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A sustainable process design to produce diethyl oxalate considering NO_x elimination

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A B S T R A C T

Diethyl oxalate (DEO) is widely used in fine chemical industry. In comparison with traditional esterification process, carbon monoxide coupling process is a novel routine for DEO production. This environmentally friendly process provides better selectivity and yield. Its unique feature is that a closed regeneration-coupling circulation is formed. Toxic byproduct-nitric oxide (NO) from coupling reaction is recycled to re-produce ethyl nitrite through regeneration reaction. This avoids significant amount of NO_x emission. However, due to a few NO_x emission, a contaminant handling system is applied for environmental protection. A systematical environmental analysis is also carried out to assess this process. Regeneration-coupling circulation brings interaction behaviors and some trade-offs including reactor size and recycle flowrate, regeneration and coupling reaction, loss of reactants and NO emission. Thus, a rigorous steady simulation is established to investigate these trade-offs. Then DEO process is optimized to obtain the optimal design. Finally a more economic flowsheet to produce DEO is proposed.

1. Introduction

Diethyl oxalate (DEO) is an important intermediate in chemical industry, especially in pharmaceutical industry, which can be utilized for the synthesis of high value drugs, dyestuff and as the useful solvent for spices (Fang et al., 2003; Meng et al., 2003). The traditional technology for the synthesis of DEO is esterification process between oxalic acid and alcohol using strong acids as catalysts, which, however, will cause serious environmental pollution and severe corrosion to equipment (Fable, 1980; Kirk, 1980). The fact that the esterification reaction is reversible decides that the per-conversion is low, thus a large amount of recycle and toxic methylbenzene or benzene is required to obtain adequate conversion. Moreover, oxalic acid as main raw material is of high production cost. Therefore, a more environmentally friendly and economic process for DEO production is significantly valuable.

A sustainable process based on carbon monoxide (CO) coupling reaction has been considered as an alternative method for DEO production. Furthermore, it has been regarded as a key intermediate step to revolutionize traditional route for ethylene glycol (EG) and oxalic acid production. DEO can further hydrogenated to synthesize EG and hydrolyzed to form oxalic acid (Yu and Chien, 2017). This process consists of two reactions: coupling and regeneration reaction. In coupling reaction, the catalytic reaction of CO and ethyl nitrite (EN) forms a desired product DEO and diethyl carbonate (DEC) as byproduct as well as toxic component- nitric oxide (NO). In regeneration reaction, NO is recycled and react with ethanol (ETOH) and oxygen to form EN and water. The schematic concept of DEO process is shown in Fig. 1. The surprising feature of this process is that a closed stream circle arises and NO from coupling reaction is recycled to re-produce EN. This feature leads to high atom utilization and less waste produced. From the perspective of product separation, the boiling point difference of products is quite large, therefore it is easy for purification of products. Notice that raw materials have wide range of sources and relatively low price. CO can be derived from syngas that can produced by various sources such as coal, biomass and natural gas while oxygen can produced from air separation. Therefore these main reasons contribute to the fact that the coupling-regeneration circulation draw great interests, especially coupling reaction.

Notice that there are a few amount of NO_x emissions to environment in this process. Nitrogen oxides (NO_x) is major air pollutants that can cause serious environmental problems, for instance, acid rain, smog formation, global warming, and ozone layer weakening (Skalska et al., 2010; Boningari and Smirniotis, 2016). Moreover, the fact that public awareness of environmental protection is getting stronger results in more stringent environmental laws and

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Nomenclature

Acronyms
AC Condenser area (m^2)
AR Reboiler area (m^2)
CO Carbon monoxide
DEC Diethyl carbonate
DEO Diethyl oxalate
EG Ethylene glycol
EN Ethyl nitrile
ETOH Ethanol
HP High-pressure steam
LP Low-pressure steam
ID Column diameter(m)
NO Nitric oxide
NO_2 Nitrogen dioxide
NO_x Nitrogen oxides
NF Feed location into the column
NF_{opt} Optimal feed location into the column
NT Total number of trays
PEC Pollutant emission cost
QC Condenser duty (kW)
QR Reboiler duty (kW)
RIO Incremental return investment
SNCR Selective non-catalytic reduction
SCR Selective catalytic reduction
TAC Total annual cost

Capital letters
E_a Activation energy(kJ/kmol)
A Pre-exponential factor
NH_3 Ammonia

Lower case letters
k_i Rate constant of reaction($i = 1$-4)

Greek symbols
$\Re_i$ Reaction rates ($i = 1,2,4$) (kmol/kgcat-s)
$\Re_i$ Reaction rates ($i = 3$) (kmol/m^3-s)

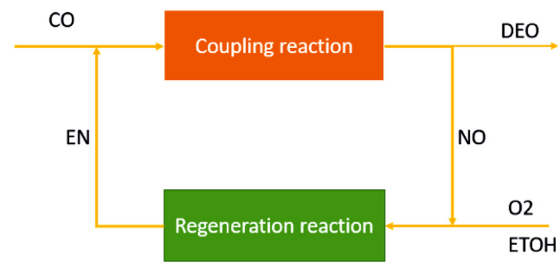

Fig. 1. Schematic process of DEO.

regulations. Thus, environment issues should be considered during the design of process.

There are fairly numerous literatures and books contributed to the design and optimization of chemical process (Turton et al., 2012; Luyben, 2011; Gong and You, 2017a, 2017b, 2018; Yu and Chien, 2017; Kim et al., 2017). Gong and You combine the product distribution optimization of chemical reaction with superstructure optimization of the process flowsheet and then apply this approach to an integrated shale gas processing and chemical manufacturing process. A superstructure including different technology/process alternatives is first proposed. And a MNLP optimization model is proposed to determine the global optimal design, which is solved by a tailored global optimization algorithm (Gong and You, 2018). They also propose a general consequential life cycle optimization (LCO) model for process design and develope a tailored global optimization algorithm to obtain the global optimal design. This approach can simultaneously optimizes environmental impacts and economic performance. A case with process design of algal renewable diesel production is used to illustrate this approach (Gong and You, 2017a). Turton et.al introduce and discuss the principle of process design and optimization. They illustrate there are two type of the optimization referred to topological optimization and parameter optimization. Topological optimization deals with the arrangement of process equipment while parametric optimization focuses on the operating variables. Luyben also introduces the principle of process design. The heuristic way or a sequential iterative optimization algorithms is used to study the trade-offs of design variables (process parameters) and obtain the optimal economics in typical chemical process (Luyben, 2011). Yu and Chien propose an ethylene glycol (EG) production process by the dimethyl oxalate (DMO) hydrogenation. And then a sequential iterative optimization algorithms is applied to obtain the optimal design (Yu and Chien, 2017). A sequential iterative optimization algorithms is applied in this article. In this method, the design variable is changed one at a time and then the whole process is re-simulated using new design variables, which is regarded as more time-consuming way for optimization. There are also some other approach of simultaneous optimization through solvers which is more efficient in calculation. However, a big convergence may occur in calculation during simultaneous optimization when there are big interactions for a complex reaction-separation process with several recycled stream. Through sequential iterative optimization algorithms, the interaction of design variables and trade-off can also be illustrated clearly, which can contribute to a better understanding for this process. Hence, the authors select the sequential iterative method in this article.

There are quite numerous open literatures studying coupling reaction (Fenton and Steinwand, 1974; Chen et al., 1993; Ma et al., 1995; Uchiumi et al., 1999; Su et al., 2000; Jiang et al., 2001; Li et al., 2001, 2003, 2005; Fang et al., 2003; Meng et al., 2003, 2004; Gao et al., 2005; Gao et al., 2011; Li et al., 2011a;Ya and Zheng, 2012; Jiang et al., 2012) (Ji et.al., 2009). However, most of them focus on coupling reaction catalyst (Fenton and Steinward, 1974; Uchiumi et al., 1999; Jiang et al., 2001; Gao et al., 2011; Ya and Zheng, 2012) and reaction mechanism (Gao et al., 2005; Ya and Zheng, 2012). In addition, there are some other contributions relevant to thermodynamic (Li et al., 2011b) and kinetic analysis (Chen et al., 1993; Ma et al., 1995; Li et al., 2003, 2005; Meng et al., 2003, 2004). A few studies also contribute on concept design of the process (Wang et al., 2000a, 2000b). Nonetheless, there is no complete design flowsheet considering environment protection and systematical environment analysis. In addition, there is no optimization or further study based on economics. In this article, a complete design flowsheet with contaminant handling system is proposed and optimized. Due to the presence of EN, more moderate condition is selected considering its decomposition temperature and critical pressure. An economic index-income is proposed including pollutant emission cost and a flowsheet with better economic performance is established with a rigorous simulation study. A systematical environment analysis is also carried out to assess and compare the environment impact with and without contaminant handling system. In this article, the work can lay a solid foundation for further research.

2. Process description

The DEO process studied in this paper is a simplified version of the actual industrial process.