

# Process-oriented approach towards catalyst design and optimisation

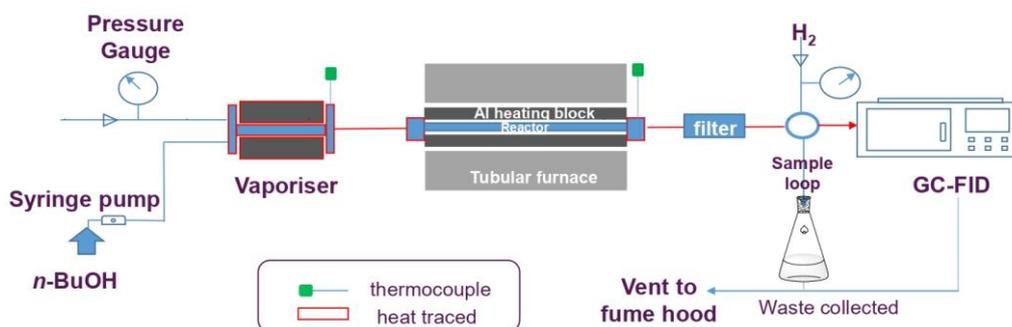
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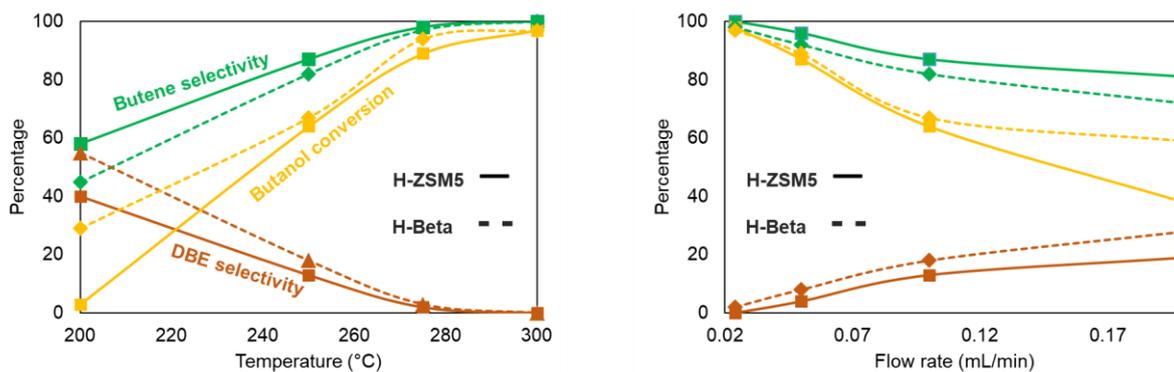
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## 1 Experimental setup and results

The experimental setup and data used in modelling the catalyst kinetics used in the process flowsheeting are shown in Figures S1 and S2. The experiments were performed using 100 mg of pressed, crushed, and sieved H-ZSM5 (Si:Al=23) or H-Beta (Si:Al=25) with particle sizes ranging between 250-500 microns. The flow reactor (internal diameter 1/4") was operated at atmospheric pressure and heated with a tubular furnace at 200-300 °C with a reactant feed flow rate of 0.025-0.2 mL/min. The catalyst was activated at 150 °C under N<sub>2</sub> flow for 1 hour. Butene in Fig S2 represents a mixture of butene isomers, whose composition depended on reaction conditions and the catalyst used. The product analysis was performed by gas chromatography.



**Figure S1:** The experimental setup used for obtaining kinetic data of catalytic butanol dehydration.



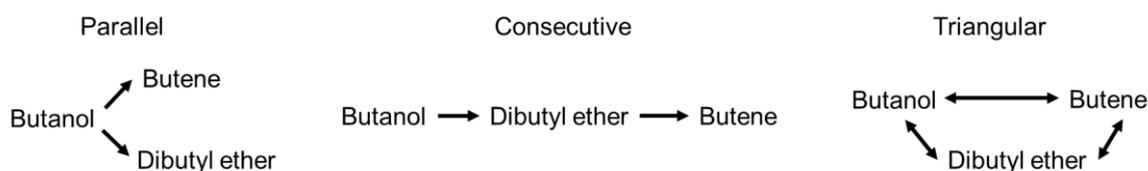
**Figure S2: Butanol conversion, butene, and dibutyl ether selectivities as a function of temperature and flow rate, (a) at 0.1 mL/min flow rate (b) at 250 °C.**

## 2 Kinetic parameter estimation

The rate of reaction can be expressed by  $-r_i = k \prod C_i^\alpha$  while the temperature dependency of each kinetic constant can be evaluated using the modified Arrhenius equation given by  $k =$

$k_{ref} e^{\left(\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}$ . The estimated reaction orders, pre-exponential factors, and activation

energies for the three possible reaction pathways considered (see Figure S3) are given in Table S1.



**Figure S3: The three possible reaction pathways considered for butanol dehydration.**

As the parallel pathway showed a better fit to the experimental data, it was used in the next steps of the methodology. The statistical significance of the estimated parameters for this pathway is given in Table S2 for both H-ZSM5 and H-Beta catalysts.

**Table S1: Estimated kinetic parameters for different reaction pathways ( $\alpha$ : reaction order for 1-butanol,  $k_{ref}$ : reaction rate constant at the reference temperature (530 K),  $E_a$ : activation energy).**

	HZSM-5			H-Beta		
	$\alpha$	$k_{ref}^*$	$E_a^*$	$\alpha$	$k_{ref}^*$	$E_a^*$
<b>Parallel pathway</b>						
Butanol to butene	0.3	0.74	115	0.4	1.5	86
Butanol to dibutyl ether	1.2	0.17	96	1.4	1.9	73
<b>Consecutive pathway</b>						
Butanol to dibutyl ether	0.3	0.82	110	0.5	2.17	74
Dibutyl ether to butene	0.4	2.28	97	0.5	2.77	77
<b>Triangular pathway</b>						
Butanol to butene	0.3	5.91	226	0.3	1.77	46
Butanol to dibutyl ether	1	14.31	297	1	112	200
Dibutyl ether to butene	0.4	1414	375	0.4	290	251

\*units:  $k_{ref}$  [ $h^{-1} kg_{cat}^{-1} (kmol^{-1})^{\alpha-1} (m^3)^{\alpha}$ ],  $E_a$  [kJ/mol]

**Table S2: Statistical significance of the estimated kinetic parameters in terms of 95% confidence intervals and t-values for the parallel reaction pathway considering H-ZSM5 and H-Beta as catalysts.**

	Parameter	Estimated values	95% confidence interval	t-values*
<b>H-ZSM5</b>	$E_a$ : Butanol to butene	115.03	20.64	5.57
	$E_a$ : Butanol to dibutyl ether	95.82	27.86	3.44
	$k_{ref}$ : Butanol to butene	0.74	0.15	4.90
	$k_{ref}$ : Butanol to dibutyl ether	0.17	0.09	1.96
	$\alpha$ : Butanol to butene	0.29	0.09	3.10
	$\alpha$ : Butanol to dibutyl ether	1.18	0.36	3.32
<b>H-Beta</b>	$E_a$ : Butanol to butene	85.77	11.77	7.29
	$E_a$ : Butanol to dibutyl ether	73.07	25.17	2.90
	$k_{ref}$ : Butanol to butene	1.54	0.57	2.68
	$k_{ref}$ : Butanol to dibutyl ether	1.89	1.76	1.07
	$\alpha$ : Butanol to butene	0.44	0.16	2.85
	$\alpha$ : Butanol to dibutyl ether	1.38	0.42	3.27

\*reference t-value: 1.75

### 3 Selectivity and conversion calculation

The conversion of butanol ( $X_{BuOH}$ ) is defined as

$$X_{BuOH} = \frac{F_{BuOH}^0 - F_{BuOH}}{F_{BuOH}^0} \times 100 \quad (1)$$

where  $F_{BuOH}^0$  is the molar flow rate of butanol at the inlet and  $F_{BuOH}$  is the molar flow rate of butanol at the outlet of the reactor.

Carbon selectivity ( $S_i$ ) towards the product is expressed as:

$$S_i = \frac{b_i F_i}{4(F_{BuOH}^0 - F_{BuOH})} \times 100 \quad (2)$$

where  $F_i$  is the outlet molar flow rate of product  $i$  and  $b_i$  the number of carbon atoms per molecule of product  $i$ .

#### 4 Sizing of process units and economic evaluation

The assumptions and equations used for unit operation sizing and to calculate economic Key Performance Indicators (KPIs), such as capital costs (CAPEX) and operating costs (OPEX), are given below.

The considerations in sizing the equipments and OPEX calculations are as follows:

- Heat transfer coefficients: The value of the heat transfer coefficient ( $750 \text{ W/m}^2\cdot\text{K}$ ) for calculating the heat exchanger duties, areas, and cost of heat exchangers, condensers and reboilers duties was chosen using an average value for the mix of applications [1].
- Drums: The decanter drum capacity calculation was based on a residence time of 5 min and assuming feed location was in the midpoint. The flash drum was designed based on permitted velocity and a height/diameter ratio of 4.
- Reactor size: An ideal isothermal pseudohomogeneous plug flow reactor model with no pressure drop was employed. The reactor volume was calculated based on having a 99% butanol conversion at  $250 \text{ }^\circ\text{C}$ , as we found this to be the highest temperature where isobutene and coking are not taking place. The calculated reactor size was then assumed to be fixed for scenarios B and C.
- Distillation columns: These were sized based on the number of stages and assuming a 0.6 m distance between the trays. The minimum number of stages and reflux ratios were calculated using shortcut methods. The NLPSQP optimisation solver, which uses a sequential quadratic programming (SQP) method to solve nonlinear programming (NLP) problems, was employed to find the values that lead to the maximum recovery of the desired component by adhering to a 99.9% purity constraint. An active area

fraction of 0.8, hole area fraction of 0.1, weir height of 0.04 m, tray thickness of 0.002 m, hole diameter of 0.0045 m, weir fraction of 0.7, and uniform pressure through stages were used.

- **Materials:** The construction material was assumed to be Carbon Steel (CS) (mass density of 7861 kg/m<sup>3</sup>) as it is the most widely used material in chemical industries. This, however, can be easily customised if required, depending on the corrosion resistance considerations, process life, and cost.
- **Pumps:** These were assumed to have 85% mechanical and isentropic efficiency with cast iron as the material of choice.
- **Operating costs (OPEX):** These included feedstock, steam, chilled water and cooling water. Cooling water was assumed to cost \$0.005/kWh, chilling water \$0.02/kWh, steam \$0.1/kWh, and electricity \$0.05/kWh [2].
- **Plant life and operating hours:** 10-year plant life and annual operating hours of 8000 h/yr were used as a rational value from an industrial point of view.

**Capital cost (CAPEX):** Capital cost includes the bare equipment cost of all the units considered and does not include the cost of land, control room or feedstock/product storage, interest, depreciation, etc., as they do not affect the comparison of different scenarios. The bare equipment costs were taken from the literature, and the Chemical Engineering Plant Cost Index (CEPCI) was used to bring the costs up to present costs based on equation 3 [3–5]. The bare equipment costs are typically considered as a function of mass or heat exchange area, which requires the process units to be sized first.

$$CAPEX_{new} = CAPEX_{old} \times \left( \frac{CEPCI_{new}}{CEPCI_{old}} \right) \quad (3)$$

After calculating the CAPEX and OPEX of the process, economic KPIs were calculated from equations 4 to 7:

$$\begin{aligned} \text{Total Revenue} \left( \frac{M\$}{yr} \right) & \quad (4) \\ & = \text{Mass of product per year} \left( \frac{\text{tonne}}{yr} \right) \\ & \times \text{Selling price of product} \left( \frac{M\$}{\text{tonne}} \right) \end{aligned}$$

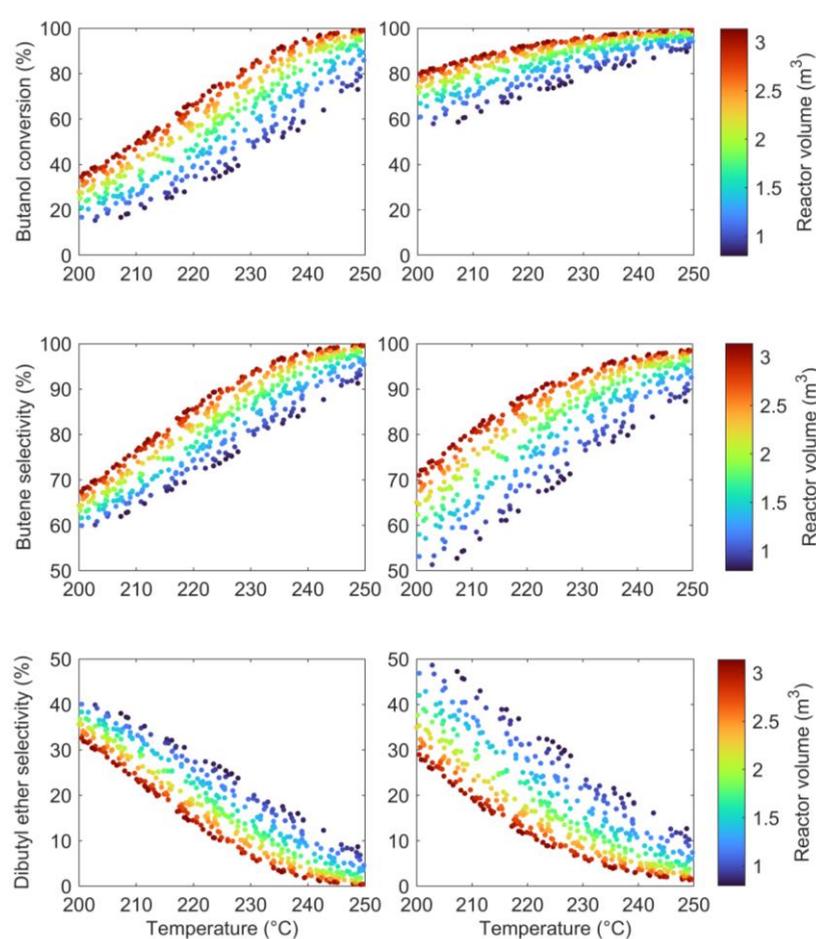
$$\text{Annualised CAPEX} = \frac{\text{Sum of equipment cost}}{\text{Plant lifetime}} \quad (5)$$

$$\text{Total Annualised Cost} \left( \frac{M\$}{\text{yr}} \right) = \text{Annualised CAPEX} + \text{OPEX} \quad (6)$$

$$\begin{aligned} \text{Total Annualised Profit} \left( \frac{M\$}{\text{yr}} \right) & \\ = \text{Total Revenue} - \text{Total Annualised Cost} & \end{aligned} \quad (7)$$

## 5 Effect of reaction temperature and reactor size on catalyst attributes

Figure S4 shows the simultaneous effect of reaction temperature and reactor size on conversion and selectivity for the H-ZSM5 and H-Beta catalysts. The 2D space of reaction temperature and reactor size was sampled. Various combinations of reactor volume and reaction temperature provide similar conversion/selectivities; hence, they need to be chosen via optimisation to minimise or maximise an objective function of interest. This is because the choice of reactor size affects the CAPEX, while reaction temperature requirement affects the OPEX, while both affect catalyst attributes.



**Figure S4:** The simultaneous effect of reaction temperature and reactor size on reactant conversion/product selectivities for the H-ZSM5 (left) and H-Beta (right) catalysts.

## References

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