ETBE synthesis reactor design

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Executive Summary

A reactor is designed for the production of ETBE over Amberlyst-15. Optimum reaction temperature is at $62\,°C$ with a reaction pressure of $1500\,kPa$ (De Sousa Melim *et al*, 2020). For the purpose of the liquid phase reaction an isothermal, single-pass shell and tube packed bed reactor was designed.

Two reactions occur in the reactor. One reaction produces the desired ETBE product, while a second, side, reaction involves the formation of TBA. Reaction kinetics are modelled for the two reactions from literature for a non-ideal mixture. The UNIFAC thermodynamic model was used to model the reaction mixture. The ETBE reaction is modelled based on work done by Fite *et al* (1994) with support from Syed *et al* (2004) and Traiprasertpong & Svang-Ariyaskul (2012). The TBA reaction kinetics are modelled based on study done by Velo, Puigjaner & Recasens (1988).

The physical model was developed with valid simplifying assumptions using viable and realisable engineering judgement supported by Domingues *et al* (2012), who provides actual reactor plant data for the production of ETBE over ion-exchange resin catalysts. Differential equations for the mole and energy balances were used for the physical model to generate axial concentration and temperature profiles along the reactor. The liquid phase pressure drop was calculated using the well-known Ergun equation. Physical parameters were obtained from De Sousa Melim *et al* (2020) where appropriate. The reactor is kept isothermal with the use of a cold water utility, having an overall heat transfer coefficient of $350\,W\,m^{-2}\,K^{-1}$.

The kinetic and physical model was simulated. The inner tube diameter was selected as $75\,mm$ with a wall thickness of $4\,mm$. The catalyst particle diameter chosen was $0.74\,mm$ (Domingues *et al*, 2012; Lenntech, 2020). Standard stock piping length was used to select the length of the reactor at $6\,m$ (Greef I.L, 2000). The simulation illustrated that to achieve $88\,\%$ conversion of isobutene, with the models developed, the optimum number of tubes was 776 with a catalyst mass of $10.3\,kg$ per tube. The simulation further includes results for temperature, pressure, conversion and concentration profiles along the length of the reactor.

Detailed reactor design is done, with selection of a square tube arrangement. The drawing and dimensions for the reactor are provided along with tubesheet layout, pitch dimensions, floating-head partitions and baffles.

Contents

1   Kinetic Model

ETBE production as a fuel additive is a relatively new breakthrough market. The ETBE is expected to be used as a replacement for MTBE as a fuel additive. The lack of literature available on the kinetics for ETBE production emphasises the fact that the ETBE market is relatively new. However, there are researchers who have conducted work on the kinetics. The ETBE production can be conducted either in the vapour or liquid phase. The reaction is generally carried out over an ion-exchange resin catalyst. The catalyst selection affects the optimal temperature and pressure for reaction. The reaction specifics chosen during the group design, was liquid phase reaction using a ion-exchange resin catalyst (Amberlyst-15) (De Sousa Melim *et al*, 2020).

Initial insight into reaction kinetics was obtained through review of work by Traiprasert-pong & Svang-Ariyaskul (2012). Traiprasertpong & Svang-Ariyaskul (2012) reviewed research conducted that explored kinetics of ETBE production under various conditions. Fite *et al* (1994), Umar, Patel & Saha (2009), and Françoisse & Thyrion (1991) studied the reaction kinetics of ETBE production from isobutene and ethanol. To determine which reaction kinetics best fit the design, reaction information needed to be inferred from the group design (De Sousa Melim *et al*, 2020). Reaction 1 and Reaction 2 illustrate the two reactions considered for the reactor design.

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Isobutene}}{C_4H_8} \rightleftharpoons \underset{\text{ETBE}}{C_6H_{14}O} \tag{1}$$

$$\underset{\text{Water}}{H_2O} + \underset{\text{Isobutene}}{C_4H_8} \rightleftharpoons \underset{\text{TBA}}{(CH_3)_3COH} \tag{2}$$

These reactions are exothermic reversible reactions. The reaction is carried out isother-mally. Therefore, in accordance with Fogler (2006), $\Delta Cp_{rxn} = 0$ is a valid assumption when modelling the kinetics. Syed *et al* (2004) suggests three possibilities for the kinetic model of ETBE production. One of these models suggested was the kinetic model developed by Fite *et al* (1994). The kinetics were selected such that the reaction conditions were similar to that of what was designed in the group design. Fite *et al* (1994) studies kinetics in a temperature range of $40\,°C$–$90\,°C$ and at a pressure of $1.6\,MPa$. These reaction conditions are similar to the reaction conditions designed. The rate equation for Reaction 1 as described by Fite *et al* (1994) and supported by both Syed *et al* (2004) and Traiprasertpong & Svang-Ariyaskul (2012) is given in Equation 3:

$$r_{ETBE} = k' \times \frac{a_{IB}a_{EtOH} - \frac{a_{ETBE}}{K}}{a_{EtOH}^3} \qquad (3)$$

where, a_i denotes the activity for the compound in terms of the activity coefficient and mole fraction, given by:

$$a_i = \gamma_i \times x_i$$

The equilibrium constant is described by Fite *et al* (1994) as seen in Equation 4.

$$K = exp(1140 - 14580T^{-1} - 232.9ln(T) + 1.087T - 1.114 \times 10^{-3}T^2 + 5.538 \times 10^{-7}T^3) \quad (4)$$

and the rate constant is described in Equation 5 (Fite *et al*, 1994).

$$k' = 4.7 \times 10^{12} exp(\frac{-10360}{T}) \qquad (5)$$

The above kinetics is described with temperature in Kelvin, the rate constant (k') has units of $mol\,hr^{-1}\,g^{-1}$. Therefore, r_{ETBE} has units of $mol\,hr^{-1}\,g^{-1}$, since activity and equilibrium constant is considered dimensionless.

The kinetics for Reaction 2 had to be modelled from a different source due to the reaction designed being specific to the project brief. Velo *et al* (1988) studied reaction kinetics for Reaction 2 in the temperature range 303 K to 333 K, which fits the designed temperature for this reaction (De Sousa Melim *et al*, 2020). Addtionally, the reaction kinetics were established for the liquid phase reversible reaction over the catalyst Amberlyst-15. Equation 6 details the rate eauqtion described by Velo *et al* (1988):

$$r_{TBA} = k \times \frac{C_{IB}C_W - \frac{C_{TBA}}{K_C}}{1 + K_A C_A} \qquad (6)$$

now, where

$$K_A = exp(26.6 - \frac{8540}{T})$$

$$k = exp(15.03 - \frac{8844}{T})$$

$$K_C = exp(\frac{3160}{T} - 6.78)$$

The kinetics are described with C_{IB}, C_{TBA} and C_W having units of $kmol\,m^{-3}$ and temperature in Kelvin. The rate equation therefore, is described having units as $kmol\,kg^{-1}\,s^{-1}$. Furthermore, from the above kinetics reaction rates for the remaining reactants can be determined using stoichiometric numbers.

2 Physical Model

A shell and tube packed bed reactor is designed for the isothermal production of ETBE (De Sousa Melim *et al*, 2020). The packed bed reactor is modelled physically to provide a platform for the simulation of the packed bed reactor design. The physical modelling, allows for complete sizing to be achieved as well as estimation of parameters that influence the simulation of the reactor. For the physical modelling to begin, a few simplifying assumptions were made. The first simplifying assumption that was made, was stated in Section 1, $\Delta Cp_{rxn} = 0$. This simplifies an isothermal reactor, as the carrying capacity of the components in the reactor do not change along the length of the reactor.

The mixture inside the reactor is assumed to be a non-ideal mixture which is modelled on the UNIFAC thermodynamic model. The kinetic model for ETBE production in Section 1, required γ values to calculate the activity for each compound in the rate equation. For simplicity of the design, and having Fite *et al* (1994) report a list of very similar γ values at different temperatures – using the UNIFAC thermodynamic model, average γ values were assumed constant. The list below provides the values selected for kinetic and physical modelling. These values were taken from the simulation provided by De Sousa Melim *et al* (2020) at the inlet to the reactor:

- $\gamma_{ETBE} = 1$

- $\gamma_{EtOH} = 2.16$

- $\gamma_{IB} = 1.29$

Physical modelling needed to be conducted for the catalyst. The catalyst selected in the group design was Amberlyst-15, the decision to design a reactor using this catalyst was well justified by De Sousa Melim *et al* (2020). Catalyst diameter has a significant affect on the modelling and simulation of the reactor design. It is important to take note that kinetic modelling was based of catalyst diameters of around 0.1 mm. Small catalyst

diameters are usually undesirable in the case of pressure drop, since catalyst diameter and pressure drop have an inversely proportional relationship. However, when external and internal mass transfer affects are considered, a trade off is encountered. The trade of is that a small catalyst diameter implies a small boundary layer that forms on the catalyst during transportation. Therefore, a smaller catalyst particle becomes desirable as it enables internal mass transfer effects to be negated at a cost of a slightly increased pressure drop. Fite *et al* (1994) and Velo *et al* (1988) state that the given reaction kinetics make a valid assumption that internal mass transfer is negligible. Due to the relation between internal mass transfer and flow rate, higher flow rates than those used by Fite *et al* (1994) and Velo *et al* (1988), imply that a slight increase in the catalyst particle size will not have a significant affect on the internal mass transfer. The catalyst particle diameter was taken from Domingues *et al* (2012), as this study modelled actual plant data for ETBE production reactors. Additional support for the selection of the particle size diameter is provided by Lenntech (2020), who states that the average particle diameter for Amberlyst-15 is between 0.6 and 0.85 mm. Concluding, the assumption that internal mass transfer is negligible holds true for the selected particle diameter and selected kinetic models are valid and applicable. The remaining physical properties associated with the catalyst are catalyst density, porosity and bed density. The porosity (ϵ) of the catalyst was taken from Ehteshami *et al* (2006) while catalyst density (ρ_c) was given by De Sousa Melim *et al* (2020). The bed density (ρ_b) can now be calculated as shown in Equation 7:

$$\rho_b = (1 - \epsilon) \times \rho_c \tag{7}$$

Further assumptions to allow for complete modelling and sizing are listed below:

- No coking of the catalyst occurs due to operating temperature well below potential cracking and coking temperatures typically encountered

- Heat exchange is one dimensional

- Temperature and concentration profiles are non-radial

- The temperature of the cold water utility (T_U) is constant (cooling water at 30 °C

- Fluids are Newtonian and in turbulence

- Molar heat capacities, heat of reactions and other flow parameters are taken from De Sousa Melim *et al* (2020) and are assumed to be constant.

- The inert compounds are grouped together and average heat capacity and molar mass is assumed for the inert mixture

- The reactor was modelled by the dynamic pseudo-homogeneous plug-flow reactor model (Domingues *et al*, 2012)

The packed bed reactor was modelled using a mole and energy balance. The mole balance is given in Equation 8, where the subscript i is used to denote the ith component:

$$\frac{dF_i}{dW} = r'_i \tag{8}$$

Following the mol balance, the energy balance is as shown in Equation 9:

$$\frac{dT}{dW} = \frac{\frac{U \times a}{\rho_b} \times (T_U - T) - (r_{ETBE} \times \Delta \text{Hrx}_1 + r_{TBA} \times \Delta \text{Hrx}_2)}{Fo_i Cp_i} \tag{9}$$

where, $a = \frac{4}{d_t}$ and d_t denotes the internal tube diameter while ρ_b is the bed density. The $Fo_i Cp_i$ term is given as:

$$Fo_i Cp_i = Fo_{ETBE} Cp_{ETBE} + Fo_{EtOH} Cp_{EtOH} + Fo_{IB} Cp_{IB}$$
$$+ Fo_{TBA} Cp_{TBA} + Fo_W Cp_W + F_{Inert} Cp_{Inert}$$

The Fo is used to illustrate that the flow rate being used is constant and is taking as the inlet flow rate to the reactor. This aligns with the assumption that $\Delta \text{Cp}_{\text{rxn}} = 0$

Heat exchanger design was integrated into the reactor design and physical modelling. The integration of heat exchanger design began with reasonable estimation for the overall heat transfer coefficient (U), from literature. Sinnott & Towler (2019) provides a range of overall heat transfer coefficients for shell and tube heat exchangers for various hot and cold fluids. Based on the assumption that cooling water is available as the cold utility at $30\,°\text{C}$, the cold fluid is water. The hot fluid is considered a product from crude oil processing and is assumed to be a light oil. This is a fair and valid assumption as light oils are used to produce petroleum gas. The hot fluid is therefore, designed as the hot fluid. Sinnott & Towler (2019) suggested that U range between 350 and 900 $\text{W}\,\text{m}^{-2}\,\text{K}^{-1}$, for light oils as the hot fluid and water as the cold fluid, in a shell and tube heat exchanger. Conservative design implies a selection of the lower value for the overall heat transfer coefficient. The conservative approach was taken based on the fact that the lower overall heat transfer coefficient implied that design would assume the worst estimated heat transfer ability for the reactor. Additional support for the conservative heat transfer coefficient approach is provided by industrial plant data for the production of ETBE, which suggested that the

overall heat transfer coefficient be in a region of $70\,\mathrm{W\,m^{-2}\,K^{-1}}$ (Domingues *et al*, 2012). Thus:

$$U = 350\,\mathrm{W\,m^{-2}\,K^{-1}}$$

Once a reasonable, fair and justifiable overall heat transfer coefficient was estimated, the physical sizing of the heat exchanger could be carried out. Greef I.L (2000) provide a table of standard pipe diameters, thickness and length. However, it needed to be kept in mind that common, viable reactors have a pipe diameter between $20\,\mathrm{mm}$ and $75\,\mathrm{mm}$. It is to be kept in mind that larger pipe diameters result in a radial temperature profile. The selection of the catalyst particle diameter steered engineering judgement when selecting the pipe diameter. The engineering judgement was based on knowledge of the pressure drop across the reactor as described in Equation 10.

$$\frac{dP}{dW} = \frac{-1}{\rho_b \times A \times N_{tubes}} \times \frac{G}{\rho \times d_p} \times \frac{1-\epsilon}{\epsilon^3} \times \left(150 \times \mu \times \frac{1-\epsilon}{d_p} + 1.75 \times G\right) \qquad (10)$$

Here, G is the mass flux through the reactor which is calculated as $G = \frac{mass_{in}}{A \times N_{tubes}}$ where A is the area of a single tube and N_{tubes} is the number of tubes. The area is calculated using the geometry of a circle where d_t refers to the internal tube diameter. The recommended wall thickness was used at 4mm (Greef I.L, 2000).

Further support for the engineering judgement used in the selection was also inferred from Lenntech (2020) and DuPont (2020) which report that the maximum pressure drop for the catalyst is $\approx 100\,\mathrm{kPa}$ across the packed bed. It was therefore, concluded, that the best fitting diameter was $d_t = 75\,\mathrm{mm}$. Bonus benefaction is that the slightly larger diameter tube, selected, is easier to clean from fouling that may occur. Greef I.L (2000) suggests that stock length of piping is $6\,\mathrm{m}$. Therefore, it was assumed that the length of the reactor (or) heat exchanger (L) was $6\,\mathrm{m}$. Having engineered the diameter of the tube (inner) and the length of the tube, the number of tubes needed to be determined. The volume of the packed bed can be determined from Equation 11 as shown:

$$V = \frac{W}{\rho_b} \qquad (11)$$

where, W represents the total mass of catalyst (kg). It is to be noted that catalyst mass was designed in order to achieve original designed conversion of 88 % isobutene (De Sousa Melim *et al*, 2020). The catalyst mass was determined by ensuring that the conversion obtained for the packed bed reactor was 88 % isobutene, knowing the equilibrium conversion is around 93 %. The reactor was therefore, designed to achieve

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a specific conversion. Once, determining the volume was complete, having made good engineering judgement on the dimensions for the diameter and length, the number of tubes could be calculated from Equation 12:

$$N_{tubes} = \frac{V}{\frac{\pi}{4} \times d_t{}^2 \times L}$$ (12)

The pressure drop is then calculated with the resulting number of tubes. The pressure drop across the bed must lie within $\approx 100\,\text{kPa}$ yet, be a reasonable pressure drop. If the pressure drop is outside the estimated limit, the diameter and length ratio is re-estimated and re-engineered to re-select the number of tubes following the same procedure beginning at Equation 11.

The arrangement of tubes in the heat exchanger was selected based on the fact that triangular and rotated square arrangement are associated with a higher pressure drop (Sinnott & Towler, 2019). Therefore, the arrangement chosen is a square arrangement. Equation 13 details the equation used to calculate the pitch length for a square arrangement - d_o denoted outer diameter:

$$P_t = 1.25 \times d_o$$ (13)

The pitch length can then be correlated with Equation 14 to size the tube arrangement. The bundle diameter was calculated for a single pass.

$$d_{bundle} = d_o \times \left(\frac{N_{tubes}}{K_1}\right)^{\frac{1}{n_1}}$$ (14)

where constants for the single pass square arrangement can be used from Sinnott (2014). The selection of a pull-through floating head (Sinnott & Towler, 2019) for the shell bundle clearance allows for easy maintenance when cleaning the reactor from fouling that may occur. It is good practise to perform regular maintenance on the equipment to ensure optimum performance of equipment. Additionally, the larger shell bundle clearance allows room for catalyst loading which needs to take place once the catalyst has degraded completely.

3   Model Solution

Table 1 summarises the sizing and parameters used for the model solution.

Table 1: Summary of model sizing and parameter estimation for packed bed reactor design

Parameter	Symbol	Value
Number of tubes	N_{tubes}	776
Overall heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)	U	350
Inner tube diameter (mm)	d_t	75
Outer tube diameter (mm)	d_o	83
Bundle diameter (m)	d_{bundle}	2.2
Nominal shell diameter (mm)	d_{shell}	2540
Length of reactor (m)	L	6
Inlet temperature (K)	T_o	335.15
Utility temperature (K)	T_u	303.15
Porosity	ϵ	0.36
Catalyst density ($kg\,m^{-3}$)	ρ_{cat}	608
Bed density ($kg\,m^{-3}$)	ρ_b	389
Particle diameter (mm)	d_p	0.74
Inlet pressure (kPa)	P_o	1500
Catalyst mass (kg)	W	8000
Catalyst mass per tube (kg)	W_{tube}	10.3
Flow rate ($m^3\,hr^{-1}$)	Q	158
Fluid density ($kg\,m^{-3}$)	ρ	598
fluid viscosity (Pa s)	μ	0.00027
Heat of Reaction 1 ($J\,mol^{-1}$)	ΔHrx_1	-64450
Heat of Reaction 2 ($J\,mol^{-1}$)	ΔHrx_2	-53486

The model solution source code is discussed in Appendix A. Several plots that were developed from the source code in Appendix A are shown in this section. Figure 1 provides insight into both reactions and the rate of consumption and formation. The concentration profile for the ETBE production (Reaction 1) is significantly greater than that of the TBA formation (Reaction 2). This implies a strong dominance from the ETBE production reaction reaction, emphasising the fact that the TBA formation due to the presence of water in the ethanol is a "side" reaction. The ETBE is continuously formed along the length of the reactor, until desired conversion is achieved. To further illustrate the dominance of the ETBE production reaction, Figure 2 shows an initial spike in the temperature of the reaction. This is indicative of dominance from a highly exothermic reaction (Reaction 1). The dominance of the exothermic reaction is slowly depleted as the utility and inert material attempts to consume the exothermic energy and return the reaction to the desired reaction temperature (335 K).
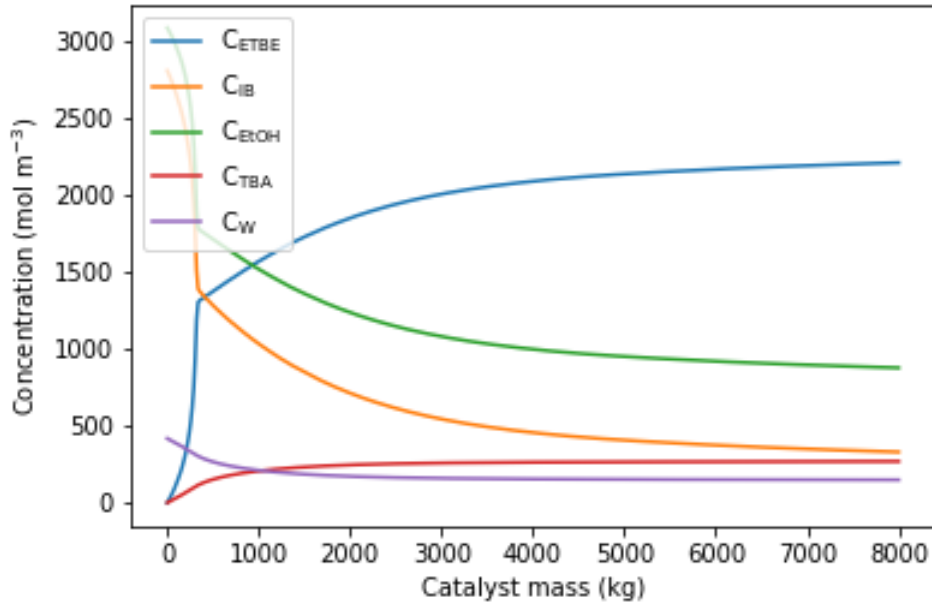
Figure 1: Concentration profiles along the length of the reactor for all components present in the reactor designed
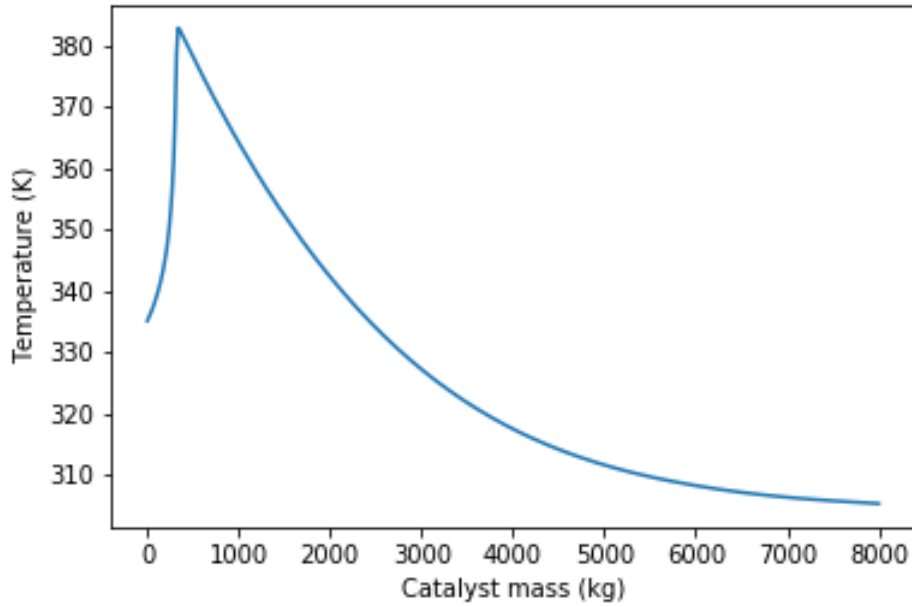

Figure 2: Temperature profile along the length of the designed reactor

Figure 3 shows similar concepts to that of Figure 2. The figure shows the conversion instead of the length of the reactor as the independent variable. Slight similarities can be seen in the two figures in terms of shape. Therefore, the two figures can be used in conjunction to infer the same information about the reactor. The reason for the significantly

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higher, isobutene, conversion is due to the presence of isobutene as a reactant in the ETBE production reaction as well as the TBA formation reaction. Thus, implying that more isobutene will be consumed in comparison to the ethanol and water consumption. The ethanol conversion is close to 75 % which agrees with engineering design reported by De Sousa Melim *et al* (2020).
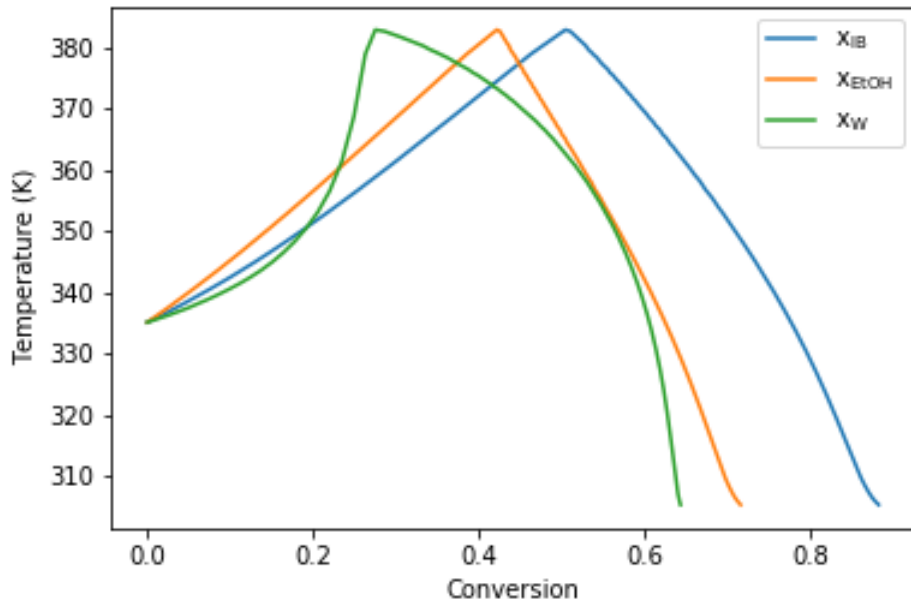
Figure 3: Temperature profile versus the conversion of the different reactants in the reactor

To prove that the conversion along the length of the reactor is not constant, Figure 4, Figure 5 and Figure 6 are shown below. The figures show how the conversion of reactant in the reactor changes as a function of the length of the reactor. Equation 15 details how the component conversion is calculated where the subscript i is used to denote the specific reactant.

$$x_i = \frac{Fo_i - F_i}{Fo_i} \tag{15}$$
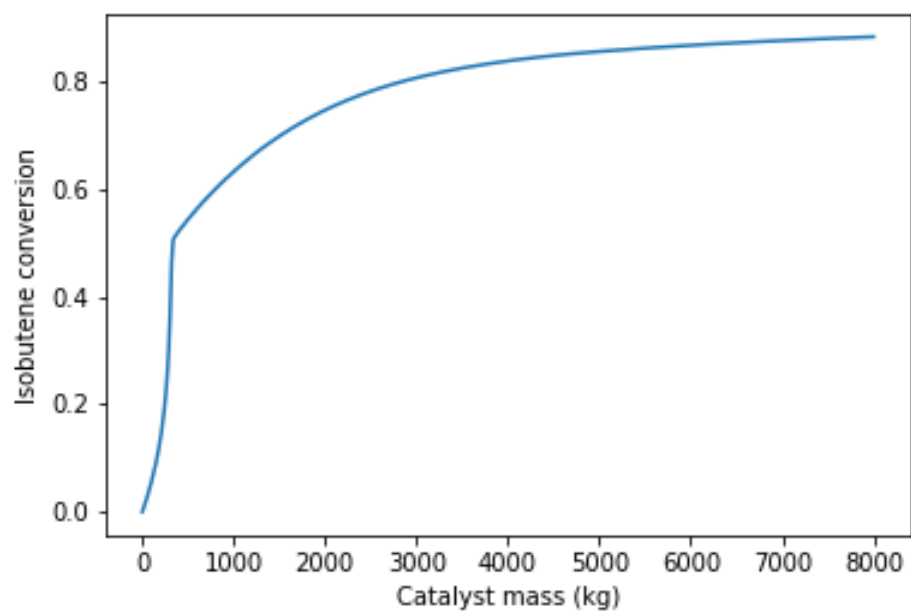
Figure 4: Conversion of isobutene along the length of the reactor
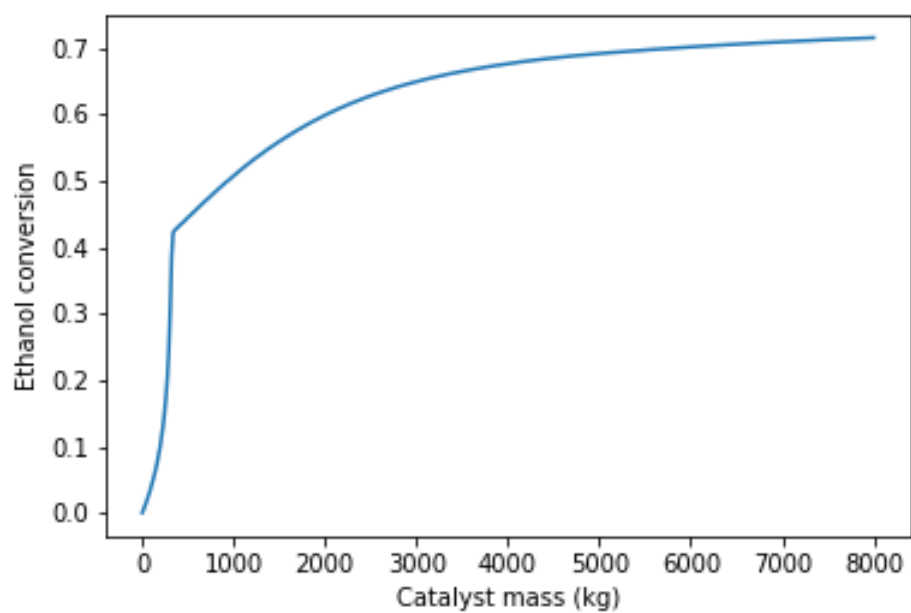
Figure 5: Conversion of ethanol along the length of the reactor
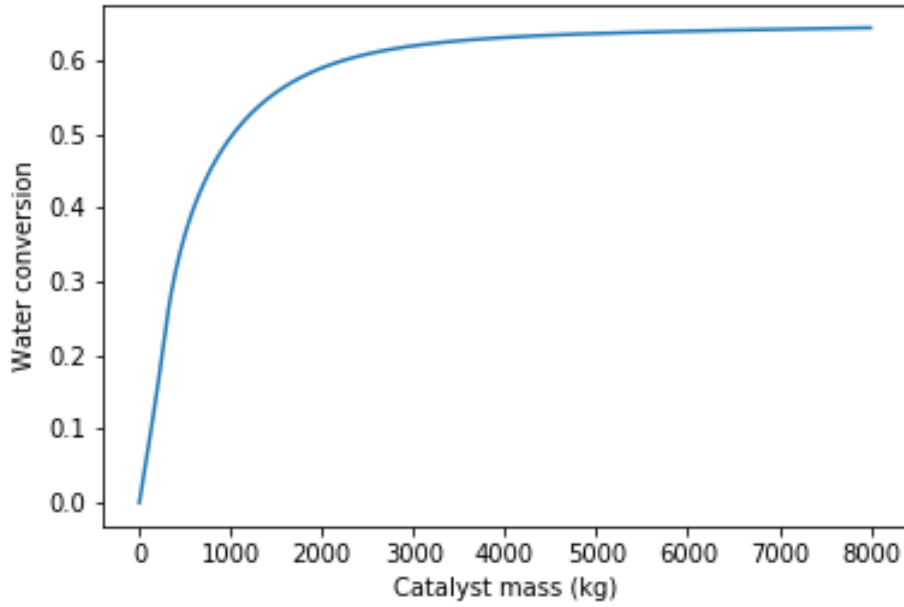
Figure 6: Conversion of water along the length of the reactor

Interesting to note, the conversion of water is relatively less when compared to the conversion of the isobutene and ethanol. This implies that the formation of TBA is not a favoured reaction and that the TBA forms in minor amounts. Therefore, conclusion can be drawn that the TBA formation reaction does not strongly hinder the reaction of ETBE formation.

The pressure profile along the length of the reactor is shown in Figure 7. The figure confirms a pressure drop that is within the limits discussed in Section 2. Therefore, the pressure drop is an acceptable pressure drop and the design parameters used to provide the model solution are valid. The reason the pressure drop is a linear function is due to the reaction occurring in the liquid phase.
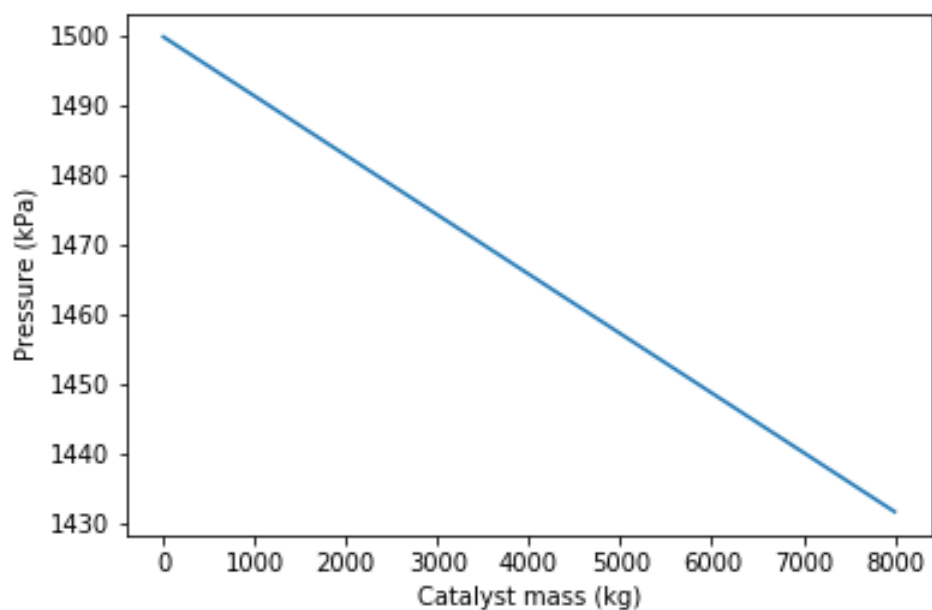
Figure 7: Pressure profile along the length of the reactor

Additional supporting graphs are Figure 8 and Figure 9. Figure 8 shows the concentration profile along the length of the reactor for the ETBE production reaction (Reaction 1). The figures further emphasise the fast, exothermic reaction with initial strong spikes with gradual plateau achieved at desired conversion. The concentration profiles gradually plateau as the conversion approaches equilibrium conversion. Figure 9 illustrates further how the side reaction has a low selectivity, with the formation of TBA being significantly smaller in relation to the conversion of isobutene. Furthermore, Figure 9 shows that the formation of TBA is rapid at the start of the reaction.
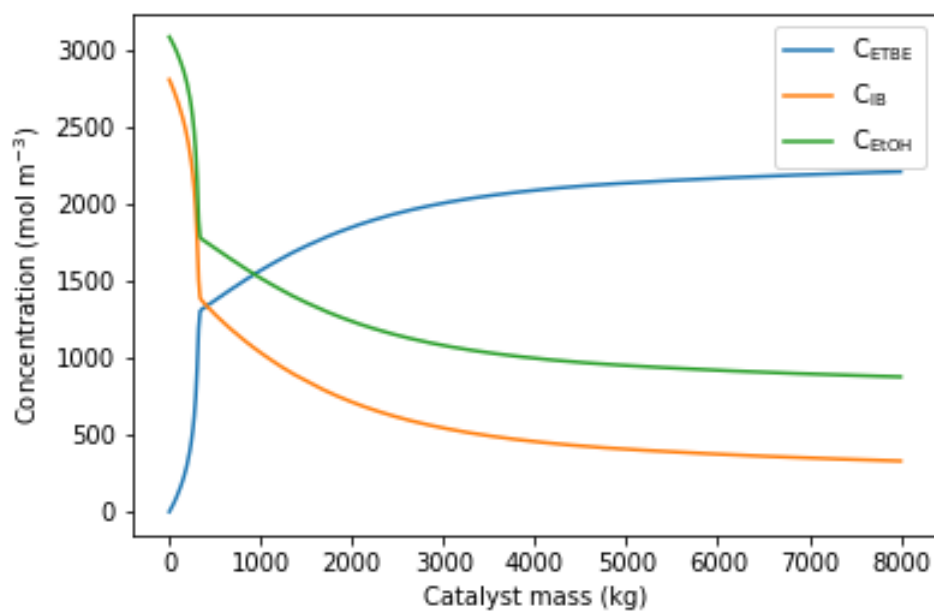
Figure 8: Concentration profile along the length of the reactor for ETBE production reaction (Reaction 1)
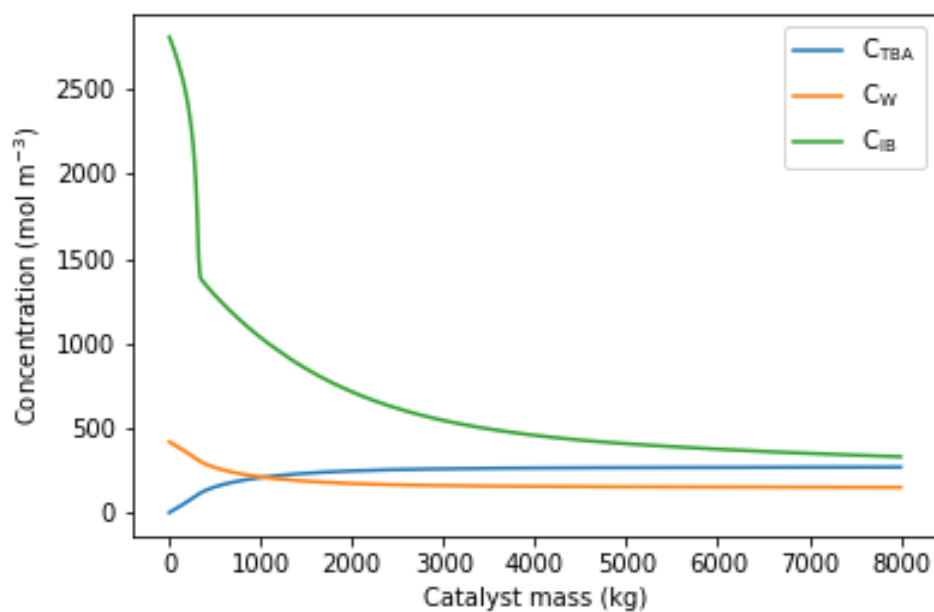
Figure 9: Concentration profile along the length of the reactor for TBA formation side reaction (Reaction 2)

4   Design Detail

The solution as provided in Section 3 allowed for construction of detailed reactor drawing. Figure 10 is a plan for a shell and tube packed bed liquid phase reactor.
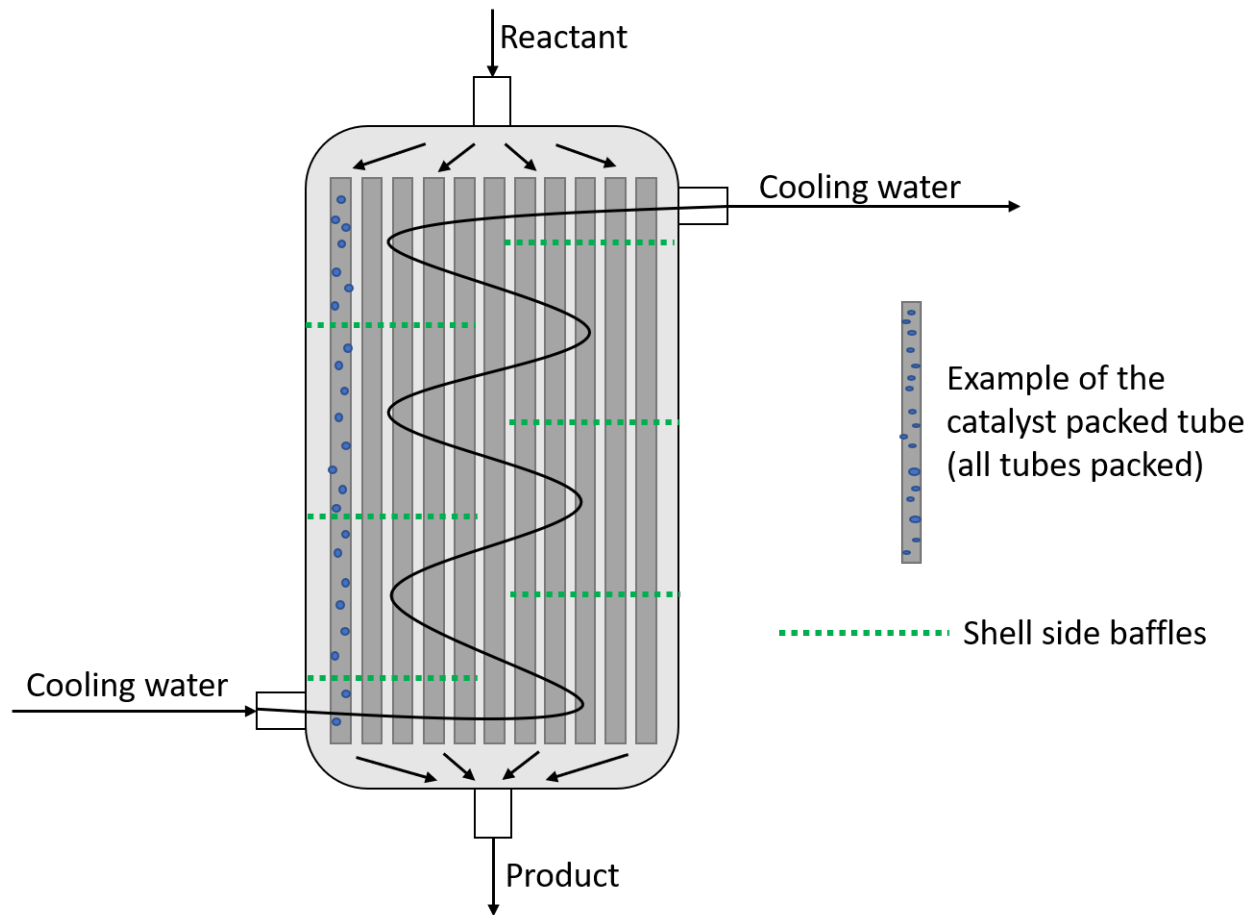

Figure 10: A plan for the reactor design, adapted from Fogler (2006)

Figure 11 provides a detailed diagram for the tube dimensions, square arrangement and pitch dimensions.
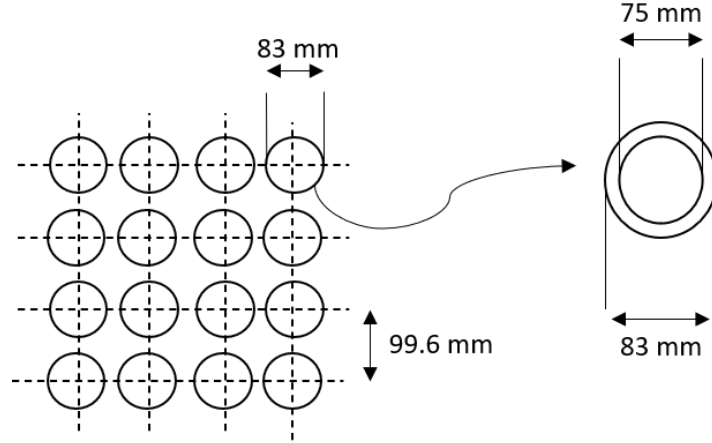
Figure 11: The square arrangement selected for the tube layout with tube and pinch dimensions (Fogler, 2006)

The detailed reactor drawing, with heat exchange integration is provided in Figure 12. The figure details the tube layout for a single-pass floating-head partitions shell and tube packed bed reactor with 776 tubes, design in Section 3. Additionally, fundamental dimensions are indicated.
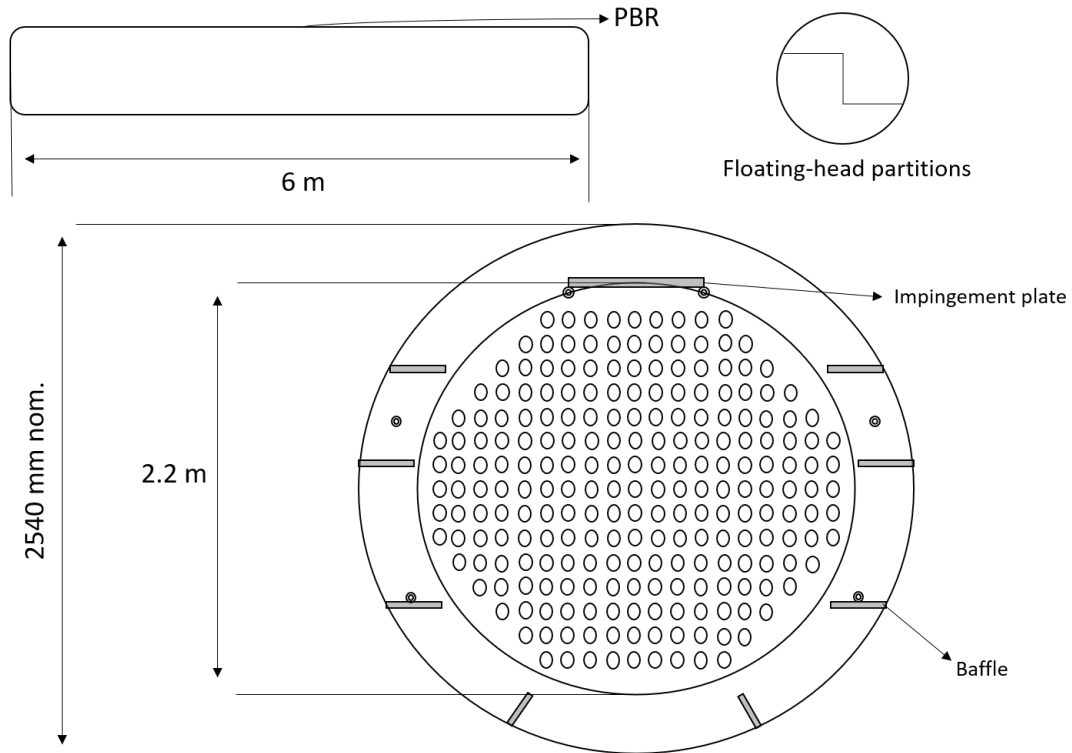
Figure 12: Tubesheet layout and reactor length for a single-pass floating-head partitioned shell and tube packed bed reactor, adapted from Fogler (2006)

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Appendix A   Source Code

The source code for the reactor design is shown in full on the next page.

In [1532]:

```python
import numpy as np
import sympy
from matplotlib import pyplot as plt
%matplotlib inline
from scipy.optimize import fsolve
from scipy.integrate import solve_ivp
from ipywidgets import interact
```

Kinetic model for Reaction 1 (ETBE formation)

In [1533]:

```python
γ_ib = 1.29
γ_etoh = 2.16
γ_etbe = 1

def rate_1(var):
    F_etbe, F_ib, F_etoh, F_tba, F_w , T, P = var
    frac_ib = F_ib/(F_ib + F_etoh + F_etbe + F_i + F_tba + F_w)
    frac_etoh = F_etoh/(F_ib + F_etoh + F_etbe + F_i + F_tba + F_w)
    frac_etbe = F_etbe/(F_ib + F_etoh + F_etbe + F_i + F_tba + F_w)
    a_ib = γ_ib*frac_ib
    a_etoh = γ_etoh*frac_etoh
    a_etbe = γ_etbe*frac_etbe

    K = np.exp(1140 - 14580*(1/T) - 232.9*np.log(T) + 1.087*T - (1.114e-3)*T**2 + (5.53
8e-7)*T**3)
    kp = (4.7*(10**12)*np.exp(-10360/T))*1000/3600 # mol/kg.s
    r_etbe = kp*(((a_ib*a_etoh) - a_etbe/K)/(a_etoh**3))
    return r_etbe
```

Kinetic model for Reaction 2 (TBA formation)

In [1534]:

```python
def rate_2(C_ib, C_w, C_tba, T):
    C_ib, C_w, C_tba = C_ib/1000, C_w/1000, C_tba/1000 # kmol/m3
    k = np.exp(15.03 - 8844/T)
    Kc = np.exp(3160/T - 6.78)
    Ka = np.exp(26.6 - 8540/T)
    r_tba = 1000*k*(C_ib*C_w - C_tba/Kc)/(1 + Ka*C_tba) # mol/kg.s
    return r_tba
```

Physical model parameters

In [1535]:

```
Ntubes = 776
U = 350
dt = 75/1000 #m
To = 62 + 273.15 #K
Tu = 303.15 #K
ε = 0.36
ρcat = 608 #kg/m3
dp = 0.74/1000 #m
Po = 1500 #kPa
W = 8000 #kg
Q = 158/3600 #m3/s
ρ = 598 #kg/m3
a = 4/dt
ρb = ρcat*(1 - ε) #kg/m3
ΔHrx_1 = -64450 #J/mol
ΔHrx_2 = -53486 #J/mol
```

Flow parameters and heat capacities

In [1536]:

```
Fo_etbe = 0 #mol/s
Fo_ib = 444*1000/3600 #mol/s
Fo_etoh = 488*1000/3600 #mol/s
Fo_tba = 0 #mol/s
Fo_w = 66*1000/3600 #mol/s
F_i = (12.6 + 0.6 + 408 + 58.7 + 215 + 20 + 96.5)*1000/3600 #mol/s
Fto = Fo_etbe + Fo_ib + Fo_etoh + Fo_tba + Fo_w + F_i

MM_etbe = 102.17 #kg/kmol
MM_etoh = 46.07 #kg/kmol
MM_ib = 56.11 #kg/kmol
MM_tba = 74.123 #kg/kmol
MM_w = 18.02 #kg/kmol
MM_i = 56.2 #kg/kmol

Cp_etbe = 2.26*MM_etbe #J/mol.K
Cp_etoh = 2.78*MM_etoh #J/mol.K
Cp_ib = 2.53*MM_ib #J/mol.K
Cp_tba = 3.33*MM_tba #J/mol.K
Cp_w = 4.2*MM_w #J/mol.K
Cp_i = 2.49*MM_i #J/mol.K
```

Ergun Equation

In [1537]:

```
A = (np.pi/4)*dt**2
mass_in = 94000/3600 #kg/s
G = mass_in/(Ntubes*A)
μ = 0.00027 #Pa.s

dPdz = -((G/(ρ*dp))*((1 - ε)/ε**3)*(150*μ*(1 - ε)/dp + 1.75*G))/1000 #kPa/m
```

Model

In [1538]:

```python
def PBR(w, var):
    F_etbe, F_ib, F_etoh, F_tba, F_w , T, P = var

    C_etbe = F_etbe/Q
    C_ib = F_ib/Q
    C_etoh = F_etoh/Q
    C_tba = F_tba/Q
    C_w = F_w/Q

    r_etbe = rate_1(var)
    r_ib1 = -r_etbe
    r_etoh = -r_etbe
    r_tba = rate_2(C_ib, C_w, C_tba, T)
    r_ib2 = -r_tba
    r_w = -r_tba
    r_ib = r_ib1 + r_ib2

    dF_etbedW = r_etbe
    dF_ibdW = r_ib
    dF_etohdW = r_etoh
    dF_tbadW = r_tba
    dF_wdW = r_w

    dPdW = dPdz/(ρb*A*Ntubes)
    FoiCpi = Fo_etbe*Cp_etbe + Fo_etoh*Cp_etoh + Fo_ib*Cp_ib + Fo_tba*Cp_tba + Fo_w*Cp_
w + F_i*Cp_i
    dTdW = (U*a/ρb*(Tu - T) - (r_etbe*ΔHrx_1 + r_tba*ΔHrx_2))/(FoiCpi)
    return dF_etbedW, dF_ibdW, dF_etohdW, dF_tbadW, dF_wdW, dTdW, dPdW
```

Model Solution

In [1539]:

```python
wrange = (0, W)
ans = solve_ivp(PBR, wrange, [Fo_etbe, Fo_ib, Fo_etoh, Fo_tba, Fo_w, To, Po], dense_out
put = True)
wspan = np.linspace(0, W, 500)
F_etbe, F_ib, F_etoh, F_tba, F_w, T, P = ans.sol(wspan)

C_etbe, C_ib, C_etoh, C_tba, C_w = F_etbe/Q, F_ib/Q, F_etoh/Q, F_tba/Q, F_w/Q

x_ib = (Fo_ib - F_ib)/Fo_ib
x_etoh = (Fo_etoh - F_etoh)/Fo_etoh
x_w = (Fo_w - F_w)/Fo_w
```

```
C:\Users\Matthew\Anaconda3\lib\site-packages\ipykernel_launcher.py:14: Run
timeWarning: invalid value encountered in log
```
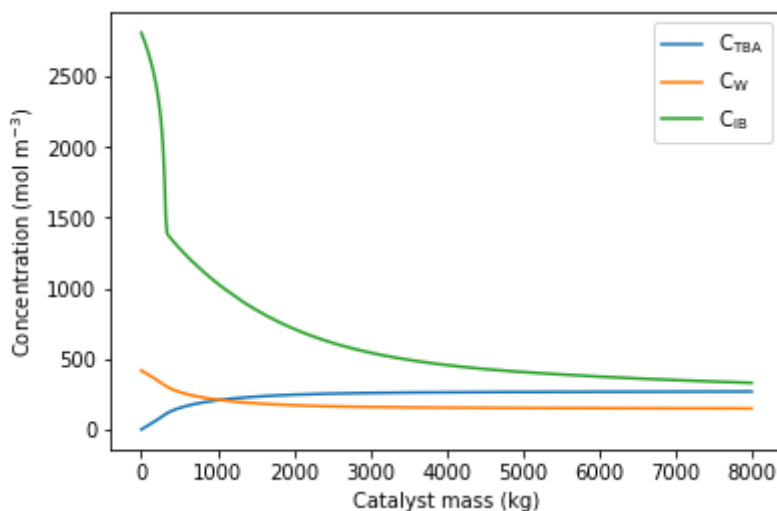
In [1540]:

```python
plt.plot(wspan, C_etbe)
plt.plot(wspan, C_ib)
plt.plot(wspan, C_etoh)
plt.legend(labels = ['$\mathregular{C_{ETBE}}$', '$\mathregular{C_{IB}}$', '$\mathregul
ar{C_{EtOH}}$'], loc = "best")
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Concentration (mol m$^{-3}$)")
plt.savefig("Concentration_Profile_R1.png")
plt.show()
```
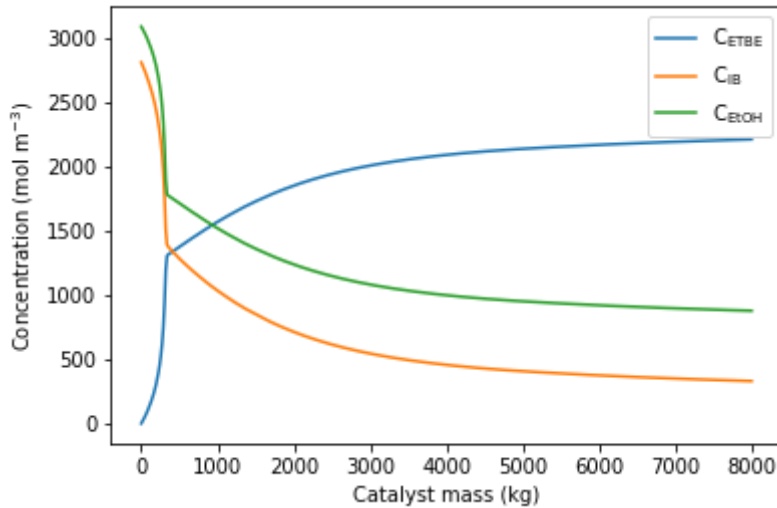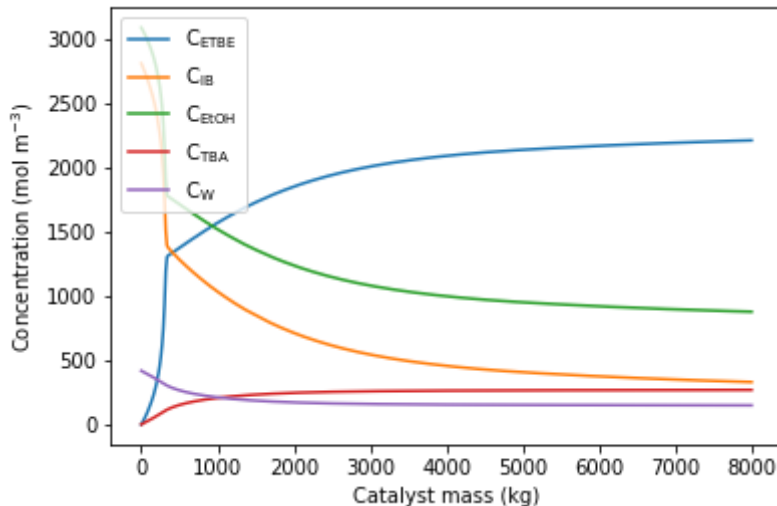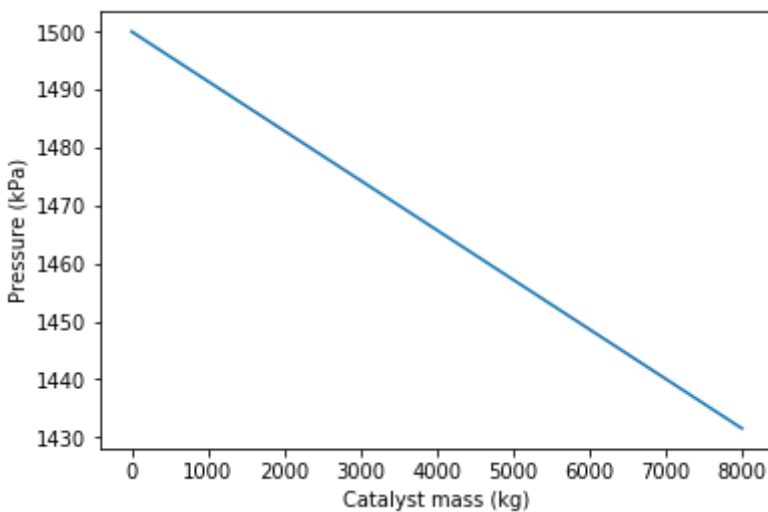

In [1541]:

```python
plt.plot(wspan, C_tba)
plt.plot(wspan, C_w)
plt.plot(wspan, C_ib)
plt.legend(labels = ['$\mathregular{C_{TBA}}$', '$\mathregular{C_{W}}$', '$\mathregular
{C_{IB}}$'], loc = "best")
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Concentration (mol m$^{-3}$)")
plt.savefig("Concentration_Profile_R2.png")
plt.show()
```
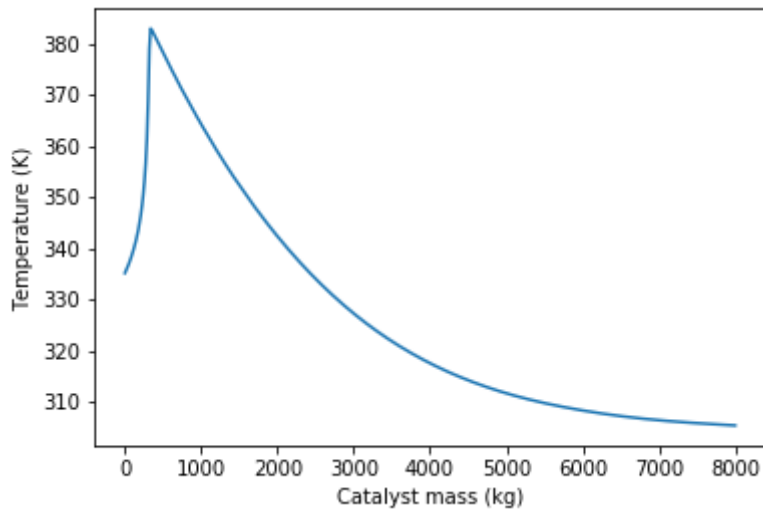
In [1542]:

```
plt.plot(wspan, C_etbe)
plt.plot(wspan, C_ib)
plt.plot(wspan, C_etoh)
plt.plot(wspan, C_tba)
plt.plot(wspan, C_w)
plt.legend(labels = ['$\mathregular{C_{ETBE}}$', '$\mathregular{C_{IB}}$', '$\mathregul
ar{C_{EtOH}}$', '$\mathregular{C_{TBA}}$', '$\mathregular{C_{W}}$'], loc = "best")
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Concentration (mol m$^{-3}$)")
plt.savefig("Concentration_Profile.png")
plt.show()
```


In [1543]:

```
plt.plot(wspan, P)
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Pressure (kPa)")
plt.savefig("Pressure_drop.png")
plt.show()
```
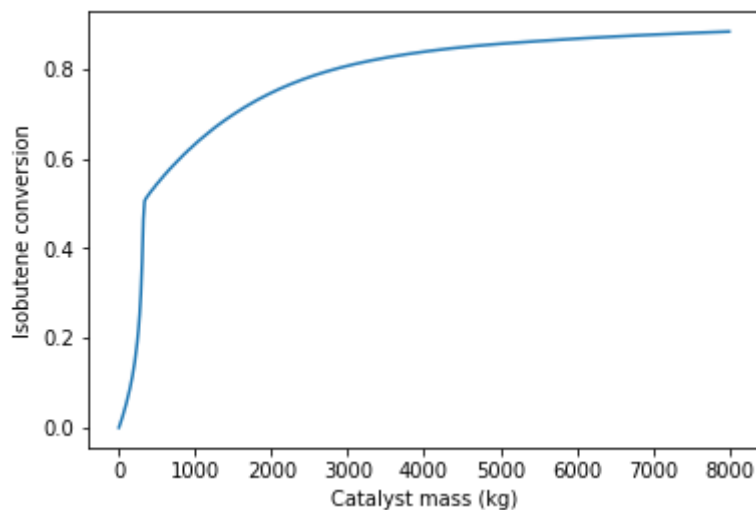
In [1544]:

```python
plt.plot(wspan, T)
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Temperature (K)")
plt.savefig("T_vs_mass.png")
plt.show()
```
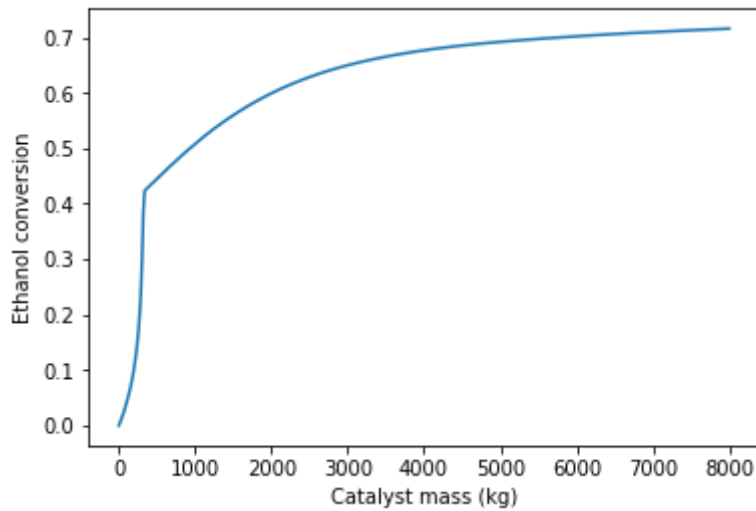

In [1545]:

```python
plt.plot(wspan, x_ib)
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Isobutene conversion")
plt.savefig("mass_vs_x_ib.png")
plt.show()
```
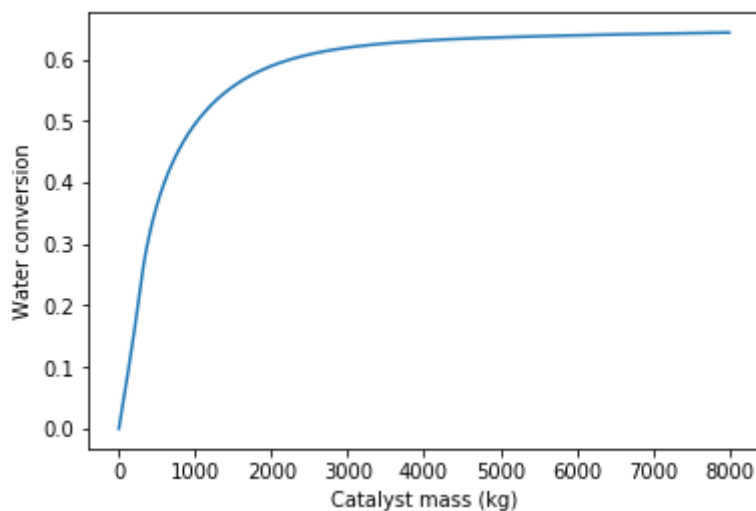
In [1546]:

```
plt.plot(wspan, x_etoh)
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Ethanol conversion")
plt.savefig("mass_vs_x_etoh.png")
plt.show()
```
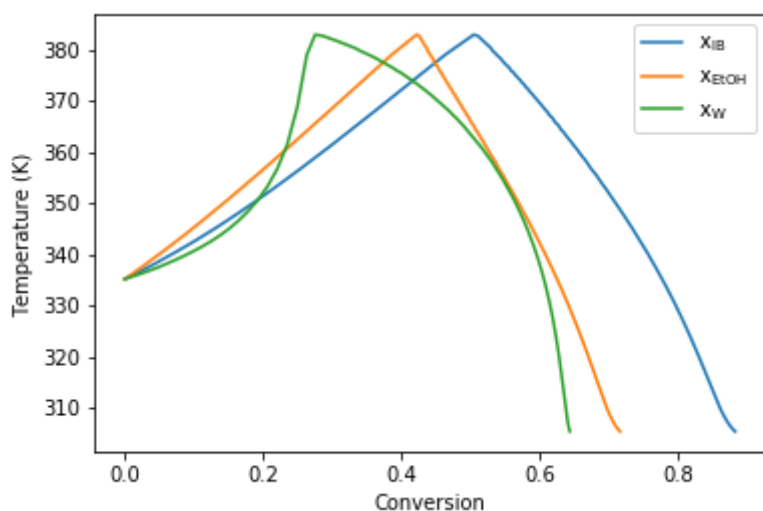

In [1547]:

```
plt.plot(wspan, x_w)
plt.xlabel("Catalyst mass (kg)")
plt.ylabel("Water conversion")
plt.savefig("mass_vs_x_w.png")
plt.show()
```

In [1548]:

```
plt.plot(x_ib, T)
plt.plot(x_etoh, T)
plt.plot(x_w, T)
plt.xlabel("Conversion")
plt.ylabel("Temperature (K)")
plt.legend(labels = ['$\mathregular{x_{IB}}$', '$\mathregular{x_{EtOH}}$', '$\mathregul
ar{x_{W}}$'], loc = "best")
plt.savefig("conversion_vs_T.png")
plt.show()
```


In [ ]:

In [ ]: