Parametric Studies of Ethylene Dichloride Purification Process

Sh. Arzani, H. Kazemi Esfeh, Y. Galeh Zadeh, V. Akbari

***Abstract*—**Ethylene dichloride is a colorless liquid with a smell like chloroform. EDC is classified in the simple hydrocarbon group which is obtained from chlorinating ethylene gas. Its chemical formula is C2H2Cl2 which is used as the main mediator in VCM production. Therefore, the purification process of EDC is important in the petrochemical process. In this study, the purification unit of EDC was simulated, and then validation was performed. Finally, the impact of process parameter was studied for the degree of EDC purity. The results showed that by increasing the feed flow, the reflux impure combinations increase and result in an EDC purity decrease.

***Keywords*—**Ethylene dichloride, purification, EDC, simulation.

I. Introduction

THERE are two major modes for EDC production: direct and indirect modes.

A. The Direct Mode

In the direct mode, ethylene and chlorine react with each other in the liquid phase in the presence of $FeCL_3$ catalyst. This reaction is exothermic and can be operated both in low and high temperature. This reaction is shown as:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

In this process the reactor product is optimized, EDC 99% is along with small amounts of trichloroethylene, HCl, ethylene, and Chlorine. In some cases, oxygen is injected into the reactor to control the free radicals and to increase selectivity in EDC production process. A scheme of this process in high temperature is depicted in Fig. 1.

B. The Indirect Mode

In indirect mode or oxychlorination, EDC is a product of ethylene with hydrochloric acid, without water and oxygen (air) in fixed bed or fluidized copper chloride catalyst [1]. Catalyst reaction of oxychlorination part is shown as:

$$2C_2H_4 + 4HCl + O_2 \xrightarrow{CuCl_2} 2C_2H_4Cl_2 + 2H_2O$$

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According to this reaction, hydrochloric acid and oxygen (air) are mixed and reacted in the process of oxy chlorination ethylene in respective mole proportion 1:4:2 and result in the production of two moles of EDC and two moles of water. The reaction happens in the gas phase and 220 centigrade temperature in fixed bed or fluidized bed reactor. A mixture of copper chloride and other chlorides are used as a catalyst.

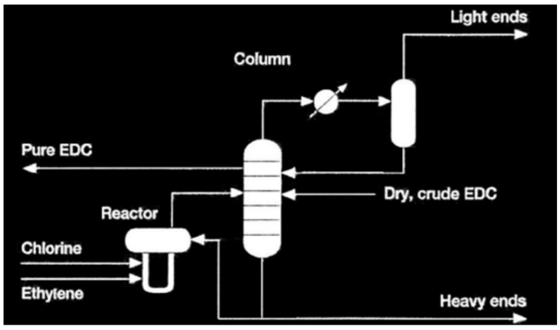

Fig. 1 Direct process of high-temperature EDC production

The products of the oxychlorination reactor are cooled by using the cooling material and sent to the knockout drum where water and EDC are turned into liquid. The liquid flow is sent to a decanter where raw EDC and acid phase solution are separated from each other. The raw EDC is sent to the storage tanks and (acid) solution phase returns to the cooling stage[2]. Nitrogen and other neutral gasses are released into the atmosphere. The EDC density in the vent is decreased by absorption and excretion towers or cooling fridge [3]. The temperature and pressure conditions in EDC indirect mode operation are usually (200-315°C) and (1.3-4.8 atm) respectively. A scheme of this process is depicted in Fig. 2.

C. The Source of Impurities in HCL Feed Oxychlorination Reactors

The source of impurities in HCL feed used in oxychlorination reactors can have different causes.

Some amount of these impurities is produced in a thermal cracking (pyrolysis) process which transforms EDC to VCM and simultaneously produces HCL. These impurities would be caused by some impurities in furnace EDC feed or lack of proper control in operational conditions of the thermal furnace. Due to the lack of proper control of thermal and pressure conditions of the furnaces, some impurities are produced which are finally sent to a side of the reactor with HCL as one of the feeds [1].

Some of the mixtures are made in determined and proper operating condition of the furnace. However, the output from the furnaces should be purified in the fracture separation phase, and HCL should be purified. However, this purification process may not be done properly due to the lack of operational control of the HCL purification tower. As a result, some impurities enter to oxy reactors with HCL. Consequently, controlling the operational conditions of the thermal cracking furnace and the used equipment (such as distillation tower and etc.) for HCL purification are very important.

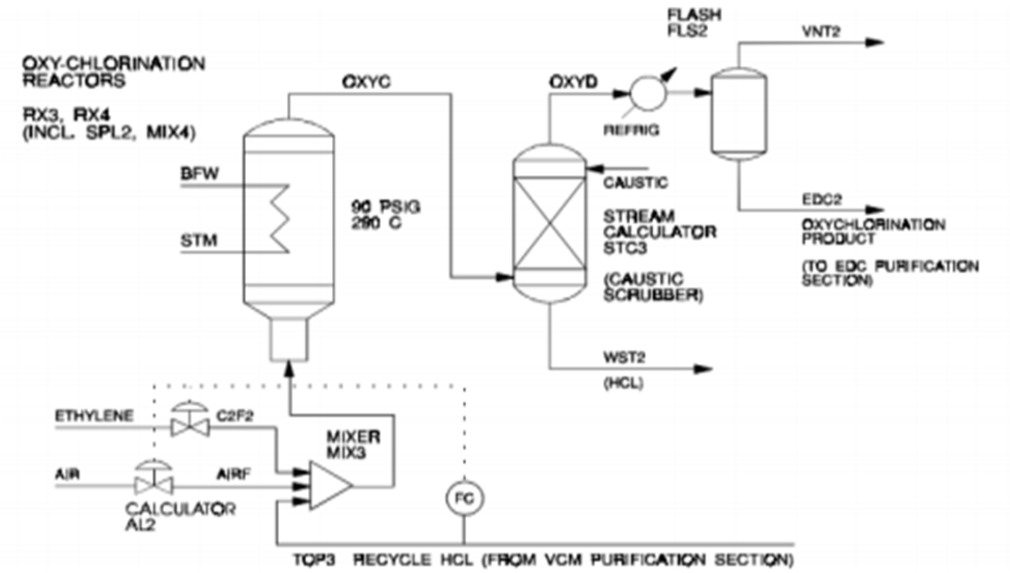

Fig. 2 Direct process of high-temperature EDC production [4]

D. The Sources of Impurities in Raw EDC

VCM is produced by breaking ethylene dichloride in an endodermal process in the furnace. The impurities in breaking EDC feed cause sediment removal and produce some unwanted lateral product such as 1,1,2 trichloroethane, tetra chloromethane, chloroform, and benzene. Controlling some of the compositions in EDC purification unit is important to maintain the ideal conditions for purification. Almost in all petrochemical companies there is a specific way in EDC purification which is gradual, and in some stages first it is dehydrated, and then the light combination is separated, and finally heavy combinations are separated from EDC [5].

II. EDC Purification Process

In EDC purification unit, first in dehydration tower, the water in EDC is absorbed in a way that the water density in EDC reaches below 10 ppm, then it enters the second phase which includes light combinations tower. In this light combination tower (combination with a low boiling point) such as 1, 1, 2 trichloroethane, chloroform, benzene, tetrachloride carbon is removed from EDC. This tower is a tray type and includes 65 trays, condenser, and reboiler. The feed of this tower which comes from dehydrating tower pores on tray number 41 and its other feed comes from a VCM purification tower and purses on tray number 25 and other feed which comes from EDC reactor production pores on tray 51. The output product goes to next phase from the bottom of the tower and light combinations exit from the top of the tower. The output product from the bottom of the second tower (the light combination tower) enters into the third tower (ethylene dichloride tower). In this tower, the heavy combinations enter the fourth tower from the bottom (heavy combinations tower) and the main product- ethylene dichloride- goes out from the top of the tower into the saving tanks to be used in cracker unit. There is still some amount of ethylene dichloride with heavy combinations in the fourth tower which is separated by vacuuming the tower in low temperature and sent to tankers as the product. The bottom product of the fourth tower which is heavy combinations is also sent to incinerate.

III. Procedure

A. UNIT Simulation

The ASPEN HYSYS software is used in this study to simulate the present distilling towers and other used equipment of this unit. For the proper conformity of the simulation with real data in EDC purification, the towers are not simulated indiscreetly. In other words, first, the towers are simulated separately without appurtenant and then the rest of the equipment such as reboiler, condenser, and pump is simulated separately. In normal situations, the degree of freedom in all towers is zero except the fourth tower which uses emitting gas from the head of the tower to make the degree of freedom zero. The pressure drop in all the towers was in accordance with a unit flowchart. In the simulation, the data in flowchart such as temperature, pressure, the combination was used. The output of all the trays of the towers was considered in 100 balanced positions.

B. Selecting the Thermodynamic Model

To study the different thermodynamic effect on EDC purification unit, different thermodynamic models were used.

In Fig. 3, the process of EDC purification simulation is depicted.

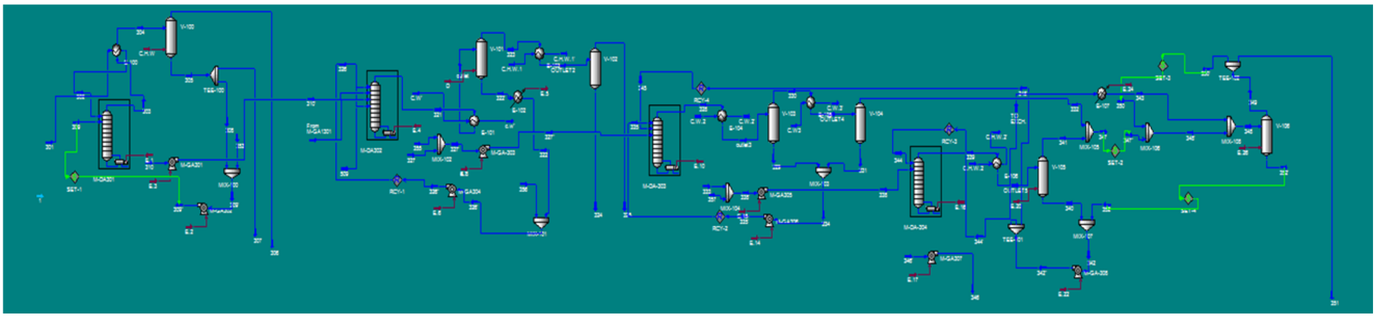

Fig. 3 The process of EDC purification simulation

IV. Discussion

A. Selecting Different Thermodynamic Models

To select a suitable thermodynamic model, the temperature of the above and below the towers was simulated by using NRTL, UNIQUAC and Lee-Kesler-Plocker models and was compared with designed amount. These results are indicated in Table I. According to the table for first, third and fourth towers both NRTL, UNIQUAC models are best for simulation, and NRTL model is used for simulation [6]. For the second tower, the comparison of the results of the simulation and the designed data shows that LKP thermodynamic is the best option which also in compliance with [7].

TABLE I
Comparison of Different Thermodynamic Models

Parameter	Design	LKP	NRTL	UNIQUAC
First tower (M-DA301)				
High Temperature (℃)	86.47	90	86.08	86.47
Low Temperature (℃)	96	98	95.5	95.5
Second tower (M-DA302)				
High Temperature (℃)	81	82	83.93	84.04
Low Temperature (℃)	100	100.6	98.8	98.8
Third tower (M-DA303)				
High Temperature (℃)	53	56	53.28	53.28
Low Temperature (℃)	65	67	64.55	64.55
Fourth tower (M-DA304)				
High Temperature (℃)	53	56	53.38	53.38
Low Temperature (℃)	95	83	95.5	95.5

B. Validation of the Data with Designed Amounts

The results obtained from the high and low temperature in the purification towers unit with the designed amount is provided in Table II. It is observed that the amount of error in the designed data is about 1%.

C. Validation of the Data with Real Amounts

To compare the real amounts with simulated ones, the diagrams of each tower against the number of trays was obtained and compared with real amounts. As it is shown in Fig. 4, there is a good compliance with real amounts and the simulated ones of the second tower. However, in other towers, there is a difference between the real amounts and the simulated ones. The obtained amount of error in each tower was respectively 6, 1, 4.4 and 10%.

TABLE II
Comparison of Design Data and Simulation Result

No. of tower	Temperature level (℃)	Simulation	Design	Error %
First tower	High	86.1	86.47	0.43
	Low	95	96	1.04
Second tower	High	81.3	81	0.37
	Low	100.4	100	0.4
Third tower	High	53.4	53	0.75
	Low	64.5	65	0.77
Fourth tower	High	53.5	53	0.94
	Low	95.6	95	0.63

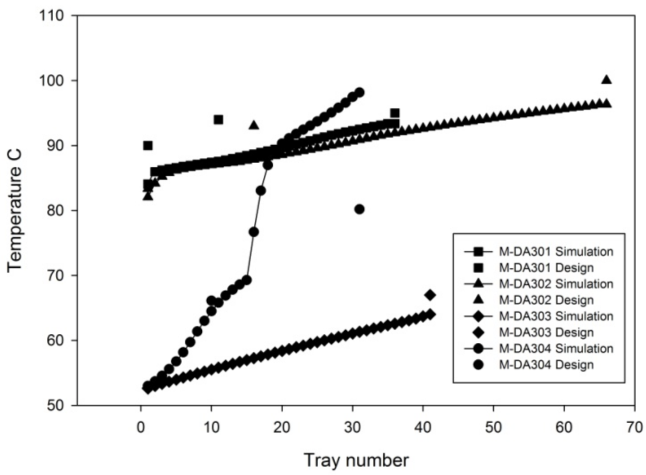

Fig. 4 Temperature-trays diagram for all four towers

D. The Evaluation of the Impurities in the Second Tower

Controlling the impurities in the output is highly important because these combinations affect EDC purity and cause coke in cracking furnace and fraction. Among these combinations, chloroform and CHCl3 have a significant impact, and their amount is higher than the allowed amounts. First, the amounts of the mentioned combinations are evaluated in the bottom of the tower, and then their effects on EDC purification are inspected. To this end, the feed flow rate (main flow) is increased, and the amount of the returned reflux to the tower is evaluated. It is observed that if the reflux density to tower increases more than 30000 kg per hour, the amounts of chloroform and CHCl3 combinations in the bottom of tower increase (Fig. 5). In addition, as shown in Fig. 6 the quality of EDC products on the head of the towers is decreased as the density flows more than 30000 kg per hour. This is depicted in Fig. 6.

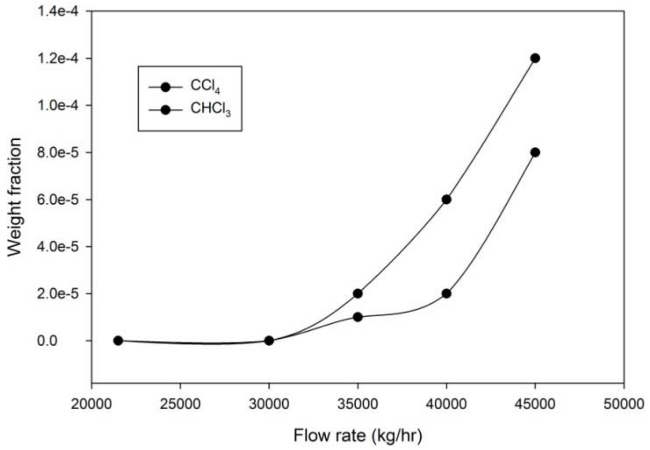

Fig. 5 Reflux flow effects on chloroform and CHCl3 combination.

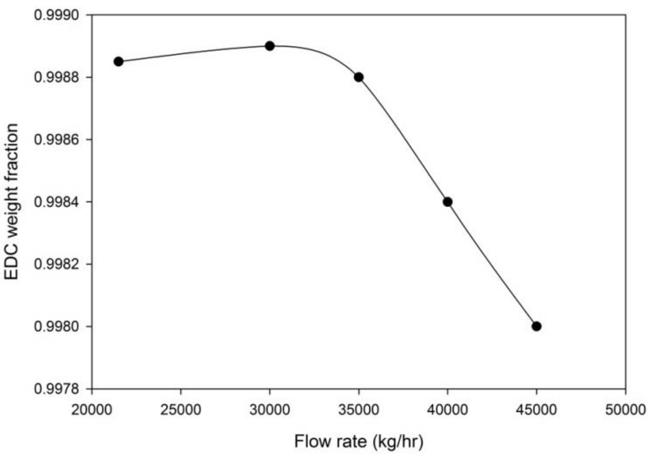

Fig. 6 Effect of feed flow rate on EDC purity

V. Conclusion

In this study, NRTL thermodynamic model was used for first, third and fourth towers and for the second tower LKP thermodynamic model was used. The results obtained from the simulation were compared once with the designed data and once with the real data and the amount of error in both conditions was evaluated. The effect of feed flow reflux on impurity and increasing purity of EDC was checked. It was observed that by increasing the flow reflux, the amount of impure combinations increased which resulted in EDC purity decrease.

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