

Design of a Process for the one-Pot Bio-Ethylene Oxide Production

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The possibility to exploit renewable sources for the production of bulk chemicals is attractive and bio-ethanol has been recently proposed as platform to produce hydrogen via steam reforming and bio-ethylene by dehydration. Another compound with huge industrial applications is ethylene oxide, which may be in principle obtained in two steps following the route bioethanol → bio-ethylene → bio-ethylene oxide. Recently, a one-pot synthesis has been proposed. Based on that, the to design from the grass roots a new production plant, including the reactive and purification sections, has been developed, to exploit it industrially after checking its economic sustainability. In this work, the first step for design, i.e. kinetic modelling and reactor design, will be presented and discussed.

A reaction pathway with parallel and consecutive reactions has been hypothesized and the kinetic parameters for the five reactions drawn have been retrieved by regression of experimental literature data. The model employed preliminarily is a power law pseudo-homogeneous one, used for a first sizing of the reactor and basic assessment of the technology. Three shell&tube heat exchange reactors were implemented to control the exothermicity of the reaction, with simultaneous steam production. Three catalyst beds were used in such reactors (200, 500 and 2,000 kg) with intercooling. 99.5 % ethanol conversion and 84 % selectivity to ethylene oxide were achieved, with ca. 90 kmol/h productivity, starting from the bioethanol production of a commercial bio-refinery as preliminary criterion for sizing.

1. Introduction

Ethylene oxide is a colourless, flammable and highly reactive gas, due to its strained ring, which is very easy to open. Nowadays ethylene oxide is used as disinfectant, sterilizing agent and fumigant when it is used as a nonexplosive mixture with N₂, CO₂, or dichlorofluoromethane, but it is mostly converted into other derivatives. Ethylene oxide is produced by direct oxidation of ethylene with air or oxygen over Ag-based catalysts with yearly worldwide production capacity of 1.5 10⁷ tons (Pinaeva, 2020).

Focusing on the green chemistry routes to produce ethylene oxide, ethanol seems to be a promising starting material. Indeed, it may be conveniently transformed into bio-ethylene (Tripodi, 2019), representing a renewable-based alternative to this product. Even more interestingly, experiments for the one-pot transformation of bio-ethanol into bio-ethylene oxide have been described by Lippits and Nieuwenhuys (Lippits & Nieuwenhuys, 2010a, 2010b) and by Martins and Mota (Martins & Mota, 2014) on the lab scale. The results show that it is possible to oxidize ethanol with O₂ to ethylene oxide over Cu, Ag or Au-based catalysts, supported on γ-Al₂O₃ and promoted by Li₂O and CeO₂. The reaction is interesting, because it could simplify present-day processes from renewables as, for example, the Croda bio-ethylene process, based upon bioethanol dehydration followed by the traditional epoxide production (Croda International Plc, 2020). This paper explores the possibility of a one-step bioethanol-ethylene oxide production, because it is a solution for a new, easier and more sustainable ethylene oxide process. The possibility to simplify in a direct conversion the process may help to improve the economic feasibility, which is the key problem of biorefinery processes when

compared with classical production plants. Hence, a fully integrated plant has been designed with target productivity of 90 kmol/h of ethylene oxide, 99.7 % pure. In this work, only the development of the kinetic model and its implementation to basically describe the reactive section will be discussed.

2. Models and methods

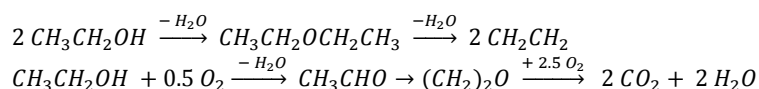
2.1 Kinetics

The calculation of the kinetic parameters has been carried out using literature experimental data based on Ag- and Cu- based catalysts (Lippits and Nieuwenhuys, 2010a) or on Au-based ones (Lippits and Nieuwenhuys, 2010b), which are not sufficiently complete to allow rigorous kinetic modelling, but allow a satisfactory representation of the catalyst performance and permit preliminary reactor design. The original study presents a comparison of different types of catalysts: for this work we have chosen the Au-Li₂O/Al₂O₃ formulation, which showed the best performance in terms of bioethanol conversion and selectivity to ethylene oxide.

Based on the analysis of the experimental data (Lippits and Nieuwenhuys, 2010b), exemplified in Figure 1, ethanol starts to convert very quickly, apparently leading to a non detected intermediate, as denoted by the incomplete carbon balance, which then forms ethylene oxide. Then over 250 °C ethanol and ethylene oxide start to over-oxidise to CO₂ + H₂O. Ethylene formation seems to follow a different pathway, independent from ethylene oxide formation, likely starting from ethanol and having diethyl ether as intermediate (De Wilde, 2013).

The carbon loss below 180 °C was attributed to acetaldehyde formation, not seen at the GC-mass analytical system (similar retention and equal molar weight of ethylene oxide (Silbaugh, 2018)), also based on other studies involving acetaldehyde formation using similar catalysts and reaction conditions (Martins & Mota, 2014; Silbaugh, 2018; Rossetti et al., 2015a and 2015b). The carbon loss over 220 °C instead, can be supposed as CO not measured or not reported.

Based on this, the following reaction pathway has been developed. Due to the intrinsic limits of these suppositions, the highest weight is given to the data in the temperature range between 180 and 250 °C, i.e. where ethylene oxide selectivity presents its maximum and the carbon loss is nearly nil, the most interesting conditions for the reaction.



A pseudo-homogeneous powerlaw kinetic model was chosen for this analysis, Eq(1), since the available dataset prevents the safe estimation of adsorption parameters in a Langmuir-Hinshelwood kinetic model. The kinetic constant k_0 at the reference temperature T_0 and the activation energy (E_a) were regressed for every reaction, leading to a total of 10 parameters for 99 entries of the global dataset.

The influence of temperature on the kinetic constant value was expressed according to the Arrhenius equation (Eq(2)):

$$r_i = k_i \prod_{\text{reagent } j} y_j^{a_j} \quad (1)$$

$$k = k_0 \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2)$$

$$\int dn_i = \int r dw \quad (3)$$

The regression was carried out by numerical integration of the mass balance of the PBR, Eq(3), using the Runge-Kutta method as implemented in the Ordinary Differential Equation function (ODE 45) of Mathworks[®] Matlab r2020 software.

The equation reported above is a formulation for a packed bed reactor (PBR) model, approximately representing the experimental mini-reactor, where n are the molar flows of the different species i , dw the catalyst mass occupying the control volume and r is the reaction generation term for species i referred to the mass of catalyst. The reaction was run at atmospheric pressure, molar ethanol/oxygen ratio equal to 1 and a 9:1 nitrogen dilution, while feeding azeotropic ethanol. Since information was not available to assess the

possible axial dispersion it was considered negligible and an ideal PBR was considered, which is consistent for a mini-plant. Also, considering the dilution and the small catalyst mass, isothermal conditions were hypothesized.

3. Results and discussion

3.1 Kinetics

At the first try, the exponents of the powerlaw rate equation were set equal to the stoichiometric coefficients, but later they were varied to improve the fit as detailed in Table 1. Data fitting returned the results shown in Figure 1 and Table 1.

Table 1: Kinetic data. Experimental runs carried out at atmospheric pressure.

ID	Reaction	Rate equation	k_0 (mol s ⁻¹ kg ⁻¹)	E_a (J mol ⁻¹)	T_0 (°C)
1	$EtOH + 0.5 O_2 \rightarrow CH_3CHO + H_2O$	$r = k y_{EtOH} y_{O_2}$	12	33,000	220
2	$CH_3CHO \rightarrow (CH_2)_2O$	$r = k y_{CH_3CHO}$	1.7	45,000	220
3	$(CH_2)_2O + 1.75 O_2 \rightarrow 1.5 CO + 0.5 CO_2 + 2 H_2O$	$r = k y_{(CH_2)_2O} y_{O_2}$	0.3	85,000	220
4	$2 EtOH \rightarrow EtOEt + H_2O$	$r = k y_{EtOH}^{1.5}$	4.0e-04	145,000	220
5	$EtOEt \rightarrow 2 (CH_2)_2 + H_2O$	$r = k y_{EtOEt}$	7.0e-05	190,000	220

The plots report an overall acceptable to good fit, better reproducing the data at lower temperature than at higher ones. They are at least suitable for the purpose of the present research, which is a preliminary design of a full scale plant for the one-pot production of ethylene oxide from bioethanol. For sure, however, the original dataset availability is the weakest part of this work, which needs improvement and a proper control on the reactor layout to refine the kinetic parameters. Moreover, it would be more appreciable to extend the dataset to include poorly assessed species (CO and acetaldehyde) and to possibly upgrade the model from a pseudo-homogeneous to a heterogeneous LHHW or Eley-Rideal one, or to make some micro-kinetic considerations. The effect of pressure should also be explored.

The fitting quality is particularly satisfactory in the temperature range of interest, well predicting the ethanol conversion and the selectivity to ethylene oxide. High temperature prevision underestimated the productivity of CO₂. However, this product does not affect the overall separation scheme, being discharged in the very first absorption column after the reactive section, allowing a sufficiently reliable design of the separation section.

3.2 Reactors layout in Aspen Plus®

The equations reported above were implemented in Aspen Plus®. An array of three packed bed reactors (PBR) with counter current cooling with water was designed. Between the first two blocks an intercooler was also included to better adjust the inlet temperature to the second stage. The PFD of the reaction section is sketched in Figure 2.

A biorefinery productivity of 50,000 tons per year of ethanol was considered as basis, thus a 133 kmol/h of 90 mol% bioethanol was considered as feed (AA.VV., Ullmann's, 2002), mixed with 632 kmol/h of air (N₂ was inert and used as thermal buffer). The feed pressure was varied up to 15 bar.

Multi-tubular heat-exchanger type reactors have been selected, with catalyst effectiveness appropriately estimated and included in preliminary sizing. Since the reaction is strongly exothermic, the first reactor was loaded with a limited amount of catalyst to ensure that the heat released must not exceed the cooling capacity, to avoid severe runaway (AA.VV., Ullmann's, 2002). A compromise between catalyst charge, tube diameter and cooling water pressure was needed to appropriately control temperature as desired. The three reactors loaded a catalyst weight of 200, 500 and 2,000 kg, respectively. AISI 304 stainless steel tubes ranging from 1" to 2.5" were considered. The first catalyst bed is the one with the highest heat exchange need but smallest size and viceversa for the third bed.

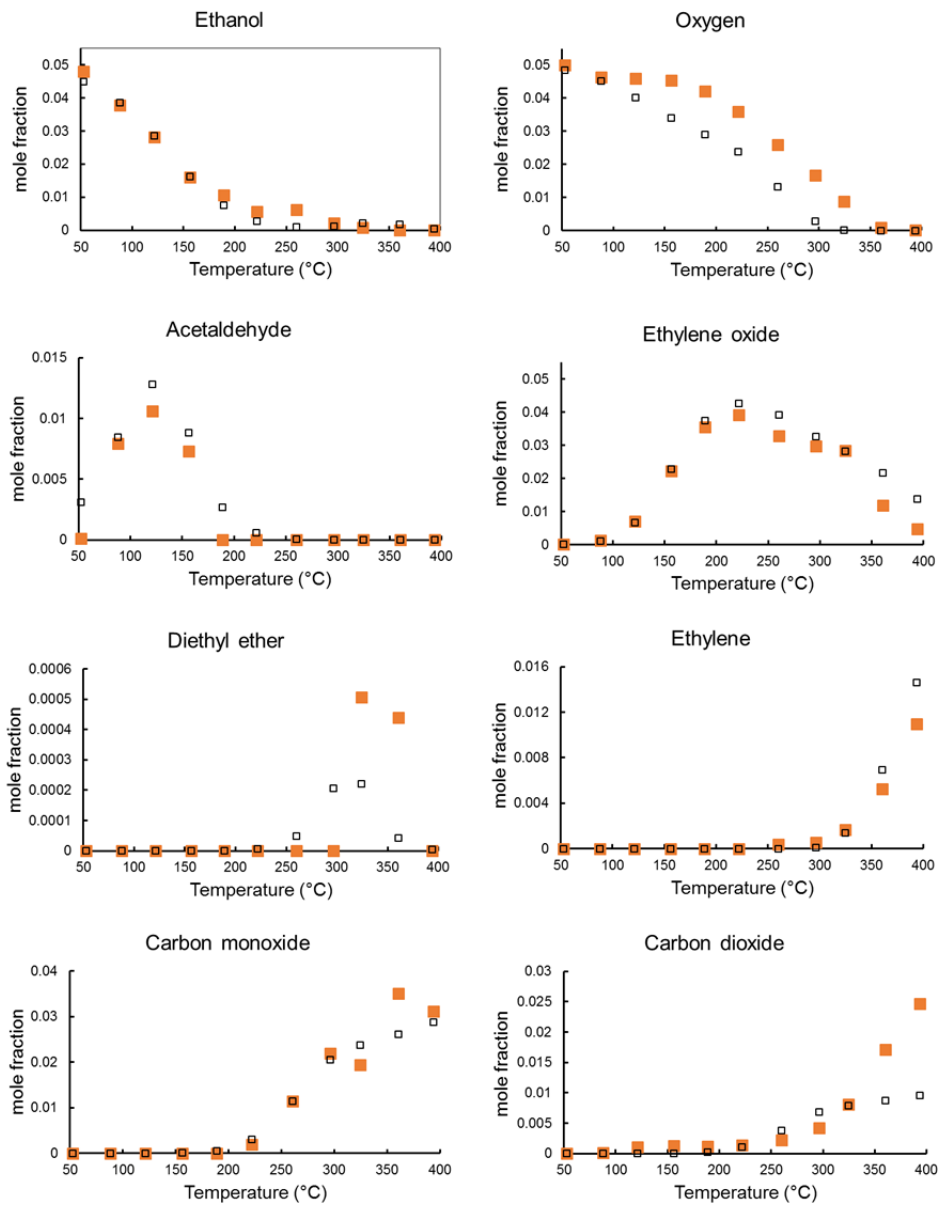


Figure 1: Comparison between the experimental data (full symbols) and calculated ones with the parameters of Table 1 (empty symbols).

Table 2: Summary of the main parameters used in reactors design.

Parameter	UOM	Reactor 1	Reactor 2	Reactor 3
Particle size	mm	6.0	6.0	6.0
Particle porosity	-	0.72	0.72	0.72
Particle tortuosity	-	2	2	2
Thiele modulus	-	8.16	6.21	3.17
Effectiveness factor	-	0.32	0.41	0.65
Pressure drop	bar	0.41	0.36	1.1
Inlet temperature	°C	165	203	220
Liminar coefficient	$W m^{-2} K^{-1}$	450	360	300
Tube number	-	600	400	200
Catalyst load	kg	200	500	2000
Bed porosity	-	0.4	0.4	0.4
Tubes outer diameter	mm	30.1	45	66.9
Boiling water P	bar	4	7	10

Acceptable pressure drops were allowed for the three catalytic beds, respectively, as calculated from the Ergun equation based on the selected particle size and the parameters reported in Table 2.

Boiling water at different pressure was used as coolant. This point however needs much better refinement since the system revealed very sensitive to boiling water pressure, so care is needed for safety assessment of the system. The addition of the intercooler helps the control of this very critical parameter.

As an example of results, in Figure 3 the temperature vs. conversion plot across the three catalyst beds is reported. Overall the system has been designed to achieve 99.4 % ethanol conversion with 84 % selectivity to ethylene oxide. The first reactor is the most sensitive to runaway, so particular care is devoted to the optimization of its catalyst particle size, pipe size and loading. A temperature raising up to 240°C was predicted for the first reactor, which falls in the high prediction capability range of the kinetic model for products distribution. The same holds for the other two reactors (always operating below 250°C), with more limited temperature excursions.

As final remark, the product can be first recovered after the reaction section with an absorption column (releasing most N₂, CO, O₂ and CO₂ in gas phase, followed by a stripping column. A further distillation column separates crude ethylene oxide as distillate, while acetaldehyde, diethyl ether and minor impurities as bottom product. Further purification options for ethylene oxide and for the recovery of by-products are also possible.

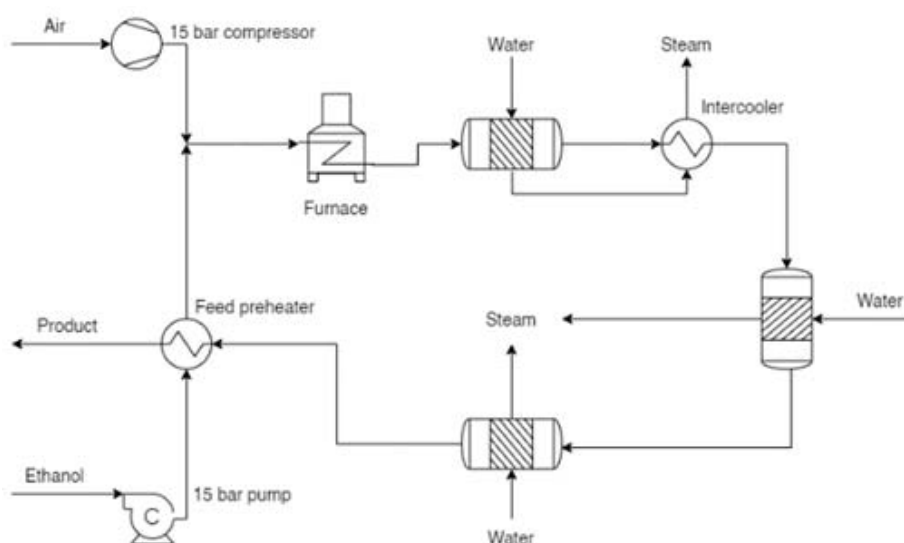


Figure 2: Process Flow Diagram of the reactors section.

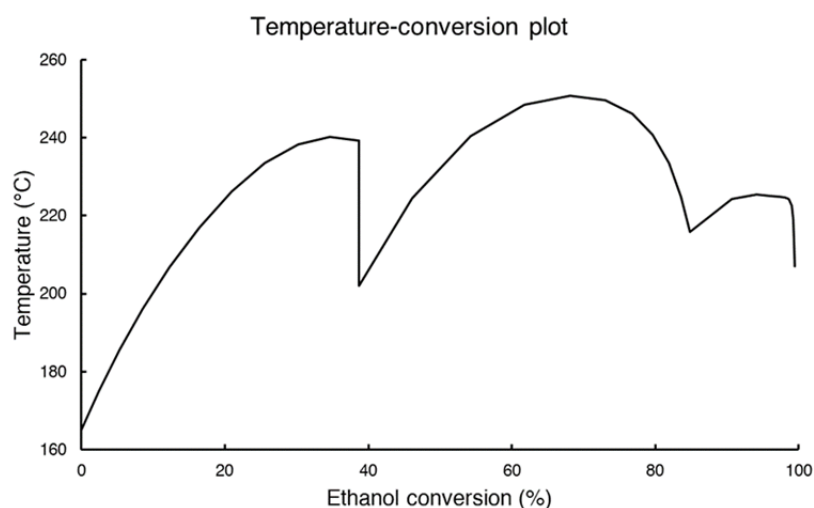


Figure 3: Temperature vs. conversion profiles of the three reactors.

4. Conclusions

A new plant concept has been designed from the grass route for the one-pot production of ethylene oxide from bioethanol, of which the reaction section is here detailed. Literature activity data were used to calculate kinetic parameters according to a set of five parallel and consecutive reactions. The fit and significance of the retrieved parameters was reasonable and the pseudo-homogeneous kinetic model was implemented in Aspen Plus® for preliminary plant design and reactors sizing. Specifically, three reactors were successfully designed: temperature and pressure drop were finely controlled by changing the particles size, catalyst load in each reactor, the coolant flowrate and pipe size. Conversion and selectivity reached satisfactory values.

A first flowsheet for the system in analysis had been successfully designed: such reactors configuration is in fact capable of converting more than 99 % of ethanol into ethylene oxide, with a selectivity around 84 %. The separation section, not described here for the sake of synthesis, can recover around the 98 % of ethylene oxide produced in the reactive section, 90 % as pure ethylene oxide and 8% as pure ethylene glycol, further recovered through a reactive distillation column.

These results can be surely improved with a more detailed analysis on robust and properly collected experimental data, with a design of experiments collected on purpose to explore the model hypothesized and with a richer dataset to allow the discrimination among different and more complete models. However, this system already allows a basic feasibility assessment of the process.

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