Explosion Limits Estimation and Process Optimization of Direct Propylene Epoxidation with H_2 and O_2

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Highlights

- Explosion limits of a multi-component gas mixture are estimated by modified proportional distribution method.
- The estimated results are validated by the classic Le Chatelier's Rule.
- Reactor optimization is carried out in gPROMS under commercially high reactant concentrations and safe operation conditions.
- Optimized results demonstrate the commercial potential of the direct propylene epoxidation with H_2 and O_2 to produce propylene oxide.

1. Introduction

Direct propylene epoxidation with H_2 and O_2 is an economic and environmentally friendly process to produce propylene oxide (PO), which is an essential and high-value added intermediate. Recently, considerable efforts have been devoted to developing active and stable catalysts, and Ti^{4+}-containing material supported Au catalysts are found to be feasible for commercial production of PO [1]. However, the process suffers from a safety problem due to the potential explosion risk of the feed gas, which is a multi-component mixture containing not only flammable gas (i.e., C_3H_6 and H_2) and inert gas (i.e., N_2), but also oxidizer (i.e., O_2). One solution to the problem is to employ membrane reactor as O_2 distributor to separately feed O_2 from C_3H_6, H_2 and N_2 [2]. Another solution is to dilute feed gas with a large amount of N_2, which would inevitably lead to low reaction performances due to the low reactant concentrations. Thus, there is a need to estimate explosion limits of the C_3H_6, H_2 and N_2 mixture in O_2 toward the process optimization of the reaction under commercially high reactant concentrations and safe operation conditions.

In this work, the explosion limits of C_3H_6, H_2 and N_2 mixture in O_2 were estimated. By using the estimated explosion limits as constraints to keep the composition of the feed gas outside explosive region, optimizations of the reaction in a packed-bed reactor were carried out in gPROMS. The optimized results demonstrated the commercial potential of the direct propylene epoxidation with H_2 and O_2 to produce PO.

2. Methods

The explosion limits of C_3H_6, H_2, and N_2 mixture in O_2 were estimated by the modified proportional distribution method (M-PDM), these results were then validated by the classic Le Chatelier's Rule (LCR).

A mathematical model of the packed-bed reactor was developed by using gPROMS to simulate the direct propylene epoxidation with H_2 and O_2. Based on the model, optimizations were carried out, where H_2 efficiency was considered as the objective, inlet temperature (T_{in}), inlet velocity (u_0) and inlet partial pressure of C_3H_6, H_2 and O_2 (i.e., $P_{in}(H_2)$, $P_{in}(C_3H_6)$ and $P_{in}(O_2)$) as the decision variables. Moreover, constraints in the optimization were set as following: the composition of feed gas mixture outside of the explosive region, 2.0% $\leq$ outlet PO fraction $\leq$ 2.8%, the hotspot temperature $\leq$ 463 K, C_3H_6 conversion $\geq$ 10% and PO selectivity $\geq$ 90%.

3. Results and discussion

For the reaction, the O_2 fraction is less than the rest gases (i.e., C_3H_6, H_2, and N_2), the composition of the feed gas could not reach the lower explosion limits of C_3H_6, H_2, and N_2 mixture. Therefore, only the upper

explosion limits of C_3H_6, H_2, and N_2 mixture (*UEL*s) in O_2 were calculated by the M-PDM, which were verified by the LCR, as presented in **Figure 1**. The *UEL*s (eight blue dots in Fig. 1c) calculated by the classic LCR were in good agreements (relative error (%) = 3.65) with those calculated by the M-PDM, which indicated the reliability of the M-PDM.

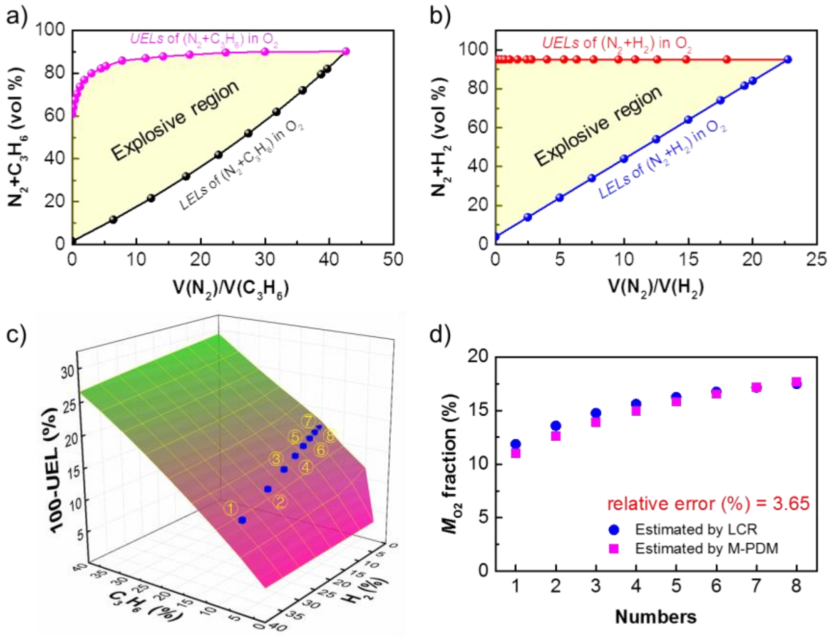

Figure 1. (a) Explosion limits of C_3H_6 and N_2 mixture in O_2; (b) Explosion limits of H_2 and N_2 mixture in O_2; (c) *UEL*s of C_3H_6, H_2, and N_2 mixture in O_2 estimated by the M-PDM (3D image) and the LCR (eight blue dots); (d) Error analysis of *UELs* estimated by the M-PDM and the LCR.

Reactor performance was further studied by the optimizations of the PBR in the gPROMS. The optimized values for the decision variables were as following: T_{in} = 423 K, u_0 =0.05 m/s, $P_{in}(H_2)$ =14.32 kPa, $P_{in}(C_3H_6)$ =17.12 kPa and $P_{in}(O_2)$ =28.02 kPa. With these optimized decision variables, the H_2 efficiency could be maximized to 17.4 %, and meanwhile all the constraints were satisfied. Moreover, the C_3H_6 conversion and PO selectivity were enhanced to 10% and 92.6%, respectively, even achieving/exceeding the targeted values (10% and 90%, respectively) [3]. The outlet PO fraction was increased to 2.8%, being comparable to that of ethylene oxide (1.0-3.0%) in commercial plants [4].

4. Conclusions

In summary, we proposed the modified proportional distribution method to estimate the explosion limits of C_3H_6, H_2 and N_2 in O_2, which were validated by the classic Le Chatelier Rule. Combined with the obtained explosion limits, process optimizations of the reaction in a packed-bed reactor were done in gPROMS under safe operation conditions. The optimized results showed that the H_2 efficiency (17.4%) was well enhanced, with the C_3H_6 conversion (10.0%) and PO selectivity (92.6%) achieving/exceeding the targeted values (10% and 90%, respectively). Moreover, the optimized outlet PO fraction reached to 2.8 %, being comparable to that of ethylene oxide (1.0-3.0%) in commercial plants. The above results showed the feasibility of commercial PO production by the direct propylene epoxidation with H_2 and O_2.

References

[1] X. Feng, X.Z. Duan, G. Qian, X.G. Zhou, D. Chen, W.K. Yuan, Appl. Catal. B-Environ. 150-151(2014) 396-401.
[2] M.K. Lu, G. Wang, Z.H. Zhang, X.Z. Duan, W.K. Yuan, X.G. Zhou, Chem. Eng. Process. (2017) In Press.
[3] A.K. Sinha, S. Seelan, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 116 (2004) 1546-1548.
[4] B. Elvers, S. Hawkins, W. Russey, Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., VCH, Weinheim, 1985.

Keywords
Explosion limits estimation; Direct propylene epoxidation with H_2 and O_2; Optimization; Safe operation