

Recent Developments on Ethylene Dimerization with Focus on Alphabutol Optimization

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Abstract: *Butene-1 is an essential compound or co-monomer typically used to regulate and control the density of both high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). The production of Butene-1 has become a significant area of interest to the industrial and educational-research sectors. Alphabutol technology is one of the Butene-1 production processes. This paper attempts to find a problem that has not been addressed by previous research on production of Butene-1 by using ethylene demineralization route focussing on Alphabutol Technology. The first part of this paper is on the ethylene dimerization techniques available in the literature. Most research on the ethylene dimerization technique emphasized on how to enhance the selectivity of Butene-1 from ethylene using different types of catalyst. The second part of this paper reviews the operational processes used to minimise fouling reported in the literature review. Most of the literatures focused ethylene dimerization and not on the operational issues to be overcome during chemical reactions to enhance the selectivity of Butene-1. Fouling problem in Alphabutol process is still an area that is not adequately addressed in the literature. There is also no literature on operating or maintenance procedure to address these problems of the technology. Therefore, there is still room for improvement on the ethylene dimerization research technology, particularly in the operational process and conditions where the improvement in the reaction parameters of the Alphabutol reactor can improve selectivity of butene-1, extend the run time of the heat exchanger and reduce the time required to clean the heat exchanger fouling.*

Index Terms: *Butene-1 Production, Alphabutol technology, Fouling, Ethylene Dimerization.*

I. INTRODUCTION

Butene-1 is a crucial petroleum-based chemical that belongs to the family of linear alpha olefins (LAO). It is typically converted into other chemicals namely; poly Butene-1 and butylene oxide. Butene-1 is principally utilized as a co-monomer along with ethylene to produce Linear Low-Density Polyethylene (LLDPE) and High-Density Polyethylene (HDPE), which accounts for nearly 80% of the global Butene-1 market [1]. In addition, Butene-1 is

Revised Manuscript Received on August 6, 2019.

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considered an essential feedstock for producing marketable products namely; plastics, surfactants, lubricants and liquid fuels, and liquid fuels [1]. In the industry, Butene-1 is generally manufactured through many chemical processes or refinery operations. These typically include cutting C4s from naphtha, C4 hydrocarbon steam cracking, and dehydrogenation of butane. Other common reactions include; co-product recovery from the manufacture of alpha-olefin, dehydration of butyl alcohol, dimerization of ethylene, along with the pyrolysis of butyl-based acetate and chloride compounds. Nevertheless, this review will highlight the dimerization of ethylene process into butene-1.

Natta and Zigler [2] first introduced the use of a catalyst to increase Butene-1 selectivity from ethylene dimerization in 1963. The authors reported that the use of the novel catalysts result in high activity and selectivity. These findings have stimulated interest in the high selectivity of Butene-1 among the global scientific and research community particularly in India [3], Russia [4], the Middle East [5] and Western [6] among others. Other than that, there is also growing research focus on the operational optimization of ethylene dimerization plants [7]. Several processes have been developed by companies such as Philips [8], Dow [9], Massachusetts Institute of Technology (MIT) [6] and others to produce Butene-1 through ethylene dimerization. One of the most common processes for ethylene dimerization is the Alphabutol process.

This review paper attempts to track two issues. The first part of the paper focuses on the ethylene dimerization technique, whereas the second part is on the process operations that may contribute to the fouling problem that occurs during the process. The emphasis is on novel advancements in ethylene dimerization specifically the Alphabutol technology.

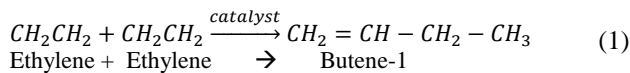
A. Ethylene Dimerization

Ethylene dimerization is a process whereby ethylene gas is dimerized to produce butene-1. The reaction of two moles of ethylene gas with modified Ziegler-Natta (Z/N) catalyst quantitatively yields Butene-1 along with a small percentage of higher molecular weight side products. Nevertheless, the yield is significantly dependent on the type of catalyst used and the selected conditions of the reaction [10].

At the selected temperature and pressure of operation, the Butene-1 product is in the liquid phase. Hence, the reaction occurs between the butene liquid phase with a dissolved catalyst. Before dimerization, ethylene gas is dissolved in the butene liquid phase as shown in Equation 1 [11].



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The Butene-1 formation reaction is exothermic with the heat of reaction 13 Kcal/mole of ethylene [12].

The alphabutol process is one of ethylene dimerization process. It has been widely used in the industry. For example, the Petrokemya company in Jubail (Saudi Arabia). In this process, titanium-based catalyst used a titanium-based catalyst. This process used titanium-based catalyst. There are two types of catalysts used in this process: TEAL - TriethylAluminiumAlkyl (C_2H_5)₃Al which is an Alkyl-Aluminum used as the main catalyst whereas LC2253 - Titanium complex + Modifier ($\text{C}_{32}\text{H}_{68}\text{O}_8$)Ti—which is a solution of Titanium complex (N-Butyl Titanate) in tetrahydrofuran type—is used as cocatalyst. This catalyst was

supplied by Axend under IFP licensor. The commercial reactor for the dimerization of ethylene functions at bubble point conditions in the aqueous phase. The feedstock ethylene and the selected homogenous based catalyst are constantly injected into the reactor operating between 50 °C and 60 °C and 20 atm to 30 atm. The exothermic heat of reaction is recovered through an outer loop furnished with a cooler [13]. Numerous research studies have focused on the catalyst with considerations for the operation of the plants.

Besides alphabutol process, there are several other processes of ethylene dimerization to produce butene-1. The different of other processes of ethylene process that are using different types of catalyst. Examples nickel, tantalum, triethyl- aluminum, chromium-based catalysts.

Table 1: Comparison of ethylene dimerization processes patented by several other companies

Process Assignee	Catalyst System	Operating Conditions		Ethylene Conversion (%)	Butene-1 Selectivity (%)	Remarks
		Temperature (°C)	Pressure (~atm)			
IFP-SABIC Alphabutol Technology	Titanium-based	50–60	20–30	80–85	93	- Low isomerization and polymerization activity
Phillips [8], [15]	Nickel-based	48	13.7	85–90	50–85	- High formation of cis/trans-butene-2 - Product super-fractionation is needed.
MIT	Tantalum	80	100	20	95	- Catalyst preparation is a complex method. - Catalyst recovery is required.
Dow	Triethyl-aluminum	277	27	25.7	95.5	- Low conversion
-	Chromium-based catalysts	79.9	13.2	8.9–31.5	53.5–82.4	- Catalyst preparation is a complex method.

II. CATALYST SELECTIVITY FOR ETHYLENE DIMERIZATION INTO BUTENE-1

There are two primary class of catalysts typically employed in the process of ethylene dimerization. These include homogeneous and heterogeneous catalysts comprising noble metals. In particular, species that contain nickel are reportedly active for the dimerization process [14].

For profitable processes, the homogeneous class of catalysts are typically employed for producing olefins with long chains. For instance, the oligomerization of ethylene involves organic solvents and homogeneous catalysts including trialkyl aluminium (Chevron and Ethyl) and nickel complexes (Shell) [11]. Table 1 shows several different types of ethylene dimerization process that are patented by several companies. Among these processes are; the process assignee IFP-SABIC process is considered the best due to its high

ethylene conversion and selectivity for Butene-1 at low temperatures and pressure. Moreover, this process produces low isomerization and polymerization.

A. Titanium-based catalyst

This class of catalysts are typically homogeneous. Also, the titanium-based catalysts ensure high activity during dimerization into Butene-1 coupled with excellent selectivity at moderate temperatures and pressures [13]. Hence, these catalysts are typically utilized commercially in the chemical industry in the form of tetrabutoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$)/Triethylaluminum (TEA)/Tetrahydrofuran (THF) at the molar ratio of THF/Ti = 4 [4]. Although the $\text{Ti}(\text{OC}_4\text{H}_9)_4$ is the critical catalyst, TEA acts as the activator or co-catalyst whereas the modifier is typically THF. The catalytic mechanism is based on the withdrawal of

the electron density surrounding the titanium metal centre by the TEA which as an activator or cocatalyst. The process subsequently generates a single or more Ti-C bonds through the replacement of its ethyl groups with the titanate complex's butoxide groups [16]. Furthermore, the modifiers function as polar additives when inserted into the $Ti(OC_4H_9)_4/TEA$ catalyst system. The subsequent addition of these species influences the active centres which exhibit strong effects on the activity and selectivity of the catalysts. Besides that, the titanium (IV) complex is stabilised by the modifier which inhibits the creation of the titanium (III) complex reportedly accountable for the formation of heavy molecular weight compounds [17].

Mahdiavani et al. [17] proposed the proximate halide (1,2-dichloroethane) as to enhance the selectivity during the production of Butene-1. This is considered dissimilar to the utilization of geminal chloro complexes as accelerants for 1-hexene and 1-octene production. The influence of reaction conditions such as temperature, pressure, and the molar ratios of Al/Ti, THF/Ti and EDC/Ti on the catalytic system behaviour was examined and optimized. In a separate study, Mahdiavani et al. [18] investigated the influence of a Ti-based catalyst on the dimerization of ethylene for the production of Butene-1 in the combination of dual modifiers and TEA (triethyl aluminum) acting as an activator. The selected modifiers used in the study were 2,5-dimethoxy tetrahydrofuran (2,5-DMTHF) and tetrahydropyran (THP). The experiment was conducted to determine which reaction parameters including ethylene pressure, temperature, molar ratio of Al/Ti, and the molar ratios of mixed modifiers/Ti can impact the total selectivity to Butene-1 [18].

The latest research on Ti-based catalyst for dimerization of ethylene was carried out by Bigdeli et al. [18]. The novelty of their research is the addition of alkylsilanes to the catalyst system, which acts as enhancement agents. The objective was also to promote high selectivity of the ethylene dimerization into butene-1. The results exhibited significant enhancement in the catalyst selectivity and productivity in the presence of the alkylsilanes compared to other unmodified catalysts [19].

Robinson et al. [19] investigated the mechanism for the ethylene dimerization for the synthesis of Butene-1 through the use of the catalyst $Ti(OR')_4/AIR_3$ based on density functional theory (DFT). The authors proposed two variant mechanisms namely: metallacycle and Cossee Arlman. The results revealed that the most probable route for the catalytic mechanism for the dimerization of Cossee-Arlman occurs through an intermediate titanium-hydride [20].

Suttill and McGuinness [20] examined the blends of Ti-alkoxide-based catalysts and $AlEt_3$. The objective was to interpret the mechanism for the dimerization of ethylene for the synthesis of butene-1. The dimerization mechanism was examined by various consecutive C_2H_4/C_2D_4 experiments on the co-oligomerization process by comparing the theoretical and experimental findings. The conclusion was that the reaction mechanism is similar to the conventional Cossee-type mechanism (insertion/ β -hydride elimination) process, which contradicts the textbook prediction [21].

B. Nickel-based catalysts

These class of catalysts are typically categorised as heterogeneous. In principle, the Ni-based catalysts are considered the most significant class of heterogeneous based catalysts for the oligomerization of ethylene. Historically,

the dimerization of ethylene through the use of Ni-based catalyst was pioneered by Phillips in 1980 [8] [11]. These catalysts convert ethylene into Butene-1 through the system of nickel-based catalyst that comprises of ethyl aluminum dichloride and bis (tri-n-butyl phosphine) nickel dichloride synthesized in desiccated n-pentane. The three-step process consists of two quenching stages and a single reaction step. In practice, the ethylene is fed to the reactor, which already contains the butane diluent and two catalysts circulated inside the reactor through an external pumping device. Due to the exothermic nature of the reaction, a cooler is typically employed to cool the mixture before it is purged into the reactor.

Ye et al. [22] investigated the atomic layer deposition (ALD) of nickel metal with the NU-1,000 metal-organic framework. The study revealed that the ALD technique could produce a substance capable of catalysing the dimerization of ethylene. Furthermore, the authors reported higher catalyst activity for the singlet state as opposed to the triplet state while using the atomic Ni catalyst and Ni4-hydroxo cluster [22].

Candran et al. [23] examined the complexes of Ni(II) based on the keto-enamine based salicylidene anilines. The authors created numerous complexes through mono-sodium salts to examine the catalyst to determine the optimal selectivity for the ethylene dimerization into Butene-1. The findings revealed that even in their complex states, the ligands were able to retain the structure of the keto-enamine. Furthermore, the complexes exhibited high activity towards ethylene when activated with methylalumoxane (MAO), which resulted in the selective dimerization but negligible yields of trimerization.

C. Tantalum-based catalyst

Schrock and Fellmann [6] made pioneering contributions to the understanding of tantalum-based catalysts. The result of which is termed the MIT (Massachusetts Institute of Technology) Process [6]. These homogeneous catalysts are prepared through a multifaceted procedure. Firstly, the synthesis of the tantalum complex is performed by the chemical interaction of tri-neopentyl tantalum dichloride ($Ta(CH_2CMe_3)_3Cl_2$) with neopentyl lithium ($LiCH_2CMe_3$) in octane to produce a quantitatively thermally stable product and yield of the catalytic complex called neopentylidene tantalum. Over the years, several tantalum compounds have been disclosed in various patents. Furthermore, these tantalum compounds are capable of selectively dimerizing 1-olefins into Butene-1 and 2,3-disubstituted-1-butenes. However, this type of catalyst is not a commercialize catalyst and has not been implemented in industries.

D. Triethyl- aluminum

Triethyl-aluminum based catalyst is used at high displacement temperature. This process is an early step for the production of low-density polyethylene by the co-polymerization of ethylene with the butene-1 product [5]. The process has been patented by Dow company [24]. Since then, they are several researchers interested on experimenting done based on triethyl-aluminum catalysts. Skinner et al. have done experiment on different concentration of

triethyl-aluminum reaction ethylene give results of product distribution of alkyl aluminums or olefins.

Furthermore, Pillai et. al. [25] found that in dimerization of ethylene, two-component systems derived from titanium alkoxide/aryloxy and triethyl-aluminum were found to be superior to triethyl-aluminum alone. They study on the influencer for catalyst concentration on dimerization of ethylene which is the $Ti(OC_4H_9)_4-A1(C_4H_9)_3$. Results from the studies shows that at high range catalyst the total ethylene conversion was in the range 71-75%. At low catalyst concentration, the selectivity to 1-butene was in the range 73-83.

E. Chromium-based catalysts

Chromium-based catalysts are also used to dimerize ethylene. According to [21, 22], organophosphine chromium (III) complex and ethyl aluminium dichloride catalysts exhibit satisfactory conversion and selectivity. The process of dimerization was performed using a 300-mL stimulated autoclave in which the synthesis of the catalysts was achieved. This was accomplished by the chemical interactions between the chromium and organoaluminum compounds such as chlorobenzene or cyclohexane solvents. The findings revealed the $CrCl_3(Py)_3$ and $EtAlCl_2$ catalyst system could successfully achieved the dimerization of ethylene into a combination of butenes. The recorded selectivity was 83% in relation to the minor yields of butene species formed when the co-catalyst was used. The throughput of 4,700 g of butene per g of Cr complex was recovered through the catalyst system comprising of $CrCl_3(4EtPy)_a$ and $EtAlCl_2$. The overall selectivity to butenes was 83% of which 50% was Butene-1, whereas the remainder was cis/trans-butene-2 [5]. Zu et al. [28] examined the potential of a carbon catalyst with Cr-promoted cobalt oxide for the synthesis of Butene-1. The overall selectivity was 53.5–82.4% compared to 8.9–31.5% ethylene conversions without the use of a co-catalyst. This is a novel finding considering the commercial dimerization of ethylene into butane-1 is typically achieved through ligand based catalysts structures which are activated by a co-catalyst. The enhanced activity and stability of the Cr-promoted catalyst was comparatively better than the un-promoted catalysts [28].

III. ETHYLENE DIMERIZATION OPERATIONAL PLANT RESEARCH

Several studies have performed research on ethylene dimerization with emphasis on the operational plant. One of the operational problems is temperature runaway in the tank reactor. Ali and Humaizi [7] examined this problem and recommended a potential solution. The authors suggested deploying a standard computer-generated proportional–integral (PI) control and linear model predictive control (MPC) to secure, control, and stabilize the reactor temperature for safe plant operations. The objective of the proposal was to maintain the computer-generated application of the standard PI control and MPC for the stabilization of the reactor temperature.

Another significant problem, which occurs in the dimerization of ethylene operations (i.e. the Alphabutol process) in plants, is the fouling of the heat exchanger. Due to

the exothermic process and reaction heat, the fluids need to be cooled down with a pump around the loop (PAL). Therefore, the polymer from the reaction can get stuck in the heat exchanger and accumulate, which increases the fouling inside the heat exchanger.

A. Fouling Problem in Alphabutol process

The fouling of heat exchanger surfaces is one of the major unresolved problems. There are six distinctively different fouling mechanisms. Firstly, it may happen due to crystallization which can be observed in process equipment, cooling towers, and steam generation plants. Secondly, it may happen in particulate sedimentation and deposition of particles on heat exchanger surfaces. Thirdly, it could happen because of chemical reaction and polymerization leading to the formation of oil sludge and organic oxidation products among others. Fourth, it could happen because of coking and hydrocarbon depositions, which usually occurs at high temperatures. The fifth is by biological and organic material growth that can cause fouling. Typically, this kind of fouling happens in several types of waste treatment systems. Lastly, fouling can be caused by a corrosion mechanism that is dependent on thermal resistance and surface roughness [29].

The associated problems of fouling result in two major effects namely: 1) hydraulic impact and 2) thermal impact. Concerning the hydraulic impact, the fouling acts by reducing or restricting flow in the cross-sectional area, which gradually blocks the tubes. Ultimately, this elevates the pressure drop thereby resulting in operational problems that lower the output. However, the thermal impact occurs as a result of fouling that gradually builds up causing increased resistance to heat transfer in the heat exchanger [30].

Heat exchanger fouling problems also occur in Alphabutol process plants. The heat exchanger fouling routinely occurs in the pump around loop (PAL) section of the process. The fouling problem can be categorized as either chemical reaction fouling or polymer fouling. This type of heat exchanger fouling problem typically occurs in hydrocarbon streams, primarily the petroleum refinery. Several studies in chemical reaction fouling have been conducted by researchers on industrial heat exchanger performance, laboratory thermal fouling, and mass deposition during heating. Other studies have examined sediment and gum formation at temperatures near ambient, along with the chemistry of organic fluid oxidation and polymerization. Table 2 summarizes the reviews by Watkinson [31] on the chemical reaction of fouling from many different resources. However, the resources are mostly focused on fouling studies in hydrocarbon process plant but not on ethylene dimerization.

Ibrahim et al. [29] investigated the fouling mechanisms that occur in the heat exchangers of the naphtha hydrotreatment unit of the Horns oil refinery. Generally, fouling is caused by polymerization. Specifically, it is caused by oxygen-initiated polymerization. On the other hand, Diaz-Bejarano et al. [30] presented an application modelling framework and thermo-hydraulic analysis methodology to the industrial case study. This analysis was performed to analyse individual shell and tube heat exchanger state of fouling.

The two-stage analysis was conducted as follows:
1) data-driven analysis to examine the extent, thermal conductivity, composition and evolution of deposits along with the equivalent rate of fouling over time; and

2) model-based analysis of the fouling rates to classify and propose appropriate models for deposition, which could be applied to performance estimation and enhancement studies such as cleaning preparation [30].

Table 2: Studies on the chemical reaction of a heat exchanger [32]

	Fouling fluids	Test rig and measurement	Temperature, pressure
1	Crude oil	Heated tube, thermal fouling	365 °C < T _s < 447 °C 345 °C < T _b < 365 °C P = 4100kPa; t < 400h
2	Crude oil refinery cuts with pitch, resin	Heated probe, rotating cylinder, thermal fouling	T _s < 287 °C 71 < T _b < 287 °C P = 2000 kPa; t = 20 h
3	Oil refinery feedstocks	Hot wire probe thermal fouling	200 °C < T _s < 340 °C T _b < 100 °C P = 1480kPa; t < 50h
4	Crude oil, kerosene, shale oils	Hotwire probe thermal fouling	175 < T _s < 400 °C T _b = 90 °C pressurized; t < 3 h
5	Crude oil with asphaltenes	Heated tube heat flow measured	32 °C < T _b < 266 °C
6	Jet fuels, hydrocarbons with heteroatoms (deoxygenated)	Heated tube and mass deposition	150 °C < T _b < 560 °C P 6990kPa; t < 4h
7	Jet fuel	Isothermal mass deposition	120 °C < T _b < 355 °C P = 4235kPa; t < 16h
8	Terphenyls and high boilers	Heated window film thickness	T _s = 483 °C 313 °C < T _b < 388 °C P = 1686 kPa; t < 56 h
9	1% Styrene in kerosene	Heated tube thermal fouling	22 °C < T _s < 249 °C 22 °C < T _b < 229 °C t = 12h
10	Styrene in heptane	Hotwire and annular probes thermal fouling	T < 180 °C T _b < 107 °C P ≈ 6.5 0 kpa; t < 72h
11	Jet fuels, hydrocarbons with heteroatoms (oxygenated)	Heating, vapor mass deposition on coupons	150 °C < T _b < 260 °C P 20.6kPa; t < 4 h
12	Kerosenes	Heated tube thermal fouling	130 °C < T _b < 243 °C t = 650h
13	Kerosene (air saturated)	Tube side vapour thermal fouling	160 °C < T _s < 380 °C 106 °C < P < 253 kPa t = 100h
14	Used lube oils	Heated rod mass deposition	343 < T _s < 455 °C P = 2850 kPa; t < 3 h
15	Gas oil	Heated tube thermal fouling	T _s < 175 °C T _b = 100 P = 101.3kPa t < 430 h

B. Cost Impact of Fouling on Alphabutol Technology

In Alphabutol technology, maintenance plays a great portion of the unit yearly cost. This maintenance is due to frequent fouling of the cooler in Pump Around Loop (PAL). From the industrial best practices, maintenance would cost around 500 manhours for dismantling and fixing back PAL. In addition, it costs about 300-500 manhours for hydro blasting the heat exchangers in PAL. In addition, it costs between USD2,000 to 5,000 for consumables such as gasket, fasteners, bullets etc with cranes and riggers.

Another major cost factor for this technology economics is the catalyst cost. The titanium based catalyst (LC2253) [33] [35] is ten times more expensive than the alumina alkyl (TEAL) co catalyst [34]. Hence the ratio of catalyst TEAL/LC should be optimised for better production and longer PAL in service and less time for cleaning. As shown in Figure -1

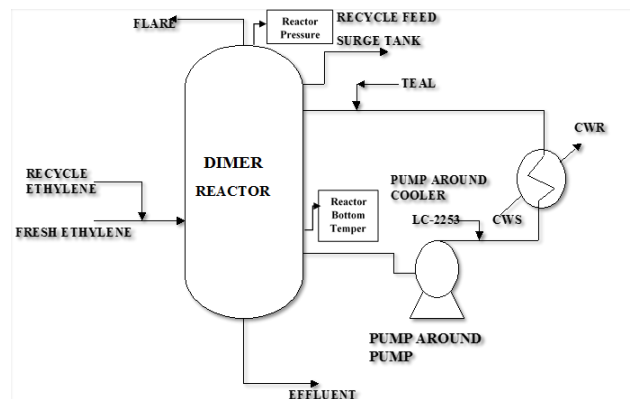


Figure -1 Alphabutol Technology Reactor system



IV. RESEARCH GAP AND CHALLENGES

In the literature, there are a few related papers about Alphabutol technology. These papers mainly describe the high selectivity of several types of catalysts. Other than that, studies on the reaction fouling that occur in the heat exchanger are general and do not specifically discuss the cause of ethylene dimerization. Furthermore, research on the operation of ethylene dimerization plants is lacking.

One research studied the process, reaction rates, and modelling of ethylene dimerization; however, this was based on a pilot plant scale [18] [20]. Although the reaction parameters were explained in the literature, the specific number of parameters was not identified. Most literature on Alphabutol technology is old, with no retrofit or experiments conducted. Even in technology manuals, the available parameters are from the pilot plants of each licenser. Also, the cleaning of fouled heat exchangers in literature is not addressed in terms of how much pressure per tube is required.

The safety aspects in terms of personnel protection while cleaning the fouled heat exchangers and piping are not addressed in the literature. Furthermore, the technology economics in terms of optimising catalyst ratio where it gives longer PAL in service and less cleaning was not address also. The economics of the technology can also be addressed in research as well as the trade-off between conversion and how long it takes for cleaning frequently fouled exchangers as mentioned above.

It is essential for the industry to address technology optimization as it is used in many countries around the worlds. It is also essential to relate reaction parameters to the selectivity using the same catalyst.

V. CONCLUSION

According to previous research, the focus on general ethylene dimerization process is to produce high selectivity of Butene-1 by improving the catalyst system. In the previous research, only few improvements were found to improve selection of butene-1 based on Alphabutol technology. However, the improvement is not focus on optimizing reactor condition nor addressing fouling issues. The only research reported so far for the heat exchanger fouling problem that is similar to Alphabutol process plant is reaction fouling in the heat exchanger. However, the researchers were focusing on the general hydrocarbon plant, which is a wide field that cannot be referenced for the Alphabutol technology. Therefore, there is still room for improvement particularly research that focuses on fouling problem in industrial Alphabutol technologies. To address the fouling problem without compromising on Butene-1 selectivity, parameters such as reactor operating condition in the Alphabutol technology industry needs to be optimized. The resulting findings could provide useful insights and guidelines to optimise and smoothen the process in a real plant.

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