Dynamic simulation of a reactor to produce 1-Butene by dimerization of ethylene

Anurag Choudhary, Avinash Shetty, Satish Oswal

Abstract

The aim of this work was to develop dynamic simulation model for reactor which is heartof 1-Buteneproduction. Theliquid phase catalytic dimerization of ethylene in 1-Butene stands as the most selective and economical route to produce polymerization grade 1-Butene.This paper identifies the components of this homogeneous system and discusses, in fair detail, the factors controlling its selectivity to 1-Butene. Other different themes covered include: structure of the active species, kinetics, mechanistic considerations and the principal reaction parameters. This dimerization is achieved thanks to a titanium compound activated by alkyl aluminum (TEAL). BY-Products are mainly hexenes formed either by reaction of 1-Butene with Ethylene or by trimerization of ethylene, and some small amount of polymer formation. The heat of reaction is removed by heat exchanger provided in pump around loop. The catalyst and TEAL is added in pump around loop in optimum ratio to increase selectivity of 1-Butene. The simulation of such a reactor was performed using the simulation program UNISIM, which does not have provision for non-standard reaction kinetic expressions. Owing to this limitation of the software, the bubble reactor had to be described by dividing reactor in five small continuous stirred types of reactor (CSTR) for optimum performance. The simulation model is very flexible and useful for the simulation and operation of this type of reactor.

Index Terms: UNISIM Simulation; Kinetic model; Dimerization of ethylene; 1-Buteneselectivity; Reactor simulation

1. Introduction

1-Butene is a basic petrochemical building block of captive requirements,not only it can be converted to polybutene-1 and butylene oxides, but also its largest utilization is as a co-monomer with ethylene for the production of higher strength and higher stress crack resistance polyethylene resins (LLDPE and HDPE).

The liquid phase catalytic dimerization of gaseous ethylene in 1-Butene stands as the most selective and economical route to produce polymerization grade 1-Butene. Titanium based Catalyst LC2253 (Trade Name) and activator Triethyl Aluminum (TEAL) are used for selective 1-Butene production.

The march in the catalytic dimerization of ethylene into 1-Butene was pioneered in 1952 by the systematic studies of Ziegler which were originally aimed at producing higher-chain polymers via the growth reaction of the organ aluminum compounds (multiple insertion of ethylene into the Al-C bonds). Ziegler type catalyst based on titanium has a tendency to polymerize ethylene to high molecular weight materials [1].Thepolymerization reaction is inhabited in the Alphabutol Catalyst by adding a modifying agent to the catalytic formula to stabilize the titanium (IV) complex, thus preventing the formation of titanium (Ill) complex which is responsible for the polymer formation. The modifier and the titanium compound LC 2253are mixed

under a well-defined ratio and form the active catalyst. The active species are realized by mixing TEAL and LC 2253 catalyst under ethylene pressure.

The aim of this work was to developdynamic simulation model of 1-Butene reactor operating at a site of RIL for various operational and engineering studies.1-Butene reactor was simulated in'UniSim Design' simulation software purchased from Honeywell International Inc.

2. Process Description:

2.1 Process Flow

Dimerisation reaction occurs in the liquid phase of the reactor and in the pump around loop. This liquid phase is formed mainly of two products: Butene and C_6+ with the dissolved ethylene feed. The catalyst injected into the pump around loop promotes the reaction. The ethylene feed enters the reactor through a distributor from the bottom to ensure good dispersion of gas bubble within the liquid. The gas will dissolve within the liquid medium where the reaction occurs. This dimerisation reaction is exothermic in nature, to remove the heat of reaction there are two heat exchangers (in parallel), through them reactor liquid is circulated by using two pumps (in parallel) called as pump around pumps. The effluent from the reactor is withdrawn from the bottom and pumped to the catalyst removal section using two effluent pumps. Fig 1 illustrates process flow of reactor

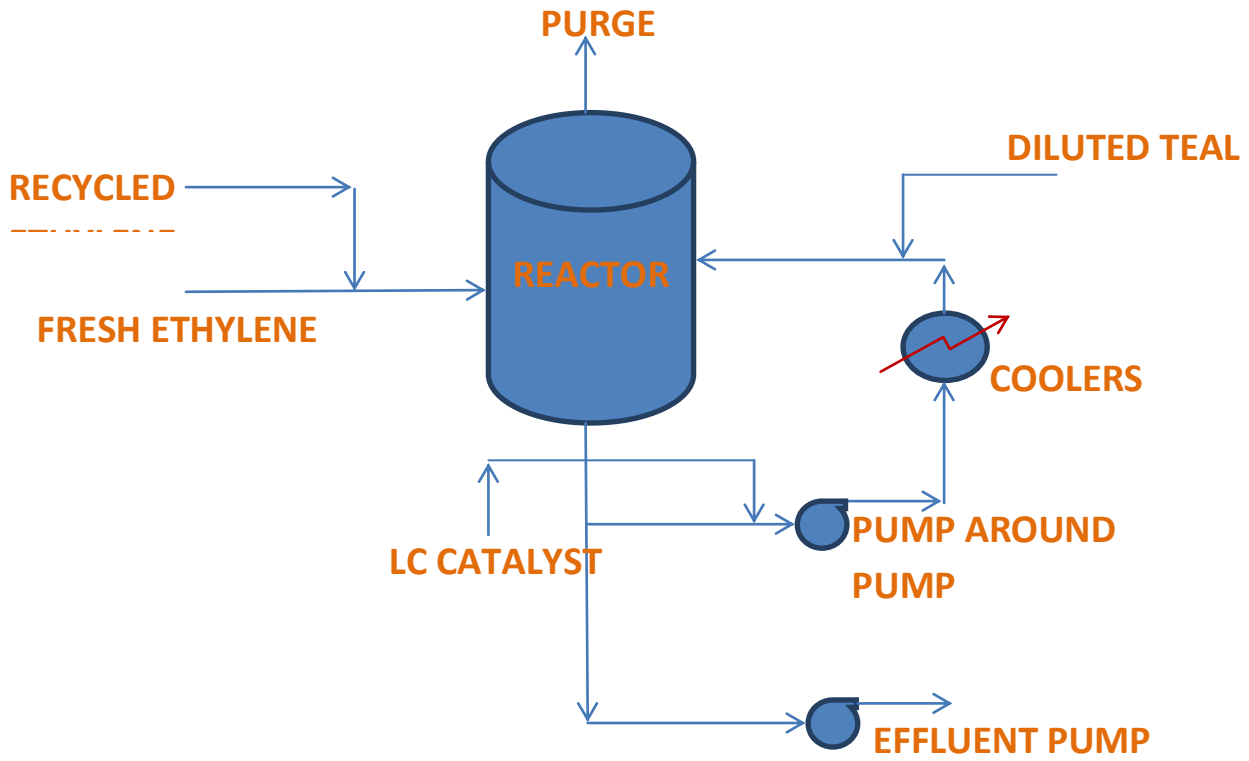

Fig 1: Schematic of Reactor

2.2 Reactor Control

The per-pass conversion in the reactor should be around 80-82%. Control of this conversion can be achieved by regulation of the temperature and pressure in the reactor. The reactor is operated at the bubble point and its composition is very close to a binary mixture of ethylene and 1-Butene. The pressure in the reactor is the sum of the partial pressure of each component. Once the temperature is fixed the vapor pressure of each component is imposed.

The temperature of the reactor can be controlled by action on the cooling water flow to the pump around exchanger. The pressure can be controlled by command of the ethylene feed valve. The residence time in the reactor is fixed by product withdrawal under level Control. The only left variable is the Catalyst flow Rate. Once the pressure and temperature fixed, the only way to increase (or decrease) the feed input will be by changing the catalyst rate. Thanks to an automatic catalyst ratio controller the required feed input can be obtained by varying TEAL catalyst flow rate until the feed rate meets the desired value. To increase the yield in 1-Butene, the unconverted ethylene is removed from the product in a distillation tower and recycled back to the reactor in vapor phase. Table 1 indicates operating and design conditions of reactor.

TABLE 1DESIGN AND OPERATING CONDITIONS OF INDUSTRIAL REACTOR

Parameter	Value
Reactor Pressure (Kg/cm^2-g)	20
Reactor Bottom Temperature (^oC)	50.5
Pump Around Liquid Temperature (^oC)	44.7
Reactor Diameter (m)	1.8
Reactor Height (m)	12.5
Reactor Level (%)	77

3. Simulation of Reactor

3.1 Simulation Basis

UNISIM was selected as a process simulator for both its simulation capabilities and its ability to incorporate calculations using the spreadsheet tool. The starting step in developing the process simulation was selecting the chemical components for the process, as well as a thermodynamic model. Additionally, unit operations and operating conditions, plant capacity and input conditions must all be selected and specified.

UNISIM library contained information for the following components used in the simulation: Nitrogen, Ethylene, Ethane, 1-Butene, n-Butane, 1-Hexene, 1-Octene and water. Components not available in the UNISIM library were specified using the ‘‘Hypo Manager” tool. Catalyst, TEAL, Active and Active* were all specified in this manner. Specification of a component requires input of a number of properties, such as normal boiling point, density, molecular weight, as well as the critical properties of the substance.

Although equation of state models have proven to be reliable in predicting properties of most hydrocarbon based fluids over a large range of operating conditions, their application is limited to primarily non-polar or slightly polar components. Polar or non-ideal chemical systems are traditionally handled using dual model approaches. In this approach, an equation of state is used for predicting the vapor fugacity coefficients (normally ideal gas assumption or the Redlich Kwong, Peng-Robinson or SRK equations of state, although a Virial equation of state is available for specific applications) and an activity coefficient model is used for the liquid phase. The non-random two liquid

(NRTL) thermodynamic/activity model was selected for use as the property package for the simulation. Since some binary interaction parameters were not available in the simulation databanks, they were estimated using the UNIFAC vapor–liquid equilibrium and UNIFAC liquid–liquid equilibrium models where appropriate. Plant capacity was specified at 2000 kg/hr of ethylene.

3.2 Reaction Mechanism:

A kinetic scheme was proposed listed below. This consists of four principal reactions with ethylene as a reactant and 1-Butene as a product and hexene-1 as a byproduct.

Reaction I:
The catalyst is a titanium compound (LC2253) activated by an alkyl-aluminum (Triethylaluminium or TEAL).

$$Catalyst + 2\,TEAL \rightarrow Active\ Catalyst$$

Reaction II:
The Titanium-based active catalyst proceeds with formation of active sites by ethylene on a valence IV titanium atom

$$Active\ Catalyst + Ethylene \rightarrow Active\ Complex$$

Reaction III:
The active complex proceeds in two steps:

1. Attack of ethylene on active site to give the metalocyclic intermediate species.
2. Intra-molecular beta-hydrogen transfer, which gives 1-Butene.

$$Active * + Ethylene \rightarrow Active + 1 - Butene$$

Reaction IV:

1-Hexene can be formed by combination of 1-Butene with active Complex.

$$Active\ Complex + 1 - Butene \rightarrow Active\ Catalyst + 1 - Hexene$$

3.3 Kinetic Parameters

Based on the experimental data, the kinetic model and its parameters were determined. Using the experimental data and analysis of the experimental reactor, by the proposed model, the following requirements for the CSTR were derived and listed below in Table 2.
Rate of reaction can be written as

$$r = k * fn(Basis)$$

Where $k = A\ e - (\frac{Ea}{RT}) * T\hat{}\beta$

TABLE 2: PARAMETERS FOR REACTION KINETICS

Reaction	A	E(kJ/kgmole)	β
I	200000	9500	1.62
II	5000	22000	2.37
III	30000	20000	1.527
IV	10800	85000	0.2

3.4 Simulation Model

To meet all the requirements mentioned above, the reactor issimulated as a bubble reactor divided into five CSTR's. Due to the high recirculation rate around the reactor (the pump around flow-rate which is equal to about 120-150 times the feed Input), the composition can be taken as constant in small sections of reactor effectively working it as a CSTR. The gaseous ethylene feed mixed with recycle ethylene from

distillation column (downstream of reactor) is fed to the bottom CSTR working as a gas distributor for above reactors. The pump around liquid consisting of catalyst and TEAL is fed to top CSTR working as a liquid distributor for below reactors. Gaseous ethylene is flowing in counter direction to liquid from top that effectively dissolve ethylene in liquid phase.

It is possible to simulate the CSTR with chemical reactions in both liquid and gas phases by the UNISIM program. This requires the knowledge of the reaction rates in the power-law expression. The matrix of stoichiometric coefficients, the reaction rate constants (frequency factor and activation energy) and the matrix of all partial orders are employed as input parameters. The selectivity of the process depends only on the temperature and the molar ratio Al/Ti in the pump around feed directed into the reactor as volume of the reactor is taken same as in the plant.

4. Results and Discussion

4.1 Performance of Model

Reactor for production of 1-Butene from gaseous ethylene dissolved in liquid phase was simulated as 5 CSTR each has a diameter of 1.8 m and height of 2.5 m.The temperature profile for each reactor is given below in table 3and reactor inlet and outlet specification are listed below in Table 4.

The temperature difference across Reactor-1is maximum as reaction is exothermic which means maximum reaction is taking place in Reactor-1 (In case of industrial reactor it is in the top part of the reactor).It is due to the availability of active catalyst sites as TEAL is added just before pump around liquid is inserted into reactor which ensures that formation of active sites in top most part of reactor.

TABLE 3: REACTOR TEMPERATURE

Parameters	**Reactor-1**	**Reactor-2**	**Reactor-3**	**Reactor-4**	**Reactor-5**
Temperature (^oC)	47.18	48.32	49.25	49.98	50.5
ΔT (^oC)	2.35	1.14	0.93	0.73	0.52

TABLE 4: REACTOR INLET AND OUTLET STREAM SPECIFICATIONS

Stream	**Feed**	**Recycle Ethylene**	**LC Catalyst**	**TEAL**	**Liquid Effluent**
Pressure (kg/cm^2-g)	33	22	20.6	22	20.6
Temperature (^oC)	32.9	31	25	40	50.5
Molar Flow (kgmole/h)	72.8	15.4	2.3	0.2	55.3
Mass Flow (kg/h)	2042	500.7	127.8	12	2682.5
Component fraction	**Feed**	**Recycle Ethylene**	**LC Catalyst**	**TEAL**	**Liquid Effluent**
Nitrogen	0.00006	0.00831	0	0	0.00278
Methane	0.00002	0.0022	0	0	0.00129
Ethylene	0.99948	0.69825	0.01548	0	0.29446
Ethane	0.00043	0.0104	0.0009	0	0.0037

1-Butene	0	0.28069	0.98024	0.95304	0.67087
n-Butane	0	0.00014	0.0014	0	0.00008
1-Hexene	0	0	0	0	0.02671
LC Catalyst	0	0	0.00198	0	0
TEAL	0	0	0	0.04696	0.00002
H2O	0	0	0	0	0

The reaction parameters, which have a manifest influence on the course of the ethylene dimerization, was found by simulation listed below

4.2 Reaction Temperature:

The effects of reaction temperature on ethylene conversions, overall selectivity to total products were investigated. The increase of temperature has a good influence on the dimerisation reaction activity (ethylene flow into the reactor) but is detrimental to the selectivity (increases the formation of byproducts).The decrease of temperature will affect the rate of conversion with the consequence to increase the rate of catalyst to keep constant production rate of 1-Butene as illustrated in Fig.2. The ethylene dimerization reaction exhibits a strong dependence on temperature. With the increase in the reaction temperature, the conversion of ethylene and the selectivity to 1-Butene decreases. The decline in the ethylene yield as illustrated in Fig 2 is attributed to the decrease in the monomer solubility at higher reaction temperature. On the other hand, the poor selectivity to 1-Butene could be attributed to the fact that increasing the reaction temperature (at constant pressure) provokes an increase in the partial pressure of the formed 1-Butene and a concomitant decrease in the ethylene partial pressure, which leads to the subsequent decrease in the concentration of the latter in the liquid phase. The higher proportion of polymer generated at higher reaction temperature could be ascribed to the higher deactivation rate of the active dimerization species leading to the quantitative generation of the Ti^{III} and Ti^{II} species, which are known to promote polymerization. A similar profile has been observed by Pillai et. Al. [2] in systematic study of titanate catalyst.

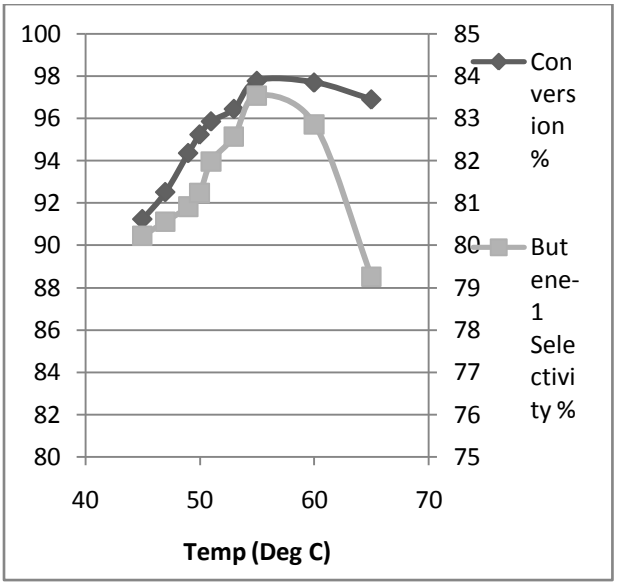

Fig 2: The effect of reaction temperature on yield of reaction

4.3 Reaction Pressure:

The effects of reaction pressure on ethylene conversions, overall selectivity to total products and are reported at Fig 3. The ethylene dimerization over TEAL and Catalyst is carried out in a liquid phase, the composition of which is determined by the ethylene pressure which, in turn, determines the ethylene conversion rate. Higher pressure is associated with an increase in the ethylene conversion rate [2]. This observation from Fig 3 could be interpreted as an indication that higher pressure ensures higher activity of the catalyst due to an improved diffusion of the monomer through the reaction mixture to the active dimerization sites.This account has been evidenced by the observation of Sergienko et al. [3] of a higher yield of 1-Butene and hexenes at higher pressure. The initial ethylene pressure has apparently no influence on the catalyst's selectivity to butene-1, but on the other hand an increase in the level of the generated polymer was detected at higher reaction pressure

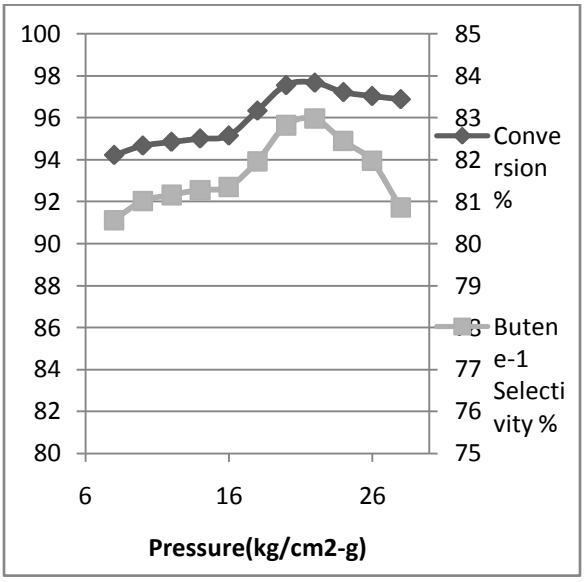

Fig 3 the effect of reaction pressure on yield of reaction

4.4 Al/Ti Molar ratio:

The effect of Al/Ti molar ratios on ethylene conversions, overall selectivity to total products wasstudied and illustrated in Fig 4. The Al/Ti molar ratio is believed to be the most critical factor which determines the course of the ethylene dimerization over the Teal catalyst. This is in agreement with a long-standing assumption advanced by Natta [4]which suggested that the reaction is selective to 1-Butene when the Al/Ti molar ratio is < 10, whilst a mixture of dimer, oligomer and polymer are produced at higher ratios, with the balance tipped toward the formation of high-molecular-weight polyethylene when Al/Ti > 20. This has later been confirmed by several studies which concluded that ethylene dimerizes selectively to 1-Butene at lower Al/Ti ratios, whereas higher Al/Ti ratios are associated with a marked loss in the activity of the dimerisation centers, due to the presence of free $AlEt_3$. An optimal catalyst activity has been detected at A1/Ti range of 3.0-5.0 (subject to the reaction temperature).

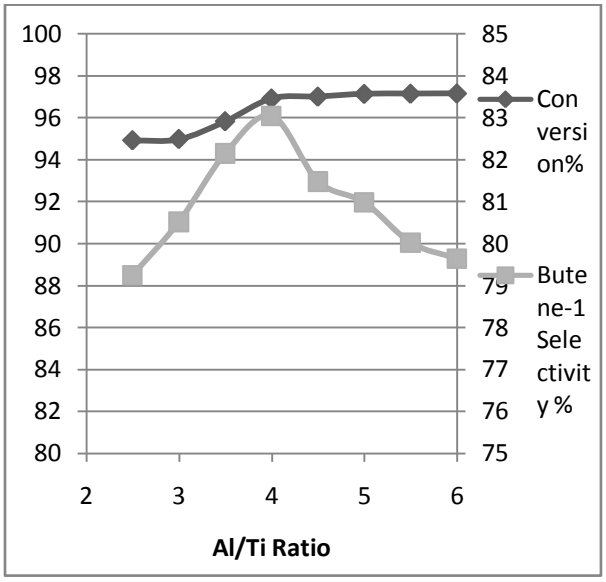

Fig 4the effect of Al/Ti on yield of reaction

5. Conclusion

In the paper, a reactor for the dimerization of ethylene to 1-Butene is proposed. The performance of this reactor was simulated by the program UNISIM. The dimerization is described by a very simple kinetic model, which involves four principal chemical reactions. There is a lack of vapor-liquid equilibrium data in the literature. Therefore, these data were predicted theoretically using the UNIFAC group contribution method. In the simulation model, the heat exchangers were all optimized. From different stages of the solution of the problem, it can be concluded that the simulation program is very flexible and robust and it converges to the solution from different starting values of variables estimated. Simulations show that the reactor divided in five CSTR's could exhibit high selectivity and high yield of 1-Butene. From the practical point of view, the design of the reactor should provide ahigh interfacial area between liquid and gas phase.

6. Notations:

Al: Aluminum
Ti :Titanium
Catalyst: Ziegler type of Alphabutol catalyst (LC2253),
TEAL Alkyl aluminum compound,
Active Catalyst Active site formed by catalyst (LC2253) and TEAL
Active Complex Active site formed by Active Catalyst and ethylene
r : Rate of reaction
k:Rate constant
A : Frequency factor
E_a: Activation Energy
R :Universal gas constant
β : Unit less coefficient of temperature

References

[1] A Hennico, J. Leonard, A. Foreatiere, and Y. Giaize, Hydrocarbon. Process. 69 (1990) 73.

[2] S.M. PilIai, G.L. Tembe, M. Ravindranathan and S. Sivaram, Ind. Eng. Chem. Res., 27(1988)1971

[3] G.S. Sergienko, V.I. Zhukov and G.P. Belov, Neftekhimiya, 3 1 (1991) 50.

[4] P. Natta, J. Polym. Sci., 34 (1959) 1