

# Selective Ethylene Dimerization Toward 1-butene by a New Highly Efficient Catalyst System and Determination of Its Optimum Operating Conditions in a Buchi Reactor

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**Abstract**—The quantity of heavy and polymeric compounds produced in the industrial reactor is the most important problem of 1-butene plants that leads to the fouling formation and shutting down of the pertinent reactor. Accordingly, a systematic study has been made of the Ti catalyzed dimerization of ethylene using a vicinal halide compound as a new promoter. This study revealed that the addition of 1, 2-dichloroethane (EDC) as new promoter had marked impact on the catalyst performance which led to the improvement of overall 1-butene selectivity, yield of reaction and remarkable decrease of by-products and polymer. It is proposed that the spatial effects of weak coordination of EDC on the Ti active species lead to the decomposition of dimeric TEA into monomeric TEA and the facile generation of the increased number of the active metal sites of responsible for the dimerization of ethylene. The relevant mechanism and reaction between TEA and EDC was disclosed in detail. More specifically, the effects of various operating conditions (i.e. reaction temperature and pressure, molar ratios of TEA/Ti, modifier/Ti and EDC/Ti on ethylene conversion, overall selectivity to 1-butene, byproducts, weight of polymer and yield of reaction were fully assessed and the optimum reaction conditions were determined.

**Index Terms**— ethylene dimerization, vicinal halide, promoter, heavy and polymeric compounds.

## I. INTRODUCTION

1-butene is a four-carbon mono-olefin that is produced by a variety of methods as follows [1], [2]:

- 1) Refinery operations (isolation from fraction of C<sub>4</sub> of crude oil and petroleum products),
- 2) Steam cracking of C<sub>4</sub> hydrocarbons,
- 3) Butane dehydrogenation,
- 4) Catalytic ethylene dimerization,
- 5) Co-product from  $\alpha$ -olefin manufacturing,
- 6) Butyl alcohol dehydration, and
- 7) Pyrolysis of butylacetate and butylchloride.

It is noteworthy that the selective dimerization of ethylene has been considered as economic route for the production of 1-butene with higher purity. The dimerization of ethylene is

governed by three essential features that influence the formation of 1-butene. There are: a) the degree of polymerization, b) the mode of linking ethylene molecules and c) the position of the double bond [1]. 1-butene can be converted to products such as poly 1-butene, butylene oxide and valeraldehyde. The main application of 1-butene is as a comonomer with ethylene in the production of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) [3]. It determines the density of the resin by controlling the amount of short-chain branching in the polymer. The 1-butene catalyst converts gaseous ethylene dissolved in a liquid phase into 1-butene which is the desired product of reaction. The only commercial process of the ethylene dimerization is the IFP Alphabutol process (titanium based catalyst). Other processes based on different catalytic systems are assigned to Phillips (nickel based catalyst), MIT (neopentylidene tantalum complex) and Dow (triethylaluminum catalyst) [1]. Among several mechanistic postulations for the ethylene dimerization, the most generally accepted are:

- Bimetallic intermediate mechanism: This classical mechanism was originally proposed by Cossee who suggested an alkoxy bridge Ti-Al model as the active dimerization complex [6]. This model was later evidence by quantum-mechanical studies. The self-consistent all valence electrons molecular orbital calculations revealed that the coordination of ethylene to the vacant site imparts a rearrangement of the catalyst complex from its original trigonal-bipyramidal structure into octahedral complex with titanium-ethyl bond at an intermediate position between two octahedral sites (see Fig. 1) [7], [8].
- Cyclic intermediate mechanism: The mechanism was accepted as part of Alphabutol process relevant to IFP in four steps as shown in Fig. 2 [3]:
  - 1) Complexation of two molecules of ethylene on a titanium atom.
  - 2) Concerted coupling of the two ethylene molecules by means of titanium (IV) metallocyclopentane intermediate species.
  - 3) Intra-molecular  $\beta$ -hydrogen transfer which gives 1-butene.
  - 4) Ligand dissociation

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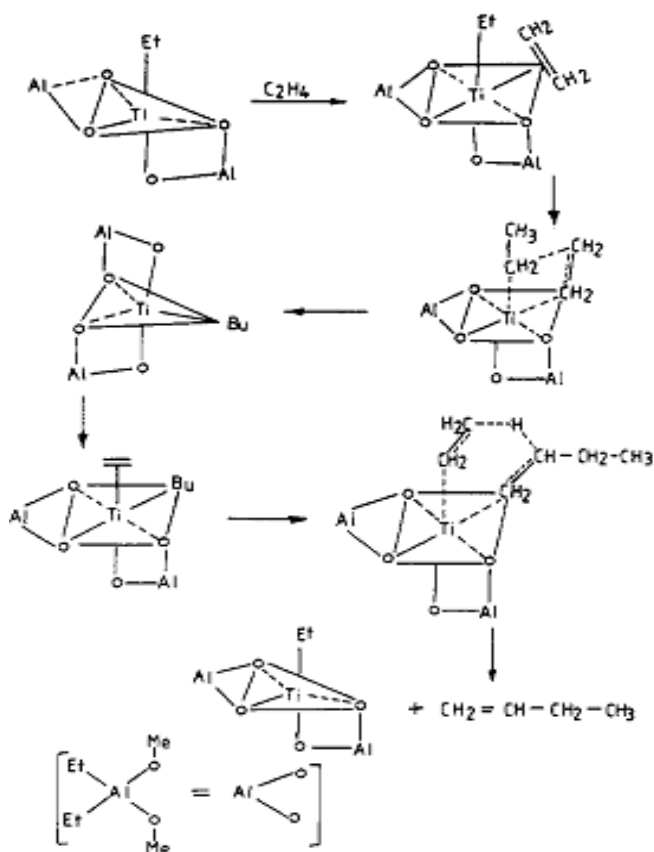


Fig. 1. A schematic representation for the bimetallic mechanism [6]

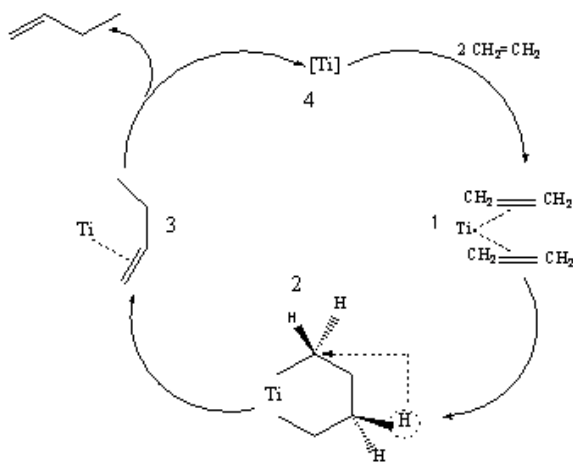


Fig. 2. Schematic representation of the cyclic intermediate mechanism

The selective ethylene dimerization reaction uses a commercial homogeneous catalytic system based on titanium tetrabutoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ )/Triethylaluminum (TEA)/Tetrahydrofuran (THF) with molar ratio of  $\text{THF}/\text{Ti}=4$  which is typically called Commercial Catalyst [4], [5].  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is as main catalyst. TEA is an activator or cocatalyst which can withdraw the electron density surrounding the titanium metal center and generate one or more Ti-C bonds by exchanging its ethyl groups with the butoxide groups of titanate complex [3]. THF is a modifier. Substantially, modifiers are polar additives when added to  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ /TEA catalyst system are known to effect changes in the nature of active centers and have a profound effect on the catalyst activities and selectivities. On the other hand, modifier stabilizes the titanium (IV) complex and prevents from the

formation titanium (III) complex which is responsible for the production of heavy compounds [1], [9].

Promoters which almost are halide compounds, have been widely studied in tri- and tetramerization of ethylene [10], [11]; but up to now, there is no report on their use in the ethylene dimerization for production of 1-butene. The promoters play an important role to assist central metal of pertinent catalyst system to achieve high desired product formation selectivity and highly catalytic activity.

In this paper, we introduced EDC as a suitable vicinal halide for the increase of conversion and 1-butene selectivity different from application of geminal chloro compounds as accelerants at production of 1-hexene and 1-octene. The effects of reaction temperature, reaction pressure,  $\text{Al}/\text{Ti}$ ,  $\text{THF}/\text{Ti}$  and  $\text{EDC}/\text{Ti}$  molar ratios on performance of catalytic system were investigated and the optimum conditions were determined.

## II. EXPERIMENTAL

### A. Material

Titanium tetrabutoxide and THF were obtained from Axens and Fluka companies, respectively. TEA was purchased from Crompton Chemicals and was diluted to a heptane solution of 1 M before use. EDC was bought from Merck Company. N-heptane (from Fluka) was dried over molecular sieve 4 Å. Also, polymerization grade ethylene was supplied from Arak Petrochemical Company (ARPC) and was checked for purity by Gas Chromatography (GC).

### B. Instrument

The set up consists of a stainless steel 1 liter buchi reactor equipped with a speed-controlled, a jacket circulating cooling fluid, a thermocouple, a pressure gage, gas inlet and outlet ports and a liquid sampling port. Meanwhile, the reactor was set up with a buchi data multi channel system (bds mc) to display and record the temperature, pressure and stirrer speed with reaction time. GC (CP-3800 Varian) with CP-Sil 8 capillary column ( $25 \text{ m} \times 0.53 \text{ mm}$ ) was used for product analysis.

### C. Reaction procedure

Before conducting a catalytic batch experiment, the reactor was heated to  $100^\circ\text{C}$  for an hour to eliminate traces of water, air and impurities. Then, it was cooled to ambient temperature and was swept with nitrogen purge for 30 minutes. After evacuation and flushing, the reactor was charged with 400 ml n-heptane as solvent. Subsequently, the reactor was heated and when it was brought to the desired temperature, ethylene was introduced into the reactor to the desired pressure and then ethylene flow was shut. The inside temperature of the reactor was controlled through cooling fluid if required. Then, calculated quantities of TEA, THF, EDC and  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  were immediately injected into the reactor. At this moment, agitation was rapidly started. The speed of the stirrer was initially set to 900 rpm. As the reaction progressed, a drop in ethylene pressure was observed. Also, the speed of stirrer was reduced with reaction time. It is noteworthy that the reaction temperature due to the exothermic reaction increased slightly and was then reduced

to the set point of the reaction. The volume of inlet ethylene was measured using a Brooks Mass-Flow Controller (MFC). Finally 30 min later, the reaction was terminated by stopping of stirrer and was quenched by adding methanol/HCl solution. In the end of reaction, the total volume of gaseous components of the reactor was measured by means of a gas flowmeter.

#### D. Product analysis

The gas portion product and liquid portion product were analyzed. Indeed, a gas sample was taken into a 150 ml stainless steel bomb and was analyzed by GC. Also, a liquid sample was washed and purified with deionized water in order to remove catalyst, TEA, alcohol and HCl. Finally, it was taken for GC-FID analysis. The polymers formed in certain runs were filtered, washed with hexane, dried in a vacuum oven at 100 °C for two hours, weighed and ultimately characterized by DSC. Note that the melting and destructive points were 129 and 221 °C, respectively, and the degree of crystallinity was 57%. It was found that the polymers formed were Linear Low-Density Polyethylene (LLDPE).

The conversions and product selectivities were determined from the mass balance for ethylene consumption based on measured values from the MFC and GC analyses of the gaseous and liquid products, the liquid product weight and gas volume. The yield of the reaction was calculated as:

$$\text{Yield (\%)} = \frac{(\text{ethylene conversion (\%)} \times (\text{overall selectivity to 1-butene (\%)}))}{100}$$

### III. RESULTS AND DISCUSSION

The effects of reaction temperature and pressure, molar ratio of THF/Ti, Al/Ti and EDC/Ti on catalytic properties of the novel four-membered homogeneous [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>/THF/TEA/EDC] catalytic system were investigated in detail and ultimately the optimized operating conditions was extinguished.

#### A. The effect of reaction temperature on catalytic properties

The effects of reaction temperature on ethylene conversions, overall selectivities to total products and weight of polymers were investigated. The Relevant results are shown at Table I.

TABLE I. EFFECTS OF REACTION TEMPERATURE ON ETHYLENE CONVERSIONS AND OVERALL SELECTIVITIES TO TOTAL PRODUCTS

Run No.	T (°C)	Conversion (%)	Product selectivity (wt %)				PE (mg)
			1-C <sub>4</sub>	C <sub>6+</sub>	C <sub>8+</sub>	≥C <sub>10+</sub>	
1	50	95.24	81.24	18.29	0.44	0.03	15
2	55	97.78	83.54	16.08	0.36	0.02	18
3	60	97.70	82.86	16.54	0.51	0.09	27
4	65	96.90	79.25	19.87	0.68	0.20	65

Reaction conditions: ethylene pressure: 22 bar, stirrer speed: 900 rpm, reaction time: 30 min, solvent: n-heptane, Ti (IV)/Al/THF/ EDC molar ratios=1:4:4:5.

It was observed that with the increase of reaction temperature up to 60 °C, ethylene conversion and overall

selectivity to 1-butene were increased but when it was further increased, overall selectivity to 1-butene was decreased and weight of polymer was increased. The decline in ethylene conversion might be attributed to decrease in the monomer solubility at higher reaction temperature. Also, poor selectivity to 1-butene at higher temperature could be ascribed to the higher deactivation rate of active dimerization species which led to generation of oligomer and heavy compounds [3].

Fig. 3 shows the effect of temperature on yield of reaction. It is observed that the further increase of temperature leads to the decrease of efficiency.

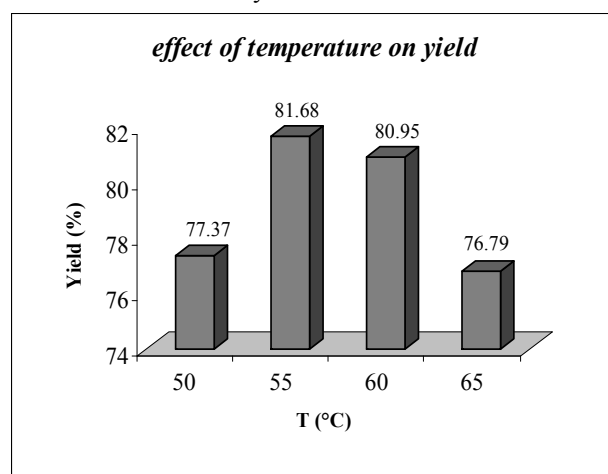


Fig. 3. The effect of reaction temperature on yield of reaction

#### B. The effect of reaction pressure on catalytic properties

The effects of reaction pressure on ethylene conversions, overall selectivities to total products and weight of polymers are reported at Table II.

TABLE II. EFFECTS OF REACTION PRESSURE ON ETHYLENE CONVERSIONS AND OVERALL SELECTIVITIES TO TOTAL PRODUCTS

Run No.	P (bar)	Conversion (%)	Product selectivity (wt %)				PE (mg)
			1-C <sub>4</sub>	C <sub>6+</sub>	C <sub>8+</sub>	≥C <sub>10+</sub>	
1	10	94.87	81.12	18.35	0.47	0.06	12
2	16	95.20	81.25	18.32	0.39	0.04	14
3	22	97.78	83.17	16.45	0.36	0.02	16
4	28	97.10	81.86	17.69	0.35	0.10	20

Reaction conditions: reaction temperature: 55 °C, stirrer speed: 900 rpm, reaction time: 30 min, solvent: n-heptane, Ti (IV)/Al/THF/ EDC molar ratios=1:4:4:5.

Improving ethylene pressure increased both ethylene conversion and overall selectivity to 1-butene. This observation could be interpreted as an indication that higher pressure ensures higher activity of catalyst due to improved diffusion of the monomer through the reaction mixture to the active dimerization sites [1], [3]. The effect of pressure on yield of reaction was investigated in Fig. 4.

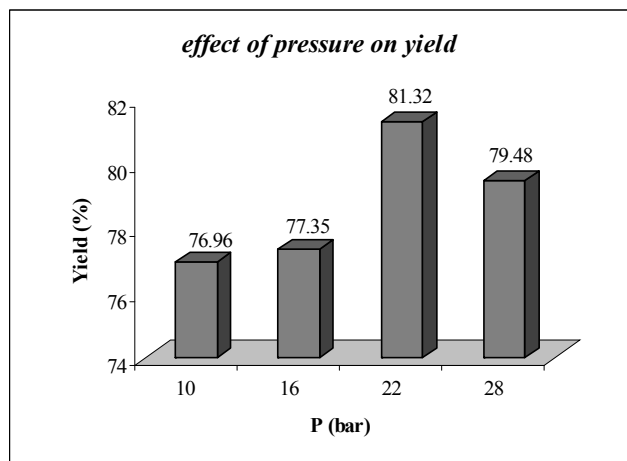


Fig. 4. The effect of reaction pressure on yield of reaction

### C. The effect of Al/Ti molar ratio on catalyst performance

The effect of Al/Ti molar ratios on ethylene conversions, overall selectivities to total products and weight of polymers were investigated. The results are shown in Table III.

TABLE III. EFFECTS OF AL/TI MOLAR RATIO ON CATALYST PERFORMANCE

Run No.	Al/Ti	Conversion (%)	Product selectivity (wt %)				PE (mg)
			1-C <sub>4</sub>	C <sub>6</sub> +	C <sub>8</sub> +	≥C <sub>10</sub> +	
1	3	95.12	80.55	18.85	0.47	0.13	25
2	4	97.15	83.14	16.43	0.41	0.02	28
3	5	97.24	81.11	18.40	0.44	0.05	37
4	6	97.28	79.73	19.64	0.50	0.13	75

Reaction conditions: reaction temperature: 55 °C, ethylene pressure: 22 bar, stirrer speed: 900 rpm, reaction time: 30 min, solvent: n-heptane, Ti (IV)/THF/EDC molar ratios=1:4:5.

As demonstrated in Table III, with the increase of Al/Ti molar ratio, ethylene conversion was increased. In addition, with the increase of Al/Ti to 4, overall selectivity to 1-butene was increased but when the molar ratio of Al/Ti was further increased, overall selectivity to 1-butene was decreased and weight of polymer was remarkably increased. This was expected that due to the presence of free AlEt<sub>3</sub> at high Al/Ti molar ratios, a rapid deactivation process of catalyst might be occurred [12]. On the other hand, at high Al/Ti molar ratio Ti (III) complex was stabilized. This causes which the polymer and heavy compounds are further formed. Of course, as seen in Table III, in the obtained optimum molar ratio i.e. Al/Ti=4, the weight of PE is more than Al/Ti=3 but with the depth investigation, It is observed that the yield of reaction for Al/Ti=3 is very less than Al/Ti=4 (see Fig. 5).

### D. The effect of THF/Ti molar ratio on catalyst performance

The THF/Ti molar ratio also had significant effect on ethylene conversion, overall selectivity to 1-butene, yield and weight of polymer. The results are shown in Table IV.

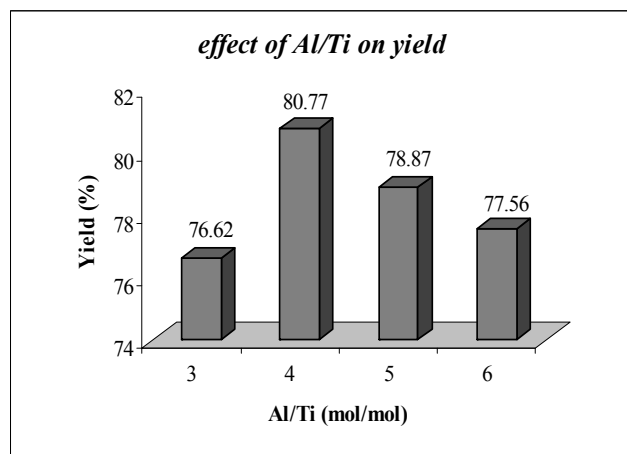


Fig. 5. The effect of Al/Ti on yield of reaction

TABLE IV. EFFECTS OF THF/TI MOLAR RATIO ON CATALYST PERFORMANCE

Run No.	THF/Ti	Conversion (%)	Product selectivity (wt %)				PE (mg)
			1-C <sub>4</sub>	C <sub>6</sub> +	C <sub>8</sub> +	≥C <sub>10</sub> +	
1	2	94.12	79.46	20.23	0.26	0.05	43
2	3	95.38	80.56	19.20	0.21	0.03	30
3	4	97.78	83.54	16.08	0.36	0.02	15
4	5	95.20	80.37	19.32	0.28	0.03	40

Reaction conditions: reaction temperature: 55 °C, ethylene pressure: 22 bar, stirrer speed: 900 rpm, reaction time: 30 min, solvent: n-heptane, Ti (IV)/Al/EDC molar ratios=1:4:5.

It was clear that the increase of THF/Ti molar ratio from 2 to 4 led to the increase of ethylene conversion and 1-butene selectivity. When THF/Ti molar ratio was 4, the selectivity to 1-butene afforded the highest value but the further increase of THF/Ti molar ratio resulted in an evident decrease of catalytic activity. This is expected any excess modifier can interfere with the formation of the active Ti species or may prevent coordination of ethylene at the active dimerization sites [13], [14].

Fig. 6 demonstrates that THF content has the pronounced impact on the yield of reaction. It is observed that the further increase of THF/Ti molar ratio (i.e. ratio of 5) leads to the remarkable decrease of efficiency.

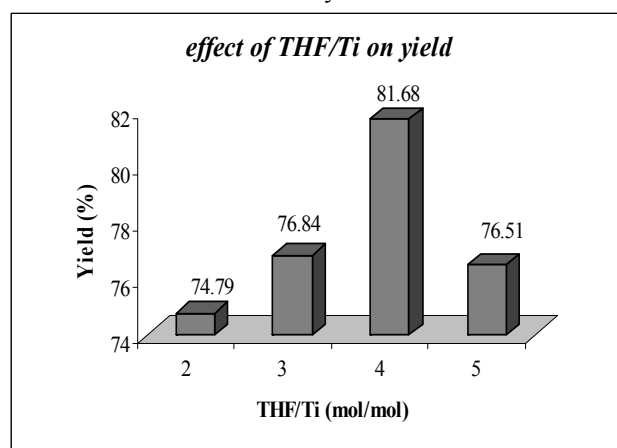


Fig. 6. The effect of THF/Ti on yield of reaction

### E. The effect of EDC/Ti molar ratio on catalyst performance

In this research, we found that the increase of vicinal halide compound led to the acceleration of reaction. In this

regard, we investigated the effect of EDC/Ti molar ratios which were listed in Table V.

TABLE V. EFFECTS OF EDC/Ti MOLAR RATIO ON CATALYST PERFORMANCE

Run No.	EDC /Ti	Conversion (%)	Product selectivity (wt %)				PE (mg)
			1-C <sub>4</sub>	C <sub>6</sub> +	C <sub>8</sub> +	≥C <sub>10</sub> +	
1	1	94.15	80.76	18.55	0.55	0.14	24
2	3	95.95	81.94	17.74	0.30	0.02	20
3	5	97.78	82.86	16.75	0.38	0.01	15
4	7	96.82	81.72	17.90	0.35	0.03	20

Reaction conditions: reaction temperature: 55 °C, ethylene pressure: 22 bar, stirrer speed: 900 rpm, reaction time: 30 min, solvent: n-heptane, Ti (IV)/Al/THF molar ratios=1:4:4.

As reported in Table V, with the increase of EDC/Ti molar ratio to 5, both ethylene conversion and overall selectivity to 1-butene were increased but further increase of EDC/Ti led to the adverse performance of the catalyst.

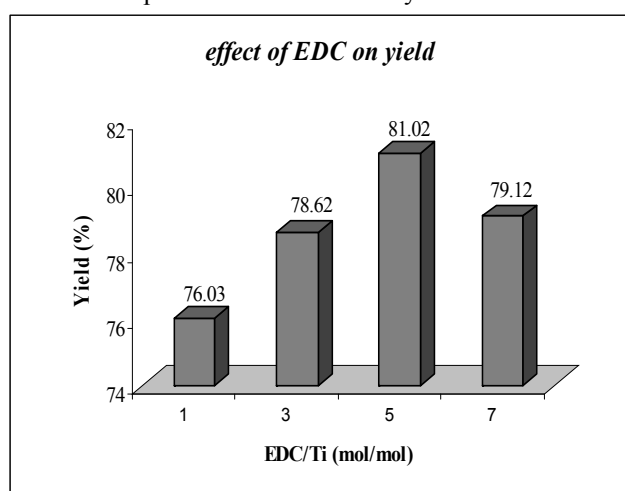


Fig. 7. The effect of EDC/Ti on yield of reaction

As seen in Fig. 7, it is apparent that the increase of EDC/Ti molar ratio results in the increase in yield to a maximum value (i.e. 81.02 %). but, when the EDC/Ti molar ratio is increased further, the yield percent falls.

The mechanism of reaction between catalytic system and EDC is complicate but the following items can be postulated:

- Because of compatibility of aluminum alkyls and chlorinated hydrocarbons, there is the effective interaction mode between EDC and dimeric TEA which is expected to accelerate the decomposition of dimeric TEA into monomeric TEA. Since the catalyst system of ethylene dimerization is dual functional catalyst, monomeric TEA can modify spatial and electronic properties of Ti active sites [15]. Thereupon, the dimerization component of dual functional catalyst is provoked and finally heavy and polymeric compounds are decreased.
- An electrophilic process generating what may be looked on as a carbonium counter ion pair, a free carbonium ion, or a polar complex (\*) which then may react further depending on the reaction conditions and the nature of the reactant [16]. On the other hand, complex (\*) can release monomeric TEA which modifies spatial and electronic

properties of Ti active sites which leads to decrease of heavy and polymeric compounds.



- Since the reaction of TEA with C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (EDC) gives high energy release, the reaction rate is increased and ethylene conversion is improved.  
 $(\text{C}_2\text{H}_5)_3\text{Al} + 3/2\text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{AlCl}_3 + 3\text{C}_2\text{H}_6 + 3/2\text{H}_2 + 3\text{C}$

The research on the other vicinal halide compounds as efficient accelerants in the ethylene dimerization reaction is ongoing. Also, the measurement of bond energy between Cl groups of EDC and titanium center of catalyst, and the recognition of possible molecular complexes in the reaction media need to be disclosed by the further study.

#### IV. CONCLUSION

In this research, a novel four-component homogeneous [Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>/TEA/THF/EDC] catalyst system was introduced. The aforesaid catalytic system displayed high activities in ethylene dimerization with good selectivities to 1-butene. EDC, a new promoter for dimerization of reaction, could significantly enhance ethylene conversion and yield of reaction. Also, oligomer compounds and polymer were remarkably decreased. The optimum conditions were obtained as follows:

T= 55 °C, P=22 bar, Al/Ti molar ratio=4, THF/Ti molar ratio=4 and EDC/Ti=5.

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