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Experimental Study of Ethylene Epoxidation in a Catalytic Fixed Bed Reactor using Response Surface Methodology (RSM)

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Research Article

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ABSTRACT

Simultaneous effect of operation conditions on the ethylene epoxidation reaction is studied in this research. Effect of temperature (190°C-210°C), inlet carbon dioxide (up to 6 mol%) and ethylene dichloride concentration (0.75-1.7, ppm chlorine) through Response Surface Methodology (RSM) is investigated. The negative effect of carbon dioxide on selectivity and conversion is obvious on ethylene oxide yield. F-test results releases that carbon dioxide concentration, temperature and temperature-carbon dioxide interaction are important factors, respectively. Temperature of 208.7°C, chlorine moderator of 1.3 ppm and no carbon dioxide in the reactor feed are predicted by RSM model as an optimum operating condition for maximizing the yield of ethylene oxide. In this situation, ethylene oxide selectivity of 93% and ethylene conversion of 14.85% is predicted by model, which agrees well with those obtained by the experimental data with the relative error of 7.2%.

INTRODUCTION

Ethylene Oxide (EO) is an important compound in different industries such as production of petrochemical compounds, sterilization of medicine instrument, antifreeze, etc. Todays, this valuable organic compound is produced more than 26 Months in the worldwide [1]. About 65% of produced EO is used for production of ethylene glycol. Production of ethylene oxide was started by chlorohydrin process in 1914, industrially. Nowadays, direct oxidation of ethylene by air or pure O_2 is dominated in industrial scale. Ethylene oxide is a high cost product; hence, selectivity is an important factor in this process. Besides, conversion of ethylene should be maximized at acceptable selectivity value. In this reaction, silver metal due to high oxygen adsorption is used as an active phase, while alumina is the support of this catalyst [2].

Effect of different halogenated hydrocarbons on ethylene oxide catalyst showed that chlorine compound leads to better selectivity and activity relative to Fluorine, Bromine and Iodine compounds. In fact, higher electron affinity of chlorine (3.36kJ/mol) leads to this enhancement. A chlorinated hydrocarbon such as ethylene dichloride, methylene chloride and vinyl chloride in the range of less than 10 ppm is a non-negligible compound in ethylene oxide reactor feed. Optimum value of this compound in the reactor feed leads to reduce both partial and complete oxidation reactions. By adding ethylene dichloride from 1 ppm to 3 ppm, selectivity increases from 79% to 88%, while work rate decreases about 30 ton/day in an industrial plant [3-5].

On the other hand, excess chlorine compounds on the catalyst surface are considered as one of the silver catalyst deactivation agents by some researchers. Chlorine concentration strongly depends on catalyst composition such as cesium and impurities of reactor feed. Therefore, optimum value of moderator is crucial parameter in ethylene epoxidation reaction.

Carbon dioxide as an impurity in the reactor feed (up to 10%) influences on catalyst performance. Some researchers proposed that ethylene oxidation reaction rates are involved carbon dioxide concentration, which proves significant of carbon dioxide role in partial and total oxidation of ethylene. CO_2 improves selectivity through blocking undesirable sites as claimed by some researchers. However, high values of carbon dioxide in the reactor feed impacts negatively on catalyst performance. Optimum concentrations of carbon dioxide and halogenated hydrocarbon at desirable temperature can be improved selectivity and conversion of ethylene epoxidation reaction.

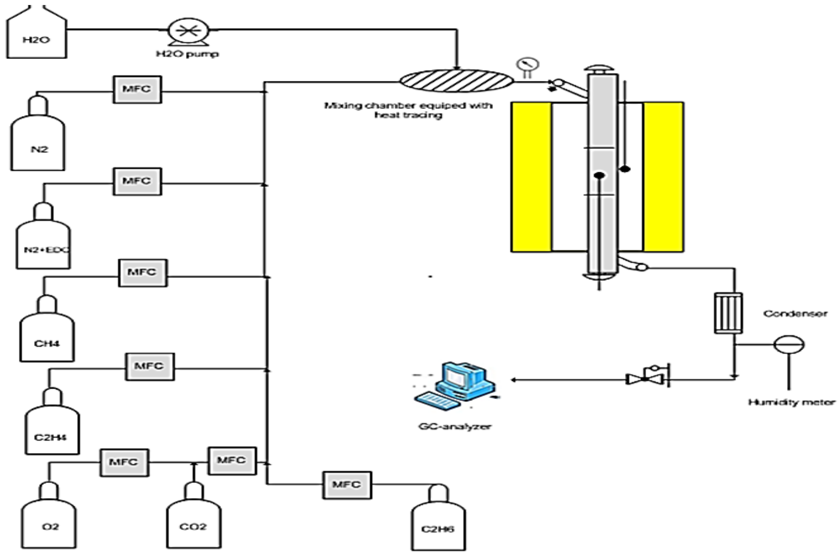
Response Surface Methodology (RSM) as a robust tool for investigation of parameters effects and their interactions with each other is proposed by many researchers. Design of experiment by RSM is a time saving and reliable method for survey of nonlinear behavior of variables in a case study.

As mentioned above, concentrations of carbon dioxide and halogenated hydrocarbon and temperature are three significant parameters in ethylene epoxidation reaction. Enough information about interactions between these factors can lead to obtain an optimum condition in the ethylene epoxidation reactor. Effect of these factors and their interactions are investigated by RSM method, in this study. As no before study is done in this area, the results can be useful in catalyst and process studies of this reaction.

MATERIALS AND METHODS

A schematic diagram of experimental setup used in this study is shown in Figure 1. A fixed bed reactor equipped with molten salt bath is charged by a commercial Ag/Al_2O_3 catalyst. Heating and cooling of the reactor is achieved using this molten salt with melting point of 180°C. Reactor feed contains six gases, which are mixed in a tracer-heating chamber with water vapor. Ethane, water vapor and carbon dioxide are impurities of recycled feed in the industrial plant. In order to supply chlorine moderator, N_2^+ethylene dichloride cylinder is prepared with specific concentration of chlorine. A flow rate of each gas is adjusted with Brooks MFC. Pressure of reactor is adjusted in 17.5 barg using GO backpressure regulator. Two thermocouples for indicating and control of the temperature in catalytic bed and molten salt bath are installed. Outlet product is analyzed by two gas chromatography (Varian-CP 3800) columns; after passing water vapor condenser equipment. Besides, outlet humidity is measured by MICHELL instrument for determination of produced water in the reaction.

Figure 1. Schematic diagram of fixed bed catalytic reactor setup.



Three effectiveness factors are considered in the design of experiments. According to the nonlinear behavior of each factor on ethylene oxide selectivity and ethylene conversion, Response Surface Methodology (RSM) is used in this study. As full factorial design is a time consuming and expensive method, it seems that RSM is a good choice for proper investigation in this area. Besides, study of factors interaction with each other is reliable and simple through DOE studies [6-8]. To our knowledge, no study was achieved in ethylene epoxidation reactor performance using RSM. Reactor temperature is an important factor in the oxidation reaction. Adjusting temperature to some extent depends on reactor cooling and heating system. In our experimental setup, temperature is chosen in the range of 190°C-210°C.

Carbon dioxide concentration in the reactor feed has a controversial effect in this reaction. CO_2 varies between 0-6 mol%, in this study. Chlorine compound (Ethylene dichloride) as reaction moderator changes between 0.75 ppm-1.7 ppm. The range of factors which are used to design of experiments by RSM. Box-Behnken method proposes 15 test runs for survey of the factors. It should be noted that each experiment were repeated two times and the average values of selectivity, conversion and yield were used.

RESULTS AND DISCUSSION

Catalyst characterization using SEM analysis is described in this section. Besides, the results obtained from RSM analysis (Minitab, 18 Software) through ANOVA table, the effect of each factor and their interactions on selectivity and yield of EO and investigation of the proposed model by RSM are described, here.

Catalyst characterization

Commercial 14% Ag/Al_2O_3 inclusive promoters such as cesium and lithium metals is used in this study and shows good dispersion of silver particles in the fresh catalyst surface through Scanning Electron Microscopy (SEM) using Phenom World G2 pro Desktop SEM device. Particles diameter in the fresh catalyst is less than 0.3 µm. After reaction and increasing temperature up to 215°C, SEM of catalyst surface was done. Agglomeration of silver particles and increasing particles size is observed in the image. Decrease in metal dispersion is the result of metal agglomeration. It seems that increasing temperature and reaction of ethylene and oxygen on the active phase in the presence of chlorine moderator are the reasons of the metal agglomeration. Presence of chlorine moderator in the reactor feed and formation of AgCl compound in the catalyst surface is declared as one of the metal sintering factors and consequently ethylene epoxidation catalyst deactivation. Large pores of alpha alumina is obvious in the SEM image which proves the SEM images in research on Cs-Prompted silver catalyst [9,10].

Ethylene oxide selectivity

According to importance of ethylene oxide selectivity in the epoxidation reactor performance, main effect of each factor on selectivity. It is expected that by increasing temperature, both total and partial reactions increase. Investigation of temperature effect on selectivity showed a decrease in selectivity from 60% to less than 20% when temperature increases from 180°C to 210°C. However, a different trend is observed in the response surface methodology results, in this study. The selectivity drop, when temperature increases from 190°C to 200°C. Increasing selectivity from 81% to more than 86 % is observed when temperature increases from 200°C to 210°C. According to consideration of factors interaction in calculation of main effect plot in RSM analysis, presence of a minimum point declares interaction between temperature with chlorine or carbon dioxide compound. These interactions are investigated in the following.

By increasing chlorine from 0.75 ppm to 1.225 ppm, selectivity is approximately constant. While, an increase from 82% to 94% by increasing Cl (ppm) from 1.225 to 1.7 is observed, as it expected. This trend accompanied with Campell and Paffett results around chlorine effect on ethylene oxide selectivity. By increasing carbon dioxide up to 6 mol%, selectivity decreases sharply from 93% to less than 76%. Hence, unlike literature review, the negative effect of carbon dioxide on selectivity is inferable. Investigation of carbon dioxide effect on selectivity. released the selectivity improvement about 4% to 8% by increasing carbon dioxide from zero to 6 mol%. In design of experiments by statics methods, main effect for each factors calculated based on responses of all test runs at the range of chosen factors. Hence, the main effect of carbon dioxide on selectivity in the range of selected factors (which similar to the industrial operation condition) is more reliable and applicable. That's the reason why the new generations of ethylene oxide catalysts are produced based on less carbon dioxide concentration in the reactor feed by great manufacturers of ethylene oxide catalyst such as SHELL Company.

Interactions of each two factors are shown as chlorine moderator and carbon dioxide have the most interaction with each other. According to literature, these two compounds lead to decrease in total and partial oxidation of ethylene. It is also observed that in the absence of carbon dioxide, selectivity remains unchanged by increasing chlorine moderator and reaches to a maximum value at about 93% for this commercial catalyst in the temperature range of 190°C-210°C. When carbon dioxide increases up to 6mol, different behavior is observed. In this situation, increasing chlorine moderator reveals positive effect on selectivity: so that, this value increases from less than 60% to more than 92%. However, chlorine moderator must be determined according to inlet carbon dioxide concentration for each catalyst. These two compounds (carbon dioxide and chlorine moderator) certainly must be considered in reaction rate equation of ethylene epoxidation. On the other hand, interaction of temperature with chlorine and interaction of temperature with carbon dioxide are not significant in this operating condition range.

According to high exothermic nature of ethylene oxidation, ethylene conversion should be controllable and not excess more than 13% in the industrial plants. High selectivity at acceptable conversion of ethylene is desirable in the ethylene oxide catalytic reactor. Hence, the yield of ethylene oxide production is an important parameter in reactor performance. Analysis of Variance (ANOVA) for investigation of factors effect on yield percent of ethylene oxide. Effect of each factor, 2-way interaction and nonlinearity of factors are calculated. For confidence level (C.L) of 0.95, F-critical value is 4.26. Factors with F-value of the higher than 4.26 are significant and vice versa. Hence, carbon dioxide, temperature, carbon dioxide square and interaction of temperature and carbon dioxide concentration are significant factors, respectively. While, other factors such as chlorine moderator has no significant effect on the responses in this operational condition range. Besides, P-value less than 0.05 (1-C.L) for temperature (0.009), carbon dioxide (0.001) and carbon dioxide-temperature interaction (0.04) shows enough accuracy in analyzing effect of these factors on ethylene oxide yield percent.

Main effect plot of each factor on the yield of ethylene oxide. Increasing temperature shows positive effects on ethylene oxide production. By comparing this figure, it can be concluded that ethylene oxide production increases, albeit selectivity decreases. Hence, operating temperature of the catalyst for ethylene epoxidation reaction is close to upper bond of our temperature range for producing more ethylene oxide. Chlorine moderator increasing from 0.75 ppm to 1.7 ppm does not appreciably change yield of reaction while shows significant effect on selectivity. So, the decline effect of chlorine moderator on ethylene conversion is obvious. As chlorine moderator can be one of the catalyst deactivation agents using less value of this compound leads to improve catalyst life. In addition to negative effect of carbon dioxide on selectivity, yields of ethylene oxide production declines by increasing carbon dioxide. Hence, it is another reason of carbon dioxide decrease in the reactor feed for improving catalyst performance.

The two-way interaction between factors on the yield of ethylene oxide. The least interaction observes between chlorine moderator and carbon dioxide concentration. The yield of ethylene oxide declines with the same slope by increasing carbon dioxide from zero to 6 mol% in all three levels of chlorine moderator (0.75, 1.22 and 1.75). Temperature interaction by two other factors is obvious. Yield of EO at temperature of 190 °C and 200°C have the same trend when carbon dioxide or Chlorine moderator changes. While, yield percent shows an optimum value of more than 10% at Cl content of 1.22 ppm at 210°C. On the other hand, increasing CO_2 concentration leads to decrease in yield more than 10%. However, this value for temperature of 190°C and 200°C is less than 5%. Therefore, it seems that this interaction is related to simultaneous effect of carbon dioxide and chlorine moderator on ethylene oxidation kinetics rates. The high value of R^2 (93.9) shows enough accuracy for model prediction. In order to maximize ethylene conversion at ethylene oxide selectivity of 93%.

CONCLUSION

Performance of ethylene oxide catalytic reactor depends on operational condition such as temperature, inlet carbon dioxide and chlorine moderator concentration at reactor feed. Design of the experiment through Response Surface Methodology (RSM) showed that carbon dioxide concentration was the most significant parameter in this process. Increasing carbon dioxide up to 6 mol% led to decrease selectivity more than 15%. Increasing chlorine moderator resulted in selectivity increase about 10%. However, ethylene oxide yield did not increase significantly. According to ANOVA table, strong interaction between temperature and carbon dioxide represented dependence of ethylene oxidation reaction rate on carbon dioxide concentration. Besides, low interaction of chlorine moderator by carbon dioxide was observed in ethylene epoxidation reaction yield. It was also found that the yield of EO and ethylene conversion predicted by the proposed model agree well with those obtained by the experimental.

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