

Short communication

## Process-oriented approach towards catalyst design and optimisation

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## ABSTRACT

Translation of catalysts developed in academia to industrial end-users remains a challenge due to a lack of knowledge about the impact of catalyst attributes on the whole process and vice versa. A systematic methodology is proposed that assesses these in terms of Key Performance Indicators (KPIs). As a case study, the dehydration of butanol to butenes and dibutyl ether is considered over H-ZSM5 and H-Beta catalysts. It is demonstrated that catalysts should be designed for complete conversion and high butene selectivity, as removal of unreacted 1-butanol requires a complex separation due to the thermo-physical properties of the product mixture.

### 1. Introduction

Catalysis is a fundamental but societally under-recognised technology that impacts upon the present and future aspects of everyday life, especially in the food-water-health-energy nexus. Without effective catalysts, the sustainable manufacture of many pharmaceuticals, agrochemicals, commodity chemicals and polymers would not be possible [1]. Considerable resources are expended in the invention, development, and application of catalysts, and it is essential to consider the efficiency with which this is done. The traditional catalyst design approach is often based on a discovery by serendipity. This usually starts in a research lab by identifying a valuable chemical transformation, then iteratively synthesising, modifying, and testing to improve the activity, selectivity, and scope of an application using simple model compounds, and finishes with the publication of the data. When industry identifies a product that it seeks to make, the project team draws on the literature and tries, in preference, to source rather than make the catalysts de novo. The problem is that comparatively few catalysts are commercially available and, whether homogenous, heterogeneous or biological, many are difficult or time-consuming to manufacture. Additionally, reproducing research lab-scale data on an actual plant can be difficult even when a commercial catalyst is employed. Furthermore, the complexity of the chemical systems considered in the industry is often far more significant than in the research lab, with the latter often using pure, idealised feed streams, without consideration of potential issues posed by impurities that may act as poisons. Also, due to the scale and duration

of production, the industrial process is far more demanding in terms of the productivity, consistency and lifetime required, which impact upon the projected product cost, quality, and the overall sustainability of the process.

One of the most significant difficulties with this approach is the uncertainty with which the desired performance can be achieved at an industrial scale due to many route and/or process selection options being available during the early stages of development, particularly related to downstream separation. Furthermore, a small change in the catalyst can completely alter the design of the downstream separation operations [2]. For these reasons, catalyst development is resource-intensive, with a long and linear path giving only incremental improvements through screening, mechanistic, and process understanding. Even the catalyst with the “best” lab-scale performance (e.g., high activity and stability) might never find its way into industrial practice as the specific process details required for its implementation might not be commercially attractive or might necessitate employing solvents, reagents, and/or conditions that may be partially or fully incompatible [3]. Given the significant effort in lab-scale catalyst development, steering research and development resources towards more commercially viable options is vital and is the subject of this work. The global catalyst market was valued at USD 33.9 billion in 2019, and it is expected to grow at a compound annual growth rate of 4.4% from 2020 to 2027 [4]. Even though thousands of academic papers are published each year on catalyst development, industrial adaptation remains comparatively low, with commercial catalysts currently in use

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numbering in the few hundreds only [5].

Catalysis research is a multi-layered problem. Modelling coupled with a systematic process design methodology can tackle the shortcomings in the traditional catalyst design approach. Experimentation alone is not sufficient but needs to be combined with kinetic and process modelling at various scales and stages with different degrees of complexity, which considers the whole process to discover or modify catalysts more efficiently. In this regard, combinatorial chemistry is a potential solution, creating likely catalyst candidates, which in combination with optimisation algorithms and data mining tools, can scan and narrow down catalyst candidates to those that best match the desired properties [6]. However, this does not guarantee that catalyst

candidates will be efficient when taken to the industrial scale and used in a plant. Similarly, the application of kinetic and process modelling methods can aid catalyst development at all steps; however, the right level of model complexity is a crucial decision to be made, which depends on factors such as resources and quality of available data [7]. Irrespective of the catalyst development tools employed, involving engineers from the start, and considering the overall impact of a catalyst on the process, is the key to success [8,9].

By utilising the latest innovations in process systems engineering, the current work aims to tackle the deficiencies in catalyst development workflows outlined above by developing an in silico methodology based on the integration of catalyst and catalytic process design to quantify the

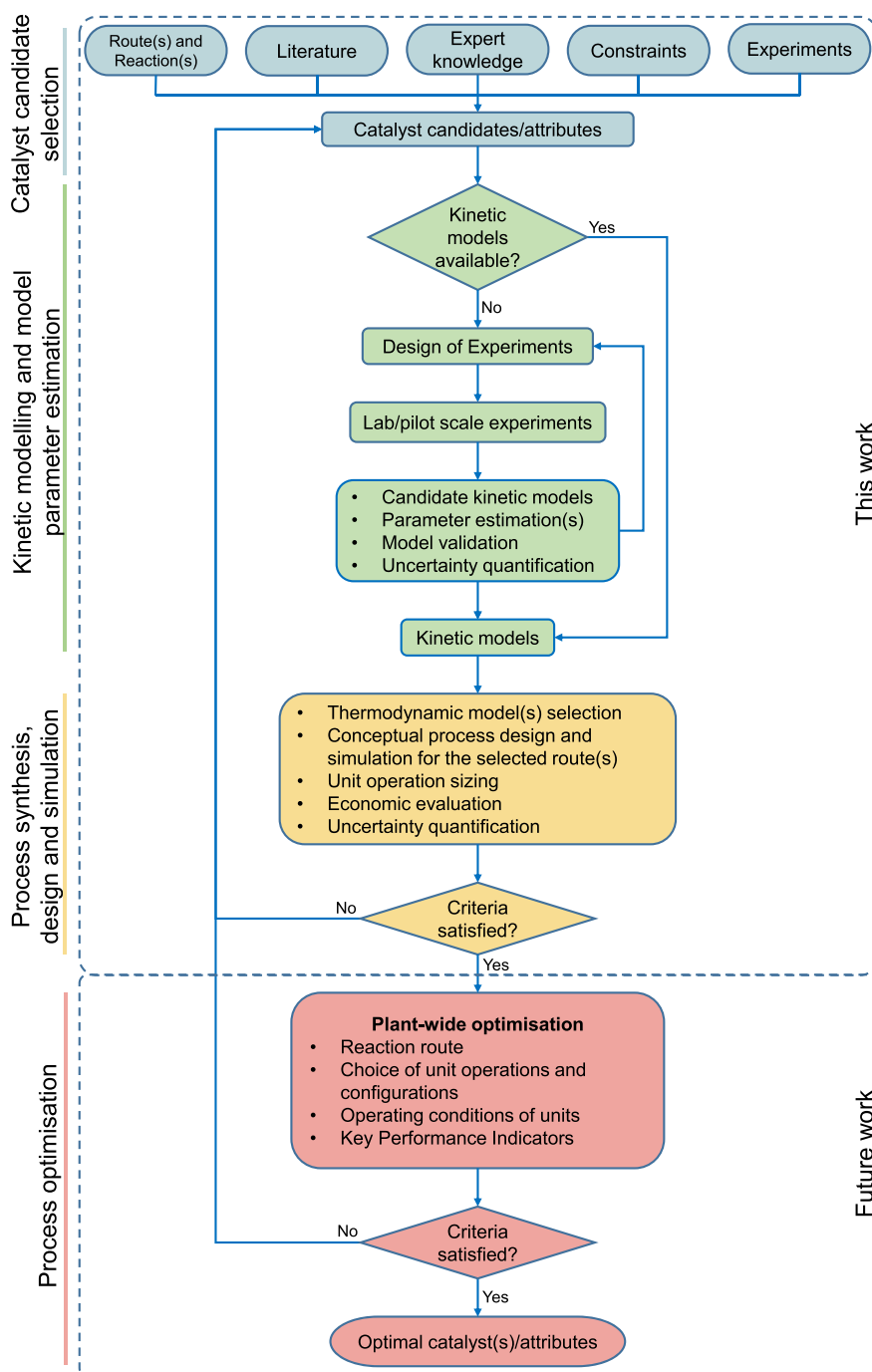


Fig. 1. Systems-oriented catalyst design and optimisation methodology proposed, also indicating the focus of this work.

impact and optimise the use of a given catalyst on the overall process flowsheet. By turning catalyst design on its head, starting with the end-product and working backwards to the ideal catalyst, this approach will be an invaluable tool for catalyst development in academia and industry alike, helping to reduce the cost and timescales involved in catalyst design or selection, by focusing the efforts on commercially viable alternatives from the outset.

## 2. Methodology

### 2.1. Catalyst candidate selection

The holistic, systems-oriented methodology to catalyst design we propose is shown in Fig. 1. The first step is to investigate the design space of the available catalysts. After considering the reaction and catalyst constraints, such as catalyst/reaction mixture phases, reagent solubility and operating conditions, the catalyst candidates can be narrowed down through knowledge gained from the literature, prior expertise, computational modelling, initial experiments, and/or a combination of experimentation and data analytics.

### 2.2. Kinetic modelling and model parameter estimation

The reactor's nature and mode of operation in the catalytic step will significantly impact a chemical process, and kinetic models are essential for its design. Consequently, developing *in silico* kinetic models for catalytic processes is a field receiving significant industrial and academic interest [10]. If a reliable set of reaction kinetic data is unavailable, experiments can be carried out on the chosen catalysts with, or without, further modifications. In this context, Design of Experiment (DoE) methodologies can be employed to carefully select an appropriate target set of experiments, aiming to reduce the number of experiments required to explore the design space and gain the data needed for kinetics estimation. Choosing a suitable kinetic model depends upon the modelling and simulation requirements and the quality of available data required for model identification and parameter estimation activities. Often in a catalytic process development programme, only a limited set of experimental data is available during the initial catalyst selection, and design phase and the use of complex kinetic models is therefore not feasible. Compared to microkinetic or other complex reaction mechanistic models, the power-law model, coupled with a suitable reformulation of the Arrhenius equation, requires the fewest number of parameters to be estimated. Thus, particularly when only preliminary data are available, it can be used initially to estimate the reactor size and performance and thereby enable an overall plant model including downstream separation steps within a single process flowsheet to be developed and used for simulation and optimisation purposes.

In the kinetic model parameter estimation step (see Fig. 1), the available experimental data can be used to estimate the kinetic parameters in process simulations. Several parameter estimation techniques are available such as Least Squares, Maximum Likelihood, and Bayesian estimation methods [11]. When solving a Maximum Likelihood parameter estimation, an optimisation algorithm attempts to determine values for the model parameters that maximise the mathematical model's probability of predicting the measurement values obtained from the experiments [12]. After validating the kinetic model, the model predictions should be assessed by examining statistics on fitting performance (chi-square statistics) and kinetic parameter estimation (*t*-test, *f*-test, and parameter correlation) to quantify the uncertainty in the kinetic parameters. The results of these evaluations are then used to determine the uncertainty in the responses of interest (such as KPIs) by Monte-Carlo simulation of sampled values within the normally distributed range of uncertain factors.

### 2.3. Process synthesis, design and simulation

Process synthesis and conceptual process design and simulation is the next step in the methodology. This is a crucial stage in chemical process development, intending to generate realistic flowsheet variants and their optimisation concerning specific objectives, such as economics, environmental impacts and safety. Here, suitable reaction routes, relevant kinetic models and thermodynamic data are required to perform the necessary calculations. The catalyst attributes (e.g., activity and selectivity) affect the whole process, including, but not limited to, the choice and design of the downstream separation units, and hence the impact of these must be taken into account. Quantifying these effects, in turn, helps to identify the optimal catalyst characteristics and associated route(s) and process(es) that satisfy the specific objective(s) for the target molecule (e.g., minimise cost/waste) while abiding by imposed constraints (e.g., product/waste purity, safety restrictions). As infrastructure and operating costs are usually the primary variables of interest at an industrial scale, suitable equations must be implemented to allow unit operation sizing and cost estimation based on the process requirements. Process simulators are used at this stage of development to design the overall process(es), as they allow direct comparison of different process layout scenarios, unit operation sizing, and quantification of uncertainty in performance indicators of interest resulting from the uncertainty in the kinetic parameters.

### 2.4. Process optimisation

Assessing the alternatives for each variable in a holistic view of the process, including the reactant and product specifications, catalyst attributes, equipment configurations, operating conditions, equipment layout, and process synthesis decisions, leads to a broad process design space. Consequently, multiple decision criteria can be explored systematically using Global Sensitivity Analysis (GSA), and the best design in which desired objectives, such as cost and process sustainability, are minimised or maximised can be achieved using process optimisation [13,14].

The final step in the proposed methodology is to perform plant-wide optimisation based on the selected criteria. This step defines product purities and other required specifications as constraints, while catalyst attributes, unit specifications, and operating conditions throughout the process are defined as decision variables. Choosing a suitable optimisation algorithm depends on the equation set describing the overall process. In most cases, the algorithm must solve a nonlinear equation set (possibly including integer variables) by varying decision variables to find the optimal objective function value (e.g., minimum cost). The results of this step provide the best process route, plus optimal catalyst, unit configurations, and operating conditions, which minimises or maximises the objective function, e.g., if the objective function is product cost, then the optimal route will be the route that has the lowest costs. The effects of the uncertainties in the kinetic parameter estimations can be further studied by propagating them through the whole plant using GSA to estimate the impact of the uncertainty of kinetic parameters on the uncertainty of the overall process performance.

Depending on the availability of catalyst candidates, the methodology we propose can be applied for:

- Optimising hypothetical catalysts by manipulating catalyst attributes (e.g., activity and selectivity) in conjunction with meaningful constraints to guide the development of new catalysts.
- Comparing available catalysts under their optimal working conditions to assess the impact of the catalyst choice on the performance of the overall process in terms of KPIs, such as Total Annualised Cost (TAC).

A demonstration of our methodology applied to a comparison of available catalysts is presented in the next section. The software

gPROMS PROCESS [15] was used as the flowsheeting tool and Multi-flash v6.1 [16] to predict the vapour-liquid equilibrium (VLE).

### 3. Results and discussion

Application of the process engineering methodology (Fig. 1) is demonstrated by a case study of dehydration of 1-butanol to butenes and dibutyl ether over H-ZSM5 and H-Beta catalysts. Bio-derived 1-butanol is a renewable feed receiving considerable attention as a sustainable fuel and chemical feedstock. It can be produced using the ABE (Acetone, Butanol, Ethanol) fermentation process, although this route is still currently commercially unattractive compared to its traditional production from crude oil [17]. Dehydration of 1-butanol has been reported in the literature using different catalysts and reactor systems, and primary products are reported as mainly butene isomers, dibutyl ether and water [18–21]. The bio-derived butenes are of interest as a commodity intermediate and dibutyl ether as a bio-renewable solvent. As simple kinetic models for dehydration of 1-butanol are not currently available in the literature, some experimental data were obtained to enable building an initial kinetic model for the process simulation and optimisation studies (see SI, Section 1). The experiments were performed using 100 mg of H-ZSM5 (Si:Al = 23) or H-Beta (Si:Al = 25) at atmospheric pressure in a flow reactor (ID = 1/4") heated with a tubular furnace at 200–300 °C with a flow rate spanning the range 0.025–0.2 mL/min.

There are several possible pathways to butenes starting from 1-butanol as the substrate [22]. These could be simultaneous formation of butenes and dibutyl ether, termed *parallel* reaction; *consecutive* reaction involving the formation of dibutyl ether and water (by surface-associated hydrogen transfer) then fragmentation to give butenes and 1-butanol; reversible reactions between 1-butanol, butenes and dibutyl ether, termed *triangular* reaction (see SI, Section 2). Reaction orders, pre-exponential factors, and activation energies for power-law kinetic models were estimated using the Maximum Likelihood estimation for each of these pathways. Although the reaction yields a mixture of butene isomers, 1-butene was used in the calculations, as the preliminary experimental results did not separate isomers and because this reduces the number of kinetic parameters to be estimated. As a result, butene is assumed to represent a mixture of butene isomers for which the exact distribution depends upon the reaction conditions and the catalyst in use. The maximum reaction temperature considered was 250 °C, as we found this experimentally to be the highest temperature where isobutene formation and coking did not take place. The comparison between the kinetic model predictions and measured data are given in

Fig. 2 for both catalysts and the three considered reaction pathways.

Fig. 2 shows that the parallel and consecutive reaction pathways are more accurate than the triangular pathway in predicting conversion for the given experimental conditions for both catalysts. The triangular pathway is the most generic form, as it includes both parallel and consecutive pathways. However, the predictions of conversion for H-ZSM5 and selectivities for H-Beta (mainly at 250 °C at various flow rates) lack accuracy. This is likely due to limitations of the model and/or lack of sufficient information from the data to make the parameter estimation more accurate.

Using Global Sensitivity Analysis (GSA) in quantifying the uncertainties provides descriptive statistics such as maximum, minimum, quartiles, coefficient of variation, and mean. The box plots in Fig. 3 show these statistics for catalyst attributes (conversion, selectivities) after accounting for uncertainties in estimated kinetic parameters (see SI, Section 2). The catalyst attribute ranges are essential for guiding the design of the downstream separation stages to accommodate possible process layouts.

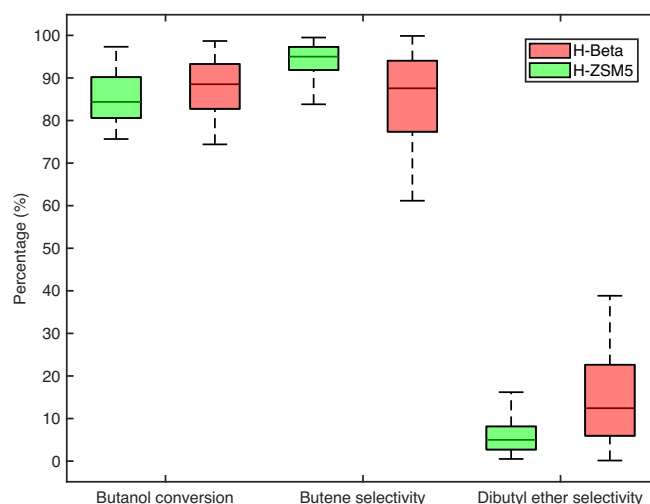


Fig. 3. Box plots showing the effect of the uncertainties in predicted kinetic parameters on conversion and selectivities using H-ZSM5 and H-Beta catalysts, considering the parallel reaction pathway. For each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively, while the whiskers show extreme data points.

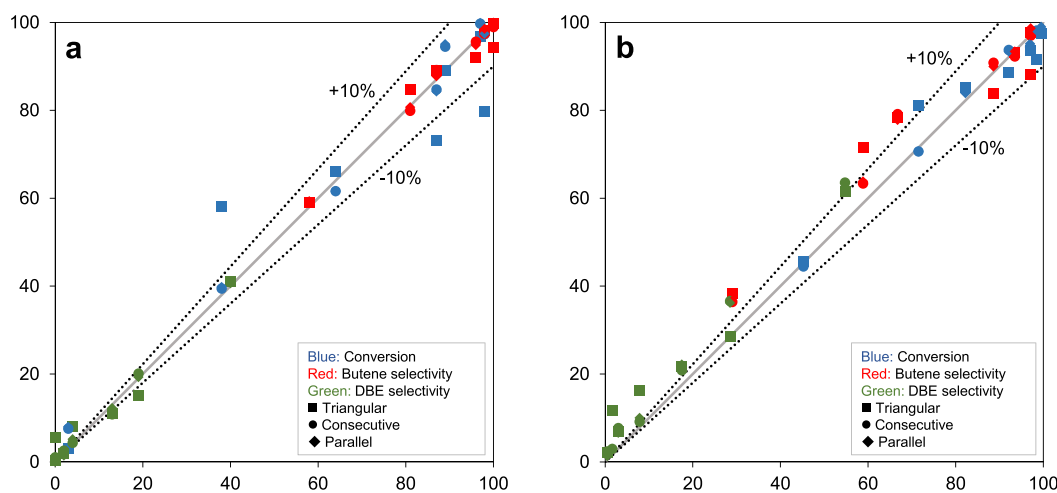


Fig. 2. Experimental data vs kinetic model predictions for the three reaction pathways considered for 1-butanol dehydration (triangular, consecutive, parallel) with  $\pm 10\%$  error lines using (a) H-ZSM5 (b) H-Beta catalysts. Experimental data and conditions are given in SI.

Thermophysical property models were evaluated using the Dortmund-modified UNIFAC model [23]. This model was chosen as it could accurately predict the vapour-liquid equilibrium of binary mixtures of components and associated azeotropes compared to experimental VLE data [24–27]. Four azeotropes exist for this mixture of butenes, butanol, dibutyl ether and water at atmospheric pressure. The molar compositions and boiling temperatures at the azeotropic points are predicted to be water(0.748)-1-butanol(0.252) at 92.6 °C, water (0.790)-dibutyl ether(0.210) at 93.52 °C, 1-butanol(0.866)-dibutyl ether(0.134) at 117.2 °C, and water(0.705)-dibutyl ether(0.174)-1-butanol(0.121) at 90.8 °C. All the azeotropes are heterogeneous except that of 1-butanol and dibutyl ether.

After exploring the physical properties of the product mixture, a suitable production process needs to be designed. When it comes to this step, one needs to consider that changing or modifying a catalyst, the reactor size, or the operating conditions will change the product composition leaving the reactor, which affects the design of the downstream separation sequence design. Thus, a process flowsheet must be established to accommodate different process scenarios. For the case study, three main possibilities were considered, which include complete conversion of the feed (scenario A), medium conversion of the feed with no feed recycle (scenario B), and complete separation of the product mixture to recycle the unreacted feed (scenario C). The process flow diagram, including the assumed scenarios, is illustrated in Fig. 4.

The first Scenario (A) simulated the process to achieve a high butanol conversion. This was done by increasing the reaction temperature or reactor size, affecting operational or capital costs, but then requiring only a simple separation sequence of a flash distillation (a single-stage separation unit) due to the high reactant conversion. The second Scenario (B) was when the reaction was performed at lower conversion by reducing the reaction temperature, with the resulting butene, water and mixture of butanol and dibutyl ether being separated by a distillation sequence using first a single column followed by a two-column and a decanter design to make use of the heterogeneous azeotropic mixture property. A third scenario (Scenario C) was considered in which the separation of butanol and dibutyl ether was also included (scenario C), requiring an additional distillation column. In the process flow diagram, and for all scenarios, the reactor outlet mixture was partly liquefied and flash distilled to remove more than 95% of the butenes produced. A distillation column (V-002) removed the remaining dissolved butenes from the liquids in scenarios B and C. Depending on the reactant conversion and product selectivity, the remaining liquids lied in the two-

liquid phase region and could be further separated in a decanter (V-003) into a water-rich and an alcohol-rich stream, with dibutyl ethers mixed in the alcohol-rich stream. Due to the existence of a heterogeneous azeotrope, water and butanol must be separated via a two-column (V-004, V-005) arrangement with a decanter. For Scenario C, the butanol/dibutyl ether azeotrope was avoided by increasing the operating pressure of the final column (V-006) as this azeotrope is pressure-sensitive [24]. Several trade-offs exist, such as reactor size vs. temperature, flash distillation operating conditions vs. butene recovery and purity, and distillation column utility requirements vs. distillation column number of stages and must be explored to achieve the desired objective (e.g., minimising cost, minimising waste, maximising safety).

The three scenarios described previously and shown in Fig. 4, were simulated and the results in terms of economic KPIs are given in Table 1. Details of the required information used for economic evaluations are shown in the SI (Section 4). In Scenario A, the reactor volume was calculated based on having a 99% butanol conversion at 250 °C, as demonstrated experimentally. The comparisons of Scenario B and C in Table 1 were based on fixing the conversion at 83.4% for both catalysts by reducing the reaction temperature while keeping the reactor size the same as in Scenario A. This lower conversion resulted from lowering the reaction temperature by 20 °C from 250 °C for H-ZSM5 and was kept similar for H-Beta for comparison purposes. As the reactor volume also affects reactant conversions/product selectivities and capital costs, its effects were also investigated. The trade-off in reactor size vs. reaction temperature is given in the SI, Fig. S4.

The results (see Table 1) show that scenario A is the best design in this case study, with the lowest capital and operating costs. This Scenario also gives the highest production rate, and therefore, the lowest production cost per kilogram of product, thus giving the highest profit (around 1.8 times the profit of Scenario C) for H-ZSM5. This suggests that for this process, due to the nature of the properties of the product stream and complex and costly separation requirements (Scenarios B and C), maximising the conversion is the most economically viable option. The desired enhanced conversion could be achieved by performing the reaction at higher temperatures, using a different catalyst with higher activity (without compromising selectivity), or increasing reactor space-time.

As is usually the case for chemical plants, the results also show that raw materials comprise the main portion of the operational costs. Consequently, reducing the fresh feed consumption through recycling the unreacted and separated 1-butanol will improve economics

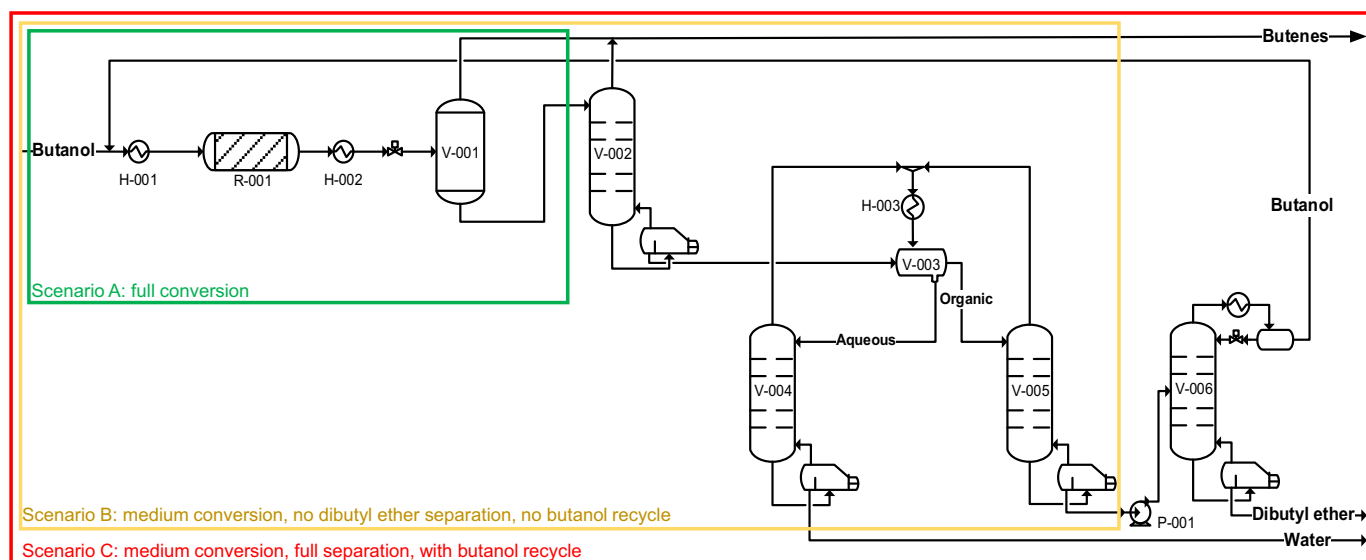


Fig. 4. Process flow diagram of butanol dehydration with 1-butanol as feed and butenes as the main product, based on three process scenarios and the associated separation requirements for H-ZSM5 and H-Beta catalysts simulated using the parallel reaction pathway.

**Table 1**

Summary of process operating conditions and associated economics for different process scenarios (see Fig. 4), and for two different catalysts, H-ZSM5 and H-Beta.

|   | H-ZSM5      |             |             | H-Beta      |             |             |
|---|-------------|-------------|-------------|-------------|-------------|-------------|
|   | Scenario A  | Scenario B  | Scenario C  | Scenario A  | Scenario B  | Scenario C  |
| <b>Operating conditions<sup>a</sup></b>             |             |             |             |             |             |             |
| H-001 outlet temperature (°C)                       | 250         | 230         | 230         | 250         | 206         | 206         |
| H-002 outlet temperature (°C)                       | 15          | 11          | 11          | 11          | 11          | 11          |
| V-002 boil-up ratio (normalised)                    | N/A         | 0.22        | 0.22        | N/A         | 0.09        | 0.09        |
| V-002 number of stages                              | N/A         | 3           | 3           | N/A         | 3           | 3           |
| H-003 outlet temperature (°C)                       | N/A         | 91.8        | 80          | N/A         | 80          | 80          |
| V-004 boil-up ratio (normalised)                    | N/A         | 0.09        | 0.09        | N/A         | 0.06        | 0.06        |
| V-004 number of stages                              | N/A         | 5           | 5           | N/A         | 5           | 5           |
| V-005 boil-up ratio (normalised)                    | N/A         | 0.52        | 0.52        | N/A         | 0.44        | 0.44        |
| V-005 number of stages                              | N/A         | 10          | 10          | N/A         | 10          | 10          |
| P-001 outlet pressure (atm)                         | N/A         | N/A         | 5           | N/A         | N/A         | 5           |
| V-006 number of stages                              | N/A         | N/A         | 20          | N/A         | N/A         | 20          |
| V-006 feed stage                                    | N/A         | N/A         | 10          | N/A         | N/A         | 10          |
| V-006 boil-up ratio (normalised)                    | N/A         | N/A         | 0.97        | N/A         | N/A         | 0.97        |
| V-006 reflux ratio (normalised)                     | N/A         | N/A         | 0.5         | N/A         | N/A         | 0.5         |
| <b>Capital costs (M\$)</b>                          |             |             |             |             |             |             |
| H-001   | 0.087       | 0.025       | 0.025       | 0.087       | 0.025       | 0.023       |
| R-001   | 0.074       | 0.074       | 0.074       | 0.074       | 0.074       | 0.074       |
| H-002   | 0.027       | 0.032       | 0.032       | 0.027       | 0.032       | 0.033       |
| V-001   | 0.022       | 0.016       | 0.016       | 0.022       | 0.016       | 0.012       |
| V-002   | N/A         | 0.019       | 0.019       | N/A         | 0.019       | 0.017       |
| H-003   | N/A         | 0.024       | 0.024       | N/A         | 0.024       | 0.024       |
| V-003   | N/A         | 0.023       | 0.023       | N/A         | 0.023       | 0.063       |
| V-004   | N/A         | 0.054       | 0.054       | N/A         | 0.054       | 0.056       |
| V-005   | N/A         | 0.23        | 0.23        | N/A         | 0.23        | 0.22        |
| P-001   | N/A         | N/A         | 0.004       | N/A         | N/A         | 0.004       |
| V-006   | N/A         | N/A         | 0.093       | N/A         | N/A         | 0.1         |
| <i>Total</i>  | <i>0.21</i> | <i>0.49</i> | <i>0.59</i> | <i>0.21</i> | <i>0.49</i> | <i>0.63</i> |
| <b>Operating costs (M\$/yr)</b>                     |             |             |             |             |             |             |
| H-001   | 3.39        | 3.26        | 3.26        | 3.39        | 3.10        | 3.10        |
| R-001   | 1.32        | 1.02        | 1.02        | 1.3         | 0.77        | 0.77        |
| H-002   | 0.61        | 0.61        | 0.61        | 0.62        | 0.59        | 0.59        |
| V-002   | N/A         | 0.35        | 0.35        | N/A         | 0.38        | 0.38        |
| H-003   | N/A         | 0.074       | 0.074       | N/A         | 0.049       | 0.049       |
| V-004   | N/A         | 0.092       | 0.092       | N/A         | 0.073       | 0.073       |
| V-005   | N/A         | 0.33        | 0.33        | N/A         | 0.29        | 0.29        |
| P-001   | N/A         | N/A         | 0.0003      | N/A         | N/A         | 0.0003      |
| V-006   | N/A         | N/A         | 0.12        | N/A         | N/A         | 0.19        |
| Raw materials                                       | 83          | 83          | 70          | 83          | 83          | 70          |
| <i>Total</i>  | <i>88</i>   | <i>88</i>   | <i>76</i>   | <i>88</i>   | <i>88</i>   | <i>75</i>   |
| <b>Economic Key Performance Indicators (M\$/yr)</b> |             |             |             |             |             |             |
| Butene Revenue                                      | 118         | 90          | 90          | 119         | 66          | 66          |
| Water Revenue                                       | 0.026       | 0.052       | 0.052       | 0.026       | 0.075       | 0.075       |
| Dibutyl Ether Revenue                               | N/A         | N/A         | 2.5         | N/A         | N/A         | 3.6         |
| <i>Total Revenue</i>                                | <i>119</i>  | <i>90</i>   | <i>93</i>   | <i>119</i>  | <i>66</i>   | <i>70</i>   |
| <i>Total Annualised Cost</i>                        | <i>88</i>   | <i>88</i>   | <i>76</i>   | <i>88</i>   | <i>88</i>   | <i>75</i>   |
| <i>Total Annualised Profit</i>                      | <i>31</i>   | <i>2</i>    | <i>17</i>   | <i>31</i>   | <i>-22</i>  | <i>-6</i>   |
| <i>Butene production cost (\$/tonne)</i>            | <i>1100</i> | <i>1400</i> | <i>1200</i> | <i>1100</i> | <i>1712</i> | <i>1468</i> |

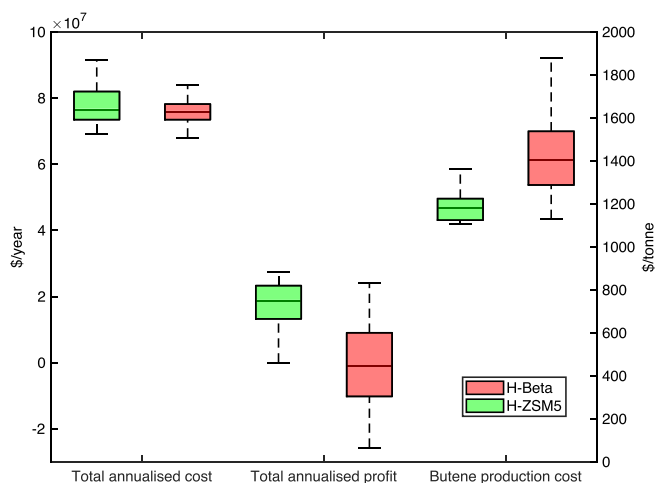
<sup>a</sup> 13.2 t/h pure 1-butanol feed, at 1 atm, 25 °C. 99.9% purity of products.

(Scenario C). Instead of implementing recycle streams, which would make the simulation challenging, we have subtracted the separated and recyclable streams from the raw material feed streams for the cost calculations.

It should be noted that when using H-Beta as the catalyst, Scenarios B and C yield an overall negative profit. This means that H-ZSM5 is the better option at a conversion similar to H-Beta due to higher selectivity to butenes. However, H-Beta is a better option at the same reactor temperature and reactor size since it gives rise to higher conversion. It should be noted that the results which are shown in Table 1 also depend on the precision of the predicted kinetic parameters, as the uncertainty in the H-Beta's predicted kinetic parameters is higher, which is apparent

when butene and dibutyl ether selectivities are compared with those of H-ZSM5.

The uncertainty in the estimated kinetic parameters (SI Section 2) can also be further propagated after the process design and optimisation stage to observe the effect on KPIs of interest. The data presented in Fig. 5 show the effect of variation in the estimated kinetic parameters on the economic KPIs for both catalysts for Scenario C. For this Scenario, when H-ZSM5 and H-Beta operate at the same conversion, H-ZSM is a better catalyst choice. Fig. 5 also shows how the higher uncertainties for H-Beta catalyst kinetic parameters result to lower accuracy in the predicted KPIs. Note that Table 1 shows the simulation results for the KPIs using the estimated kinetic parameters, while Fig. 5 shows the median of



**Fig. 5.** Box plots showing the effect of the uncertainties in predicted kinetic parameters on process economic indicators for Scenario C (see Fig. 4) using H-ZSM5 and H-Beta catalysts and the parallel reaction pathway, assuming all the other variables are fixed. For each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively, while the whiskers show extreme data points.

the KPIs obtained from GSA studies, where the set of kinetic parameters used were stochastically generated. In addition, the GSA results were obtained under unoptimised unit operating conditions.

#### 4. Conclusion

Process systems engineering tools can aid catalyst design and development by analysing the impact of the attributes of available or hypothetical catalysts on the overall process. An integrated methodology was introduced that uses advanced modelling and optimisation approaches to first develop kinetic models from limited kinetic data, then describe the required reaction, separation, and unit operations in a flowsheeting tool, providing recommendations for catalyst attributes and operating conditions of process units. A vital aspect of the methodology is the quantification of the uncertainties associated with the kinetic modelling and assessing their effect on the overall process performance by Global Sensitivity Analysis (GSA) tools. The methodology was applied to the 1-butanol dehydration process, comparing two available catalysts for catalyst selection purposes by assessing their plant-wide impacts on process economics. The results show that in the optimum catalyst/process, 1-butanol conversion must be maximised (for example, by performing the reaction at high temperature) due to the complexity of the downstream separation sequence required for different reaction conditions.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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#### Appendix A. Supplementary data

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#### References

- [1] W. Liu, Multi-scale catalyst design, *Chem. Eng. Sci.* 62 (2007) 3502–3512, <https://doi.org/10.1016/j.ces.2007.02.057>.
- [2] A. Shafiee, M. Nomvar, Z. Liu, A. Abbas, Automated process synthesis for optimal flowsheet design of a hybrid membrane cryogenic carbon capture process, *J. Clean. Prod.* 150 (2017) 309–323, <https://doi.org/10.1016/j.jclepro.2017.02.151>.
- [3] S. Hübner, J.G. de Vries, V. Farina, Why does industry not use immobilized transition metal complexes as catalysts? *Adv. Synth. Catal.* 358 (2016) 3–25, <https://doi.org/10.1002/adsc.201500846>.
- [4] Grand view research, catalyst market size & share & Trends Analysis Report by Raw Material (Chemical Compounds, Zeolites, Metals), by Product (Heterogeneous, Homogeneous), by Application, by Region, and Segment Forecasts, 2020–2027, 2020. <https://www.grandviewresearch.com/industry-analysis/catalyst-market>.
- [5] Acmite Market Intelligence, *Glob. Catalyst Mark.* (2015). <https://www.acmite.com/market-reports/environmentals/global-catalyst-market.html>.
- [6] G. Kirsten, W.F. Maier, Strategies for the discovery of new catalysts with combinatorial chemistry, *Appl. Surf. Sci.* 223 (2004) 87–101, [https://doi.org/10.1016/S0169-4332\(03\)00911-5](https://doi.org/10.1016/S0169-4332(03)00911-5).
- [7] E.J. Ras, G. Rothenberg, Heterogeneous catalyst discovery using 21st century tools: a tutorial, *RSC Adv.* 4 (2014) 5963–5974, <https://doi.org/10.1039/c3ra45852k>.
- [8] J.A. Moulijn, M. Makkee, A. Wiersma, E.J.A.X. van de Sandt, Selective hydrogenolysis of  $\text{CCl}_2\text{F}_2$  into  $\text{CH}_2\text{F}_2$  over palladium on activated carbon: Kinetic mechanism and process design, *Catal. Today* 59 (3–4) (2000) 221–230, [https://doi.org/10.1016/S0920-5861\(00\)00288-1](https://doi.org/10.1016/S0920-5861(00)00288-1).
- [9] P. Imhof, J.C. van der Waal, *Catalytic Process Development for Renewable Materials*, Wiley, Weinheim, 2013.
- [10] Eurokin. <https://eurokin.org/>, 2021 (accessed October 13, 2021).
- [11] R.C. Aster, B. Borchers, C.H. Thurber, Parameter Estimation and Inverse Problems, Elsevier, Waltham, 2013, <https://doi.org/10.1016/C2009-0-61134-X>.
- [12] I.J. Myung, Tutorial on maximum likelihood estimation, *J. Math. Psychol.* 47 (2003) 90–100, [https://doi.org/10.1016/S0022-2496\(02\)00028-7](https://doi.org/10.1016/S0022-2496(02)00028-7).
- [13] G. Dellino, C. Meloni, *Uncertainty Management in Simulation-Optimization of Complex Systems: Algorithms and Applications*, Springer, US, New York, 2015.
- [14] A. Saltelli, M. Ratto, T. Andres, F. Campolongo, J. Cariboni, D. Gatelli, M. Saisana, S. Tarantola, *Global Sensitivity Analysis: The Primer*, Wiley, Chichester, 2008.
- [15] Siemens Process Systems Enterprise, gPROMS Process, in: <https://www.pcenterpris.com/products/gproms/process>, 2021.
- [16] KBC Advanced Technologies Plc, Multiflash. <https://www.kbc.global/software/advanced-thermodynamics>, 2021.
- [17] J. Martinez-Gomez, E. Sánchez-Ramírez, J.J. Quiroz-Ramírez, J.G. Segovia-Hernandez, J.M. Ponce-Ortega, M.M. El-Halwagi, Involving economic, environmental and safety issues in the optimal purification of biobutanol, *Process. Saf. Environ. Prot.* 103 (2016) 365–376, <https://doi.org/10.1016/j.psep.2016.04.018>.
- [18] F.M. Bautista, B. Delmon, 1-butanol dehydration on  $\text{AlPO}_4$  and modified  $\text{AlPO}_4$ : catalytic behaviour and deactivation, *Appl. Catal. A Gen.* 130 (1995) 47–65, [https://doi.org/10.1016/0926-860X\(95\)00106-9](https://doi.org/10.1016/0926-860X(95)00106-9).
- [19] R.M. West, D.J. Braden, J.A. Dumesic, Dehydration of butanol to butene over solid acid catalysts in high water environments, *J. Catal.* 262 (2009) 134–143, <https://doi.org/10.1016/j.jcat.2008.12.009>.
- [20] M. John, K. Alexopoulos, M.-F. Reyniers, G.B. Marin, Reaction path analysis for 1-butanol dehydration in H-ZSM-5 zeolite: ab initio and microkinetic modeling, *J. Catal.* 330 (2015) 28–45, <https://doi.org/10.1016/j.jcat.2015.07.005>.
- [21] D. Gunst, K. Alexopoulos, K. Van Der Borgh, M. John, V. Galvita, M.F. Reyniers, A. Verberckmoes, Study of butanol conversion to butenes over H-ZSM-5: effect of chemical structure on activity, selectivity and reaction pathways, *Appl. Catal. A Gen.* 539 (2017) 1–12, <https://doi.org/10.1016/j.apcata.2017.03.036>.
- [22] M. John, K. Alexopoulos, M.-F. Reyniers, G.B. Marin, Mechanistic insights into the formation of butene isomers from 1-butanol in H-ZSM-5: DFT based microkinetic modelling, *Catal. Sci. Technol.* 7 (2017) 1055–1072, <https://doi.org/10.1039/C6CY02474B>.
- [23] J. Lohmann, R. Joh, J. Gmehling, From UNIFAC to modified UNIFAC (Dortmund), *Ind. Eng. Chem. Res.* 40 (2001) 957–964, <https://doi.org/10.1021/ie0005710>.
- [24] E. Lladosa, J.B. Montón, M.C. Burguet, R. Muñoz, Isobaric vapor–liquid equilibria for the binary systems 1-propyl alcohol+dipropyl ether and 1-butyl alcohol+dibutyl ether at 20 and 101.3kPa, *Fluid Phase Equilib.* 247 (2006) 47–53, <https://doi.org/10.1016/j.fluid.2006.06.017>.
- [25] E. Lladosa, J.B. Montón, M.C. Burguet, R. Muñoz, Phase equilibrium for the esterification reaction of acetic acid + butan-1-ol at 101.3 kPa, *J. Chem. Eng. Data* 53 (2008) 108–115, <https://doi.org/10.1021/jc700411p>.
- [26] L.H. Horsley, *Azeotropic Data*, American Chemical Society, Washington, DC, 1973, <https://doi.org/10.1021/ba-1952-0006>.
- [27] W.M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 2014.