Optimisation of sustainable epoxidation process using polybenzimidazole supported Mo(VI) complex as a catalyst via response surface methodology

Md Masud R Bhuiyan, Basu Saha*
School of Engineering, Lancaster University, Lancaster LA1 4YW, UK
**b.saha@lancaster.ac.uk*

1. INTRODUCTION

Alkene epoxidation is recognised as an essential process in chemical synthesis as the resulting epoxide can be used as a raw material or intermediate in the synthesis of a variety of valuable compounds, such as plasticisers, fragrances, and epoxy resins, as well as having significant biological activity and being useful in the production of drugs, agrochemicals, and additives [1]. The conventional epoxidation approach involves stoichiometric peracids as oxidising agents in batch reaction; however, this method is not environmentally friendly. In contrast, polymer-supported heterogeneous catalysts with *tert*-butyl hydroperoxide (TBHP) as an oxidant have demonstrated strong catalytic activity and product selectivity [1, 2]. In this study, a greener and more efficient alkene epoxidation process was developed using polybenzimidazole-supported molybdenum (VI) complex (PBI.Mo) and *tert*-butyl hydroperoxide (TBHP) for the batch epoxidation of 1,5-hexadiene and 1,7-octadiene. To optimise the reaction conditions, batch epoxidation studies were conducted to investigate the effect of reaction temperature, feed molar ratio of alkene to TBHP, catalyst loading, and reaction temperature on the yield of epoxides. Response surface methodology (RSM) using Box-Behnken Design (BBD) was used to examine the impact of the interaction of various factors on the reaction response.

2. EXPERIMENTAL

Polymer-supported Mo(VI) catalyst was prepared by reacting PBI resin with an excess of $MoO_2(acac)_2$ in the stoichiometric ratio of 2:1 in anhydrous toluene for a period of 4 days. The molybdenum content of the produced catalysts was examined. Brunauer-Emmett-Teller (BET) surface area, pore volume and pore diameter were determined by nitrogen adsorption and desorption method using Micromeritics Gemini VII. The particle size measurement was performed with Malvern Mastersizer. Response surface methodology (RSM) using Box-Behnken Design (BBD) was employed for designing experimental runs and studying the interaction effect of different variables on the reaction response. The epoxidation of 1,5-hexadiene and 1,7-octadiene using TBHP as an oxidant was systematically studied in a batch reactor using a polymer-supported Mo(VI) (PBI.Mo complex). A specific quantity of internal standard (*iso*-octane) was added to samples with known concentrations of the components in the product mixture and analysed using Shimadzu GC-2014 gas chromatography. A quadratic regression model was developed representing an empirical relationship between reaction variables and response. The yield of epoxide was selected as the response for this study.

3. RESULTS and DISCUSSION

To fit the experimental response with the independent variables, a mathematical model was defined using the general quadratic model as shown in equation (1).

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j>1}^{n} b_{ij}\, x_i x_j + \mathcal{E} \quad (1)$$

By fitting the experimental results, the generic quadratic equation shown in equation (1) was used to obtain a model of polynomial regression.

$$Yield = +52.29 + 3.64A + 5.40B + 2.56C + 27.76D + 0.8400AB + 2.63AC + 3.23AD + 0.6650BC + 2.56BD + 1.09CD - 5.27A^2 - 3.84B^2 - 3.15C^2 - 20.44D^2 \quad (2)$$

The developed models demonstrated the effect of each independent variable, variable interactions, and excess of each variable on the response. ANOVA was applied to examine the significance of the model parameters at 95% confidence level. 3D response surface plots and their corresponding 2D contour plots were created for a model equation after constructing the regression model and evaluating the model adequacy. Different contour plot shapes represent differing levels of interaction between two variables. Design Expert software was used to develop the numerical optimisation step by combining the desirability of each independent variable into a single value and then searching for optimum values for the response goals. The dependent response variable was set to be maximised to achieve the highest yield. The numerical optimisation technique concluded that the maximum yield of 1,2-epoxy-5-hexene is 64.2% at a feed molar ratio of 2.76:1, reaction temperature of 348 K, 0.56 mol% catalyst loading, and reaction time of 76 min. On the other hand, the maximum yield of 1,2-epoxy-7-octene was 66.22% at a feed molar ratio of 7.97:1, reaction temperature 347 K, 0.417 mol% catalyst loading and reaction time of 218 min. Experiments were conducted under optimum reaction conditions to validate the predicted quadratic equation's optimal response values. The experimental results showed a similar response value to the predicted optimal response with an error of 3.5% and 1.92% for both 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene, respectively. The temperature fluctuation during the reaction may have an impact on the relative error.

In order to demonstrate the yield of 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene in four independent variables, two quadratic polynomial models were developed. The optimisation results for the maximum yield of 1,2-epoxy-5 hexene and 1,2-epoxy-7-octene were validated experimentally. The experimental results showed a 62.03% yield of 1,2-epoxy-5 hexene and a 64.97% yield of 1,2-epoxy-7-octene, which confirmed the adequacy of the predicted optimum conditions from the experimental results. This study demonstrates that PBI.Mo complex could be used as an effective catalyst for a greener and sustainable epoxidation of 1,5-hexadiene and 1,7-octadiene with TBHP as an oxidising reagent.

4. REFERENCES

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