
AIDIC EFCE
ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Ethylene Oxide Production: Why tubular reactors?

Christopher DiGiulio

Honeywell UOP, 25 E. Algonquin Road, Des Plaines, IL 60017-5017

Christopher.digiulio@honeywell.com

Highlights

- Lefort's Ag-based catalyst enabled Ethylene Oxide Production by direct oxidation
- Several unique features of process made tubular reactors the preferred option
- Tubular reactors combine chemical reaction engineering and heat transport phenomena

1. Introduction

The worldwide production of ethylene oxide (EO) currently exceeds 20 MM t/yr. Since 1937, when Union Carbide opened its first EO plant, partial oxidation of ethylene has been performed using the Ag-based catalyst system developed by Theodore Lefort. The reaction network consists of the desired, mildly exothermic pathway leading to the formation of EO and the highly exothermic combustion of either ethylene or EO to from CO_2 and H_2O. On the commercial scale, the chemistry is conducted using shell and tube heat exchange reactors, or more simply just "tubular reactors." The catalyst is contained within thousands of small diameter tubes typically in the range of 20 – 40 mm. On the shell side, a cooling medium is used to remove the heat of reaction. To avoid thermal runaway, the tubular reactor must be carefully controlled by combining chemical reactor engineering and heat transport phenomena to yield a solution capable of safely producing EO, with a selectivity up to 90%.

2. Methods

Relevant kinetic parameters were obtained from existing peer reviewed literature. Modeling was performed using Athena Visual Studio.

3. Results and discussion

It may seem obvious that ethylene epoxidation should be carried out in tubular reactors, but numerous technical hurdles needed to be overcome to commercialize this technology. First and foremost, a catalyst capable of conducting the chemistry was required. Over the past 80 years, numerous advancements have been made in catalyst formulations, but no substitute for the silver based system has been demonstrated. Second, the Ag-based catalyst works under relatively mild conditions, which enables users to select boiling water on the shell-side as a cooling medium. Third, the chemistry is not limited by equilibrium, but significant flammability concerns for both the combined feed and products are present. Being able to run under mild conditions is important since the flammability envelope grows as temperature rises. Fourth, thermal destruction and/or sequential oxidation of the product encourages low per-pass conversion. Low conversion means that the partial pressures of the reactants are approximately constant. Therefore, the rate of reaction along the length of the tube and corresponding heat release also are approximately constant. Finally, the price difference between ethylene and ethylene oxide was sufficient to justify the capital expenditure and operating expenses resulting from operations at low per pass yield.

The results shown in Fig.1 illustrate the hypothetical difference between operation in a tubular, isothermal reactor (A) and a more traditional fixed-bed, adiabatic reactor (B). In the case of the tubular reactor the conversion of ethylene is approximately 10%, with a selectivity to EO of 80%. Unfortunately, the adiabatic reactor experienced a runaway, with reactor exit temperatures near 800 °C and no EO in the final product. In the runaway scenario O_2 becomes limiting the reagent and is completely consumed. In both cases ethylene conversion was approximately 10%. The inlet temperature for the adiabatic reactor could have been lowered to avoid thermal runaway, but the fixed bed reactor is still very susceptible to thermal runaway. For example, a reactor inlet temperature of 168 °C delivers an ethylene conversion of 6.9% with 82% selectivity to EO. Increasing the temperature to 170 °C triggers another runaway.

During the lecture, additional tubular reactor design parameters will be discussed including the impact of heat transfer coefficients, tube diameter, length of the catalyst bed, different modes of operation (e.g., boiling cooling medium vs high flowrate pump-around).

Research continues on identifying an alternative EO production route, but at present EO is still produced by direct oxidation of ethylene in tubular reactors. Thus, the industrial focus continues to be on catalyst improvements that benefit the tubular reactor system -- namely, higher activity and higher selectivity catalysts, with the goal to also shut down the sequential combustion pathway. Lower Ag catalysts with longer run lengths are also desired, but selectivity continues to be the primary driver, as each 1% (absolute, i.e., 89 to 90%) increase in selectivity results in approximately 1 MM $/yr reduction in ethylene destruction costs.

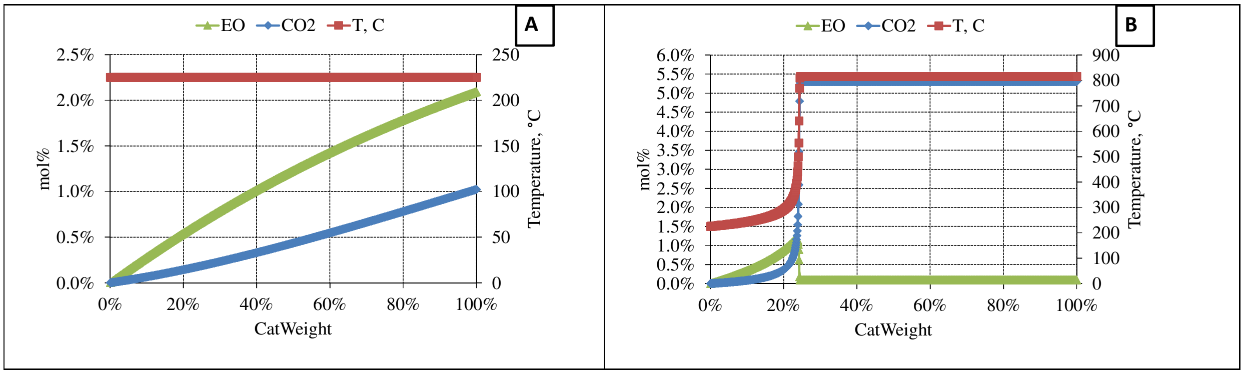

Figure 1. Identical reactor inlet temperatures (225 °C), reactor pressure (18 atm) for (A) an isothermal tubular reactor and (B) an adiabatic, fixed bed reactor. The same kinetic model and parameters were used for each simulation.

4. Conclusions

Careful control of process conditions to avoid thermal runaway and maintain high selectivity to EO are of the utmost importance. Tubular reactors are ideal for this application because the Ag-based catalyst works under relatively mild conditions and thermal destruction and/or sequential oxidation of the product encourages low per-pass conversion. Key design parameters for EO tubular reactors will be discussed with examples provided via mathematical modeling.

References

[1] C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, John Wiley and Sons, New York, 2006. p. 597.
[2] S. Rebsdat, D. Mayer. Ethylene Oxide, Ullmann's Encyclopedia of Industrial Chemistry, March 15, 2001.
[3] P.D. Klugherz, P. Harriot. AICHE Journal, Vol. 17, No. 4, pp 856 – 866.
[4] W. Diao, C.D. DiGiulio, M.T. Schaal, S. Ma, J.R. Monnier, Journal of Catalysis (2015), 322, 14-23.

Keywords
Ethylene Oxide, Tubular Reactors

CHRISTOPHER D. DIGIULIO

160 West Harrison St, Elmhurst IL, 60126
PHONE: (580) 618-2017 **EMAIL:** CHRISDIGIULIO@OU.EDU

EDUCATION

Doctor of Philosophy in Chemical Engineering, Dec. 2012

The University of South Carolina – Columbia, SC

Dissertation: "Investigation of Three-Way (TWC), Lean NO_x Trap (LNT) and Selective Catalytic Reduction (SCR) Catalysts for Control of NO_x Emissions from Lean-Burn Engines"

Advisor: Dr. Michael D. Amiridis

Bachelor of Science in Chemical Engineering / Minor in Mathematics, May 2008

The University of Oklahoma – Norman, Oklahoma

WORK EXPERIENCE

Honeywell UOP (Jan. 2013 – Present)

Senior R & D Scientist/Engineer, Olefins and Detergents Development
New Product Development Team Leader since 2015.

Technology Areas

1. Oleflex (2013 – Current)
   - Paraffin Dehydrogenation
   - Emphasis on kinetic modeling for entire Oleflex portfolio
2. Detergents (2016)
   - Linear Alkyl Benzene Complexes (Pacol, Define, Pep, Detal)
3. Oxidative dehydrogenation of Butene for On-Purpose Butadiene (2013 – 2016)
4. MTBE Decomposition for High Purity Isobutylene (2013)

HONORS, ACHIEVEMENTS AND DISTINCTIONS

- Honeywell Silver Bravo Award for Rapid Development of a kinetic model
- Honeywell - Six Sigma Green Belt

PATENTS AND PATENT APPLICATIONS

1. C.D. DiGiulio. Integration of an N-C4/N-C4=/BD Separation System for On-Purpose Butadiene Synthesis. US20150376091, 2015.
2. 20170204025 – Application – MTO process for enhanced production of Propylene and high value products
3. 20170204025 – Continuation in Part (CIP) of US20150376091 above.
4. One additional patent has been filed and two more are authorized for filing.

BOOK CHAPTERS

Myers Handbook. "TPC/UOP Oxo-D Process." J.J. Senetar, C.D. DiGiulio, J. Blommel, J. Duff, J. Horn, C. Maat, M. Nutt.

PEER-REVIEWED JOURNAL ARTICLES

1. W. Diao, C.D. DiGiulio, M.T. Schaal, S. Ma, J.R. Monnier. "*An investigation on the role of Re as a promoter in Ag-Cs-Re/α-Al_2O_3 high-selectivity, ethylene epoxidation catalysts*" **Journal of Catalysis** (2015) 322, 14-23.
2. C.D. DiGiulio, J.A. Pihl, J.E. Parks II, M.D. Amiridis, T.J. Toops. "*Passive-NH_3 selective catalytic reduction (SCR): Understanding NH_3 formation over close-coupled three way catalysts (TWC).*" **Catalysis Today** (2014) 231, 33-45.
3. C.D. DiGiulio, J.A. Pihl, J.-S. Choi, J. Parks II, M.J. Lance, M.D. Amiridis, T.J. Toops. "*NH_3 formation over a Lean NO_X Trap (LNT) system: Effects of lean/rich cycle timing and temperature.*" **Applied Catalysis B: Environmental** (2014) 147, 698-710.
4. C.D. DiGiulio, V.G. Komvokis, M.D. Amiridis. "*In situ* FTIR Investigation of the Role of Surface Isocyanates in the Reduction of NO_X by CO and C_3H_6 over model Pt/Ba/Al_2O_3 and Rh/Ba/Al_2O_3 NO_X Storage and Reduction (NSR) Catalysts." **Catalysis Today** (2012) 184, 8-19. (*Also featured in a cover story in Chemical and Engineering News: Vol. 90 (Iss. 21) pp. 10-16).