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Process Intensification for Autothermal Reaction

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UNIVERSITY OF WOLLONGONG

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Process Intensification for Autothermal Reaction

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ABSTRACT

An external heat source is often required to derive a chemical reaction. In an autothermal reactor the heat from an exothermic reaction is used to produce a self-sustaining scenario in which the use of a continuous heat source is not required. This feature makes autothermal reactors advantageous for various applications. With the proper choice of process conditions and catalyst, autothermal technology can provide high quality and efficient operation.

Recently, there has been an emphasis on developing autothermal reactor concepts for coupling endothermic and exothermic reactions. Autothermal processes have several advantages. These include not requiring an external heat source and being less expensive. The purpose of this thesis is to develop mathematical models which describe the operation of autothermal processes.

In our research we consider a cascade of two reactions occurring in a continuously stirred tank reactor (CSTR) cascade. The reaction mechanism $A \rightarrow B \rightarrow C$ consists of two steps. In the first step the reactant $A$ is converted into an intermediate $B$. In the second step the intermediate $B$ is converted into the final product $C$. The catalyst for the endothermic process is placed in reactor one whilst the catalyst for the exothermic process is placed in reactor two. Consequently the first (second) reaction only occurs in the first (second) reactor.

Several factors, including the influence of the feed temperature and the choice of catalysts, are investigated as mechanisms for increasing the product conversion in a cascade reaction. We obtain new findings and results for different reactor configurations and system operating conditions which improve the product yield. The influence of the main operating variables on the reactor performance is studied.

In this thesis we consider different model configurations in each chapter. In Chapter 2 we investigate the adiabatic reactor. In this chapter the heat-transfer across the walls
of the reactor is assumed to be negligible. The main finding of this chapter is that it is challenging to obtain high conversion of the reactant for realistic feed temperature. In Chapter 3 we analyze the diabatic reactor, where the temperature of the reactor walls are held to be constant. This relaxes the assumption that heat transfer across the reactor walls is negligible. Our most important result in this chapter is constructing the limit point unfolding diagram. This is used to find all the transitions between the steady-state diagrams. The desired autothermal region and the required conditions to achieve the desired conversion are identified from this diagram.

To further enhance the yield of the product species, in Chapter 4 we considered a model with four reactors. The advantage of increasing the number of reactors to four reactors is the possibility of achieving additional conversion of the reactant species into the intermediate species in the third reactor which results in increasing the yield. Weather introducing two additional reactors requires a good choice of the parameter values and initial conditions increases the yield. A cascade with six reactor will show insignificant improvement.

In the previous chapters we assumed that the temperature of the reactor walls is constant. In Chapter 5 we consider the placement of a jacket around the outside of the reaction vessels. This means that the feed temperature for the jackets is an independent variable. As before, we investigated the operating conditions required to achieve a high conversion. In the first reactor we found that the values of the jacket feed temperature and the jacket residence time are almost inconsequential when compared to the role played by the feed temperature. In the second reactor we found that if the residence time in the jacket is sufficiently high, then the value of the jacket feed temperature is irrelevant, i.e./ high conversions can be achieved for any value of the feed jacket temperature. In Chapter 6 we briefly analyze a model with the stream leaving reactor two is the influent stream for the jacket surrounding the reactors. This means that the feed temperature for the jacket is not an independent variable. For this reactor configuration to produce autothermal behaviour highly exothermic reactions are required to achieve the desired conversion for a realistic feed temperature.
DEDICATION

To

My Father
For honest living for me and for supporting and encouraging me to believe in myself
He taught me to work hard for the things that I aspire to achieve

My Mother
A strong and gentle soul who taught to believe in hard work
For teaching me that even the largest task can be accomplished if it is done one step at a time

My loving husband
For support and encouragement during the past three years of my doctoral journey and cheering me on when I was discouraged

My precious children
Malak, Ragad and Saja
who are indeed a treasure from the lord

My respected supervisor
For his kind guidance and encouragement to help me reach at this stage
DECLARATION

I hereby declare that I am the sole author of this thesis and this thesis represents my original work.

I clarify that, to the best of my knowledge and belief, this thesis contains no material previously published by any other person.

I declare that this thesis is a true copy of my thesis, including any final revisions. This thesis has also not been submitted for any degree in any university previously.
ACKNOWLEDGEMENTS

I would like to express the deepest gratitude to the following that without their help this project would not possible:

First, I would like to express my deepest gratitude to my supervisor, Associate Professor Mark Nelson, for his unwavering support and collegiality throughout this research.

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1. INTRODUCTION

The model we investigate in this thesis is a cascade reaction scheme:

\[ A \rightarrow B \rightarrow C. \]

We assume that the reactions take place in two separate reactors in a stepwise manner. This precise model has not been studied before. In the papers reviewed in this study the reactions proceed in the same reactor (coupled).

1.1 Reactor configuration

Our basic reactor configuration consists of two reactors. The first reaction, \( A \rightarrow B \), only happens in the first reactor and the second reaction, \( B \rightarrow C \), only happens in the second reactor. We consider different models for the reactors. In Chapter 2 we consider the adiabatic case when there is no heat loss. In Chapter 3 we consider the diabatic case where the temperature of the fluid surrounding the reactor is constant. In Chapters 5 and 6 we investigate reactor configuration where that is not true. In Chapter 4 we consider a cascade for a consequence of four reactors.

The performance of each model is affected by many aspects, such as the feed flow rate and, in Chapters 5 and 6, the coolant flow rate. The parameters of the feed entering the first reactor are the reactant concentration \( A_0 \), the feed temperature \( T_0 \) and the flow rate \( q \). The out-flow for the first reactor is the in-flow for the second reactor.

1.2 Introduction to the Sal’nikov scheme

The reaction scheme \( A \rightarrow B \rightarrow C \) is known as a Sal’nikov scheme. This model is the simplest nonisothermal chemical scheme that generates oscillatory behaviour.

The Sal’nikov scheme consists of two consecutive first-order reactions. The first re-
action is thermoneutral and the second reaction is highly exothermic. A precursor \( A \) is converted into product \( C \) through an exothermic reaction. This scheme is represented as:

\[
\begin{align*}
A & \xrightarrow{k_1(T)} B \quad (Q_1=0), \\
B & \xrightarrow{k_2(T)} C \quad (Q_2 \neq 0),
\end{align*}
\]  

where the temperature of the two reaction rates has an Arrhenius form. Thus the two rate parameters are given by the expressions:

\[
k_i = M_i \exp \left[ \frac{-E_i}{RT} \right], \quad i = 1, 2,
\]

where \( T \) is the temperature in the vessel having the dimensions of \( (K) \), \( M_i \) are constants having the dimensions of \( (\text{time})^{-1} \), and the constants \( E_i \) are activation energies having the dimensions of \( (\text{J mol}^{-1}) \). The symbol \( R \) denotes the universal gas constant, having the dimensions of \( (\text{J K mol}^{-1}) \). In equations (1.1) and (1.1) the quantities \( Q_i \) where \( i = 1, 2 \) are the heats of reaction, having dimensions of \( (\text{J mol}^{-1}) \).

In formulating a mathematical model for the Sal’nikov schemes, the precursor species is usually ignored. This gives a system of two differential equations, one for the concentration of the intermediate \( B \) and one for the temperature of the reactor \( T \). It is commonly assumed that the reactions take place in a well-stirred reactor.

Our model is different from the Sal’nikov scheme in two aspects:

- we assume that the first reaction is endothermic reaction \( Q_1 < 0 \); and
- the precursor species is not in excess.

### 1.2.1 Model equations

The progress of the reaction is described by the first-order rate equation

\[
\frac{dB}{dt} = k_1[A] - k_2[B],
\]

in which \( k_1 \) and \( k_2 \) are the rate parameters for the two reactions, given by equations (1.3) and the notations \([A]\) and \([B]\) denote the concentration of chemical species \( A \) and \( B \).
respectively. The symbol \( t \) denotes time.

The concentration of species \( A \) is assumed to be maintained as constant \((A = A(0))\). In addition, both reaction rates are temperature dependent and behave in accordance with Arrhenius kinetics (1.3).

The reaction vessel is taken to have a volume \( V \) having the dimensions of \((\text{m}^3)\) and a surface area \( S \) having dimensions of \((\text{m}^2)\), and its contents are well stirred. The fact that energy is conserved within the vessel leads to the differential equation

\[
\rho c \frac{dT}{dt} = Q_2 k_2 [B] - \chi S (T - T_a),
\]

in which the contents of the vessel have density \( \rho \), having dimensions of \((\text{kg m}^{-3})\), and heat capacity \( c \), having dimensions of \((\text{Jkg}^{-1}\text{K}^{-1})\). The first term on the right-hand side of equation (1.5) represents the heat energy generated by the second reaction in equation (1.2) and the second term is the heat energy lost to the outside environment through Newtonian cooling. The ambient temperature \( T_a \), having the dimensions of \((\text{K})\), is assumed to be constant. The remaining parameters are the heat-transfer coefficient \( \chi \) and heat of reaction \( Q_2 \), having dimensions of \((\text{Js}^{-1}\text{m}^{-2}\text{K}^{-1})\) and \((\text{kJ mol}^{-1})\), respectively.

1.3 Literature Review

The paper by Nelson [41] provides an excellent review of papers using the Sal’nikov scheme; however, all the papers reviewed therein assume that the first reaction is thermoneutral. Since we are interested in autothermal reaction, they will not be reviewed again here.

1.3.1 The single Sal’nikov scheme

The scenario in which the activation energy of the first reaction (1.1) is zero, i.e., only the second step is responsive to temperature, is known as a “single Sal’nikov scheme” [41].

• The standard single Sal’nikov scheme

Schinor et al. [55] investigated production rate enhancements in a continuously stirred tank reactor CSTR due to external periodic forcing of chemical reactions.
The long-time average of the single steady-state showed only small enhancements in the production rate, less than 1%. This is a consequence of the strong dependence of the rate constant on temperature.

McIntosh [37] investigated the effect of the drip feed rate of a fuel onto an insulation material. This system is a variant of the Sal’nikov kinetic oscillator and the equations can have one or three steady-states. The main finding is that only a very small drip feed rate is required to induce oscillatory ignition behaviour. It is very difficult to estimate the value for the evaporation/desorption reaction frequency, so it is not simple to estimate the likelihood of limit cycle behaviour. There is limit cycle behaviour when there is no evaporation/desorption from the fibres; this can be avoided by a slow feed drip. In fact, the constant supply of fuel can lead to unexpected oscillatory behaviour.

Villanueva-Marroquin and Barragan [58] studied a thermal engine by applying a second law optimization.

- **The non-standard single Sal’nikov scheme**

A non-standard Sal’nikov scheme modifies or extends the standard Sal’nikov scheme. The Sal’nikov scheme was extended in [39, 41, 42] by making the second stage an oxidation reaction with the representation

\[ F + nO_2 \rightarrow nC, \]

where \( F \) is the concentration of the precursor species in the reactor, \( O_2 \) is the concentration of oxygen in the reactor and \( C \) is the concentration of product species \( C \) in the reactor. The dynamics of this scheme were investigated in a CSTR and the steady-state structure analyzed by applying the techniques of singularity theory. Two cases were considered: adiabatic operation [41] and diabatic operation [42]. Under the assumption of adiabatic behaviour this system reduces to one equation and consequently periodic solutions are impossible. In the diabatic reactor Hopf bifurcations may occur. When the steady-state multiplicity and the degenerate Hopf points bifurcation diagrams are combined they give rise to a total of 23 generic
steady-state diagrams for the diabatic model.

In [39] the effect of an inert additive added to the reaction mixture is examined. The role of a diluent in both the adiabatic and the diabatic reactors is considered. The effect upon the flammability limit when the inert additive is replaced by a heat-sink additive is also considered.

Trenham and Forbes [57] analyzed a model describing the thermodynamic effects of a chemical stored in isolated sealed drums in a closed shipping container. They analyzed the case where the drums are identical and have a constant temperature throughout. They used a quasi-stationary approximation which reduces the system from three differential equations to a single Sal’nikov scheme. They also analyzed the case in which all drums in the shipping container start with the same temperature and behave identically. In both cases they analyzed the nature of the Hopf bifurcations found.

Olajuwon and Popoola [45] extended the model of Trenham and Forbes [57] by introducing a temperature broadening factor to the Arrhenius term in the form

\[ k(T) = MT^m \exp \left[ -\frac{E}{RT} \right], \]

where \( m > 0 \). It was shown that the self heating chemical gradually loses stability as the exponent \( m \) (\( m < 1 \)) rises and reaches maximum. No results for Hopf bifurcations were shown when \( m \geq 1 \).

Fairlie and Griffiths [21] investigated the spatial development of gas-phase and thermokinetic oscillations in a spherical reactor. They based their work on the Sal’nikov thermokinetic scheme. Dirichlet and Neumann boundary conditions were variously selected. It is shown that the rising concentration of the intermediate chemical species precedes the temperature increase for spatially uniform conditions. There is a supplementary kinetic effect of diffusive flux of the intermediate species from a low reactivity region to a high reactivity region.

Forbes [23] used both analytical and numerical methods to study the formation of spatially dependent patterns in a burning reaction. This was done by using a
simple Sal’nikov scheme as a model for burning at the face of a circular substrate. He showed that the temperature develops hot and cold circular rings and that spatial patterns can form. A shooting method was used to solve the non-linear equations. A complicated bifurcation diagram was obtained where multiple solutions occur at the same values of defining parameters.

1.3.2 The double Sal’nikov scheme

When both activation energies are nonzero the resulting mechanism is a “double Sal’nikov scheme”.

- The standard double Sal’nikov scheme

Chen et al. [16] analyzed the optimal path of a Sal’nikov scheme using optimal-control theory. Their aim was to maximize the yield of the intermediate species $B$ in the reaction

$$xA \Leftrightarrow yB \Leftrightarrow zC$$

in a given time period assuming that both reactions are reversible and taking the temperature as a control variable. They compared their results with those obtained in [5] and found that both optimal baths start with a branch at infinite temperature and that there is a curve in which switching from this temperature to a lower temperature is possible. For given parameters, there is a unique “maximal useful time” for both optimal baths that results in the largest possible yield of $B$. When the chemical reaction orders are non-unitary ($x \neq 1, y \neq 1, z \neq 1$) the maximum obtainable yield is smaller.

- The non-standard double Sal’nikov scheme

Kiryukhin [30] studied thermokinetic rate oscillations in cryochemical chain reactions theoretically and experimentally. He investigated oscillatory modes in crystalline and glassy states. It is noted that thermokinetic oscillations can occur in a solid phase at low temperatures, whereas they cannot occur in gas or liquid phases. The emergence of nonstationarity in low-temperature polymerization leads to broadening of the molecular mass distribution of the polymer. As a result, understanding
the mechanism of the process allows insights to eliminate the possibility of thermal explosion and to maintain the stationary regime.

Panfilov et al. [47] represented periodic and meandering spiral patterns in a reaction diffusion model of flames. The model focused on parameters that are representative of combustion. The evolution of spiral structures was studied as a function of parameters. It was found that spiral solutions are stable steady-state solutions of the model. The spiral disappears as its period approaches infinity.

1.3.3 The Sal’nikov scheme in fluid mechanics

Cardoso et al. [14] investigated, theoretically and numerically, the role of heat and mass transfer in the presence of natural convection. They showed how natural convection develops in an oscillatory reaction and how it affects the spatial structure and temporal evolution of the concentration and temperature fields in a closed vessel. In [15] they developed a theoretical understanding of the complex interaction between chemical kinetics, diffusion and convection for a gas-phase Sal’nikov scheme in a closed vessel. They calculated analytically the time scales for reaction, diffusion and natural convection - these depend upon the physical and chemical parameters of the system. They showed that the fluid behaviour of the system depends on the relative magnitudes of these time scales.

Campbell et al. [12] extended the analysis by Cardoso et al. [15]. The authors developed scales for the characteristic concentration of the intermediate $B$, the temperature rise and velocity when the reaction occurs for two cases: when either the diffusion or the convection transport mechanism dominates. The scales used showed that natural convection is preferred by high pressure in gas-phase reactions and in large reactor vessels.

Campbell et al. [11] extended the study of natural convection started in [14]. They investigated the phase relationship between oscillations in the temperature and the concentration of the intermediate substance for a gas undergoing a Sal’nikov reaction in a closed spherical vessel whose wall is held at a constant temperature. This phase relationship is studied at various points inside the reactor. In all, 16 cases were considered that exhibit temporal oscillations in the temperature and concentration of the intermediate substance. Three of these cases are discussed in detail; their behaviour is typical of the other 13 cases. It was found that oscillations could be in anti-phase throughout the reac-
tor, or be in anti-phase with a hot zone at the top of the reactor and in-phase with a cool zone at the bottom. These differences in phase at various points inside the reactor are due to complex interaction between the chemical kinetics and heat and mass transport, by both concentration flow and diffusion.

1.3.4 Chemical model designs

It is known that multiplicity characteristics cause process design limitations. Based on behaviour process, Yuan et al. [60] provided a strategy for classifying the operation region of chemical process design in different zones. They applied this strategy to both isothermal CSTR and exothermic CSTR models. The models’ behaviour and stability vary with the operating conditions, such as feed flow rate and coolant flow rate. Consequently, for guiding process design and operation, it is very important to know how the inherent properties change with a change in operating conditions.

Yuan et al. [61] considered a model of a two-stage-riser fluidized catalytic pyrolysis (TSRFCP) to maximize propylene yield. Their model illustrated multiple steady-state solutions and open-loop dynamics over different operating conditions. They showed that this process has at least one steady-state and a maximum of three steady-states. Steady-state multiplicity may occur depending on the choice of the input and output variables and the operating conditions. Yuan et al. [61] applied classic control theories and steady-state multiplicity analysis on TSRFCP to evaluate the maximum deviation with different combustion modes. They found that, for control system design, the output temperatures and the cooling flow rate are important to control structure.

Russo and Bequette [54] illustrated the steady-state multiplicity for a jacketed CSTR. They showed that adding a jacket equation to the model has an important effect on the steady-state behaviour. The influence of the controller behaviour of the two and three-state CSTR models on the multiplicity was considered. It was shown that a stable steady-state occurs in the two-state model and an unstable steady-state occurs in the three-state model.

As the reactor design and operating conditions play a key role in the product conversion Raganati [48] presented a model for the continuous production of Acetone, n-Butanol and Ethanol (ABE) using four reactors connected in a series. The process was carried out
for more than three months.

In boric acid production refinement of gypsum crystals is the key process to increase the production yield and purity of boric acid. Recent studies have examined the influence of gypsum crystal size growth in continuous flow experiments on the production yield in a batch reactor and continuous stirred tank reactor [10]. They compared the gypsum crystals obtained in the batch and continuous stirred systems. The crystals of gypsum obtained in the continuous process are larger than those obtained in a batch reactor for long residence time.

1.3.5 Autothermal process

An autothermal process offers a new and efficient approach for chemical reaction. In terms of coupling the endothermic reforming with the exothermic oxidation, efficient heat and mass transport between the oxidation catalyst and the steam reforming catalyst is the key to reactor design. Ma et al. investigated mathematically five different reactor configurations for autothermal production of hydrogen \( H_2 \) from methanol [35]. The results show that the arrangement, in which the oxidation catalyst is placed in the inner sphere and the steam reforming catalyst around it, is the most desirable configuration in terms of efficiency and hydrogen production maximization. Thus in order to achieve the desired conversion for a spherical pellet, coupling “egg yolk” distribution of an active catalyst with a diffusion barrier in the outer region will fulfil this objective [1]. Also, this method will maintain the reaction rate when catalyst deactivation occurs. For reducing catalyst deactivation via sintering the use of a two-stage reactor is beneficial. This reactor configuration performs over a long time when the catalyst is exposed to less extreme temperatures [49]. Also, the use of an in situ water removal process increases the exothermic catalyst life and reduces the catalyst deactivation [50]. Therefore, this technique results in improving the reactor performance and higher yield. However, the use of glycerol-water solution in a quartz reactor results in chemical failure because of catalyst deactivation and via sintering and chemical poisoning [52].

Recent studies have focused on the numerical modeling, kinetics and mechanism of the reaction. Dixit et al. studied methane autothermal reforming using a validated microkinetic mechanism to derive a single step rate equation [19]. This technique is able to predict
correctly the methane conversion as well as the outlet mole fraction. In order to maximize the production rate other techniques were used in many studies. Karimi et al. used the differential evolution technique to optimize the operating conditions of a thermally coupled reactor [27]. This model affords superior hydrogen production compared to the production obtained from a non-optimized model. Also, predicting the effect of the main operating variables, i.e. temperature, using different methods such as a non-dominated sorting genetic algorithm is a beneficial way to synthesis gas production [38]. The reform temperature has a strong influence on the system efficiency [4]. Using a water gas shift reactor (WGS) affects the fuel process efficiency positively. Thus the performance of a methane autothermal reformer is higher than that of one without WGS.

Because of global problems of energy shortage and pollution, the development of sustainable and renewable energies is vital. The implementation of new methods for hydrogen production is required. Hydrogen production by autothermal reforming holds great potential because of superior properties. For the aim of developing sustainable energies Xue et al. adopted the ethyl acetate via autothermal reforming over a series of $Ni_xLa_{10-x}O_y/Al_2O_3$ catalyst [59]. It is shown that catalyst $Ni_3La_7O_y/Al_2O_3$ was effective for autothermal reforming of waste cooking oil in hydrogen.

There has also been attention to the conversion of bioethanol to hydrogen due to its high hydrogen content. For sustainable hydrogen production via autothermal reforming of bioethanol, process design and the environmental life cycle of hydrogen has to be addressed [28, 29]. The thermal efficiency of the autothermal process indicates that about two-thirds of the energy fed to the system is converted to useful hydrogen. However, this process suffers from low performances because the environmental process is lower than similar findings previously reported for other reformates. Applying the dense membrane reactor for autothermal steam reforming shows maximum hydrogen production and stable behavior [26]. Furthermore, Fischer and Iribarren found that the counter current arrangement with sweep stream reduces the total annualized cost more than the traditional separation configuration [22].
1.3.6 Industrial model

Cantrell and Luyben [13] used the design of nonisothermal CSTR in [18] to apply their methodology to incorporate the effect of transition time into the design of a continuous multiproduct process.

Blanco and Bandoni [7] presented a new theoretical shape for the interaction between process design and operability. They applied the proposed methodology to the dynamics of typical nonisothermal CSTR provided by Devia and Luyben [18] to ensure local dynamical stability in a Lyapunov sense. In [8] Blanco and Bandoni presented an optimization approach for open loop stability. This is based on Lyapunov’s stability theory and is formulated as an eigenvalue optimization problem. The proposed technique is applied to a CSTR design provided by [18]. Under specific conditions, it is shown that the approach works well for small sized reactors in which the system’s dynamics are not very involved. However, it is not expected to perform successfully for large and complicated designs. Also, Blanco et al. [9] presented an approach to introduce a systematic technique for feedback control design. This is also based on Lyapunov’s stability theory and the non-linear problem is formulated as an optimal closed loop design.

We will apply our methodology to parameter values that are typical of an industrial CSTR [18]. These parameters are all derived from the book [33, page 110]. They are used in Russo and Bequette [53], Shacham et al. [56] and Devia and Luyben [18].

Tab. 1.1: Typical parameter values for an industrial process [18, 53, 56] and [33, page 110].

<table>
<thead>
<tr>
<th>Parameter values</th>
<th>SI Units</th>
<th>NonSI Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S )</td>
<td>23.22576 m(^2)</td>
<td>250 ft(^2)</td>
</tr>
<tr>
<td>( V )</td>
<td>1.35936 m(^3)</td>
<td>48 ft(^3)</td>
</tr>
<tr>
<td>( A_0 )</td>
<td>8008.298025 mol m(^{-3})</td>
<td>0.50 lb mol/ft(^3)</td>
</tr>
<tr>
<td>( c_{pg} )</td>
<td>3.140 J mol(^{-1}) K(^{-1})</td>
<td>0.75 btu/ lb m  R</td>
</tr>
<tr>
<td>( \rho )</td>
<td>801.554 \times 10(^3) mol m(^{-3})</td>
<td>50 lb(_m)/ ft(^3)</td>
</tr>
<tr>
<td>( \chi )</td>
<td>851.735 Js(^{-1}) m(^{-2}) K(^{-1})</td>
<td>150 btu/ h ft(^2) R</td>
</tr>
</tbody>
</table>

1.3.7 Jacketed reactor

Temperature control of a chemical reaction is often the key to obtaining the desired product. A method of temperature control for industrial reactors involves the placement of a jacket around the outside of the reaction vessel. This controls the temperature of
the reactor contents, by circulating a cooling or heating fluid through the jacket. Cooling jackets are used to remove heat from exothermic reactions and heating jackets are used to provide the heat required to drive endothermic reactions.

There are several types of jackets, depending on the design: conventional jackets, half-pipe coil jackets, dimple jackets and plate coils etc:

- **Conventional jackets:** a second shell is installed over a portion of the vessel.
- **Half-pipe coil jacket:** Pipes are split lengthwise then wound around the vessel and welded into a place.
- **Dimple jackets:** a thin external shell is affixed to the vessel shell with spot welds located in a regular pattern.
- **Plate coils:** these are very similar to dimple jackets, but fabricated separately as fully contained jackets that are then strapped to a vessel.

Jackets can be applied to the entire surface of a vessel or just a portion of it. For a vertical vessel, the top head is typically left unjacketed. Jackets can be divided into zones, to divide the flow of the heating or cooling medium.

### 1.3.7.1 The function of the jacket

A chemical reaction converts the reactant in the feed stream into the desired product as the material passes through a stirred tank. The stream exiting the vessel includes the newly created product plus that portion of the feed that was not converted.

An exothermic chemical reaction releases heat and this energy causes the temperature of the material in the vessel to rise. As the temperature rises, the conversion of the feed into product proceeds more quickly, leading to the release of even more heat.

To stop the upward spiral of hotter temperatures increasing the rate of reaction that produces even more heat, the vessel is enclosed with a jacket (or outer shell). A cooling liquid flows through the jacket, collecting heat energy from the outer surface of the reactor vessel and carrying it away as the cooling liquid exits as the jacket outlet.

Since the temperature is vital to improve the product quality, a heating system is critical for endothermic reaction. Thus the capability of the heating jacket influences the
production rate in the endothermic reaction.

1.3.7.2 Controlling conversion by controlling temperature

We seek 90% conversion of reactant feed to product. As the reactor has a constant residence time, the amount of heat energy released inside the vessel is directly related to the amount of feed converted to product. By controlling the temperature in the reactor, we can maintain the percent conversion at the desired value.

1.4 Motivation

Autothermal reactors provide considerable thermal efficiency over conventional reactors. They combine exothermic reactions, which produce heat, and endothermic reactions, which take heat out of the system. In conventional reactors energy must be supplied for endothermic reactions to proceed, typically though the use of external burners or interstage heaters. In an autothermal reactor the required heat is supplied by exothermic reactions. If the system is correctly set up then the overall process is energy neutral. A multifunctional autothermal reactor presents an attractive solution to the implementation of high temperature reactions with moderate overall exothermicity [31, 34]. The absence of an external burner and the accompanying power supplies makes the system both simpler and less expensive.

The use of autothermal reactors is especially germane to steam reforming of light alkanes for hydrogen generation in on-board vehicular fuel cells or syngas manufacture in the petrochemical industry. Another promising application of autothermal processes is in improving the operating conditions by minimizing heat consumption [25]. In particular, autothermal reactors have potential applications in the production of syngas, a gaseous fuel that is a mixture of hydrogen, carbon monoxide and often carbon dioxide [32]. Autothermal reactors are efficient in the production of hydrogen $H_2$ from steam reforming of methanol [34] and in optimising oxidation and steam reforming for methane conversion [46].

The world is currently facing critical challenges in terms of meeting future energy requirements while reducing greenhouse emissions. With rising oil prices and a possible
“peak” in oil resources, the conversion of natural gas into syngas for further production of liquid fuels and/or hydrogen will become crucial to the Australian economy and the standard of living.

The aim of this research is to develop mathematical models which describe the operation of autothermal processes.

In our research the model systems are applied in a typical continuously stirred tank reactor (CSTR) in which there is a continuous supply of reactants whilst products are continuously removed. The advantages of such reactors are:

- They may be operated continuously, which reduces running costs when compared to batch reactors as, for example, less labour is required.
- It is relatively easy to maintain good temperature control.
- Control of the equipment and grade of final product is simplified.

The CSTR can be used either by itself or as part of a series of CSTRs. In such a configuration the exit stream of one reactor is the feed stream for another reactor.

1.5 Model chemistry

We consider a chemical reaction in which a reactant \( A \) is converted to a product \( C \). The reaction mechanism consists of two steps. In the first step the reactant \( A \) is converted into an intermediate \( B \). In the second step the intermediate \( B \) is converted into the final product \( C \).

\[
A \rightarrow B, \quad (1.6)
\]

\[
B \rightarrow C. \quad (1.7)
\]

We assume that the first reaction is endothermic, i.e. heat is required to drive the reaction, whereas the second reaction is exothermic, i.e. heat is produced by the reaction.

We further assume that both reactions only take place in the presence of suitable catalysts. The reaction is assumed to take place in a cascade of two reactors. The catalyst for reaction (1.6) is placed in reactor one whilst the catalyst for reaction (1.7)
is placed in reactor two. Consequently the first (second) reaction only occurs in the first
(second) reactor.

We assume that the reactor vessels are well stirred. The notion of a “realistic” feed
temperature is not well defined. We will consider a feed temperature to be realistic if
\( T_0 \leq 1000K \).

1.5.1 Characteristic temperature

The concept of a ‘characteristic’ temperature is used to formulate the reaction parameters
associated with reactions (1.6) and (1.7). The characteristic temperature is a property of
the catalyst not the reaction. Our approach used the concept of a ‘characteristic reaction
temperature, following from [44].

Nelson and Brindley [40] considered the thermal decomposition of a polymeric material
\( A \) under a constant heating rate \( \alpha \). They assumed that this reaction is first order with
respect to \( A \) and that it is a single-step Arrehenius reaction. This system is modeled by
an “ideal thermogravimetry TG model”, expressed symbolically as:

\[
A \rightarrow B
\]

where \( B \) represents a gas-phase product. The differential form of the model system is

\[
\frac{dA}{dt} = -a_0 \exp \left[ \frac{E_0}{RT} \right] A, \quad (1.8)
\]

\[
\frac{dT}{dt} = \alpha, \quad (1.9)
\]

where \( E_0 \) is the activation energy for the decomposition reaction, \( R \) is the ideal gas
constant, \( T \) is the temperature, \( A \) is the weight of polymeric material remaining at time
\( t \), \( a_0 \) is the pre-exponential factor for the decomposition reaction, \( t \) is the time and \( \alpha \) is
the heating rate. The initial conditions are:

\[
A(0) = A_0, \quad T(0) = T_0.
\]

A polymeric material can be characterised by the temperature at which its reactivity
function, \( y = -\frac{dA}{dt} \), reaches its maximum value, e.g. \( \frac{d^2A}{dt^2} = 0 \). This temperature is called
the ‘characteristic temperature’ ($T_c$). This happens when:

$$\frac{a_0}{\alpha} = \frac{E_0}{RT_c^2} \exp \left[ \frac{E_0}{RT_c} \right].$$

The concept of a ‘characteristic’ temperature is used to formulate the reaction parameters associated with reactions (1.6) and (1.7).

### 1.6 Singularity theory

Singularity theory is a mathematical technique which can be used to investigate how the number of steady-state solutions changes as the parameter values change [1, chapter 2]. In this section we are only interested in whether the steady-state diagram contains limit points and when the limit points disappear via a cusp singularity.

All our models can be reduced to a scalar equation of the form,

$$G(X, \lambda, p) = 0.$$}

The scalar equation contains a state variable ($X$), a primary bifurcation parameter ($\lambda$), and several secondary bifurcation parameters ($p$). The parameter ($p$) consists of spaces with different steady-state diagrams.

The defining and non-degeneracy conditions for limit point bifurcations are

$$G = G_X = 0,$$

$$G_{XX} \neq 0, G_\lambda \neq 0,$$

where $\lambda$ is the selected bifurcation parameter and the subscripts denote the $n$th-order partial derivatives. The two limit points are the ignition limit point and the extinction limit point. Figure 1.1 is a steady-state diagram which contains three steady-state branches and two limit point bifurcations. The steady-state branches represent ‘low’ conversion of the reactant $A$ into product $C$, ‘intermediate’ conversion and ‘high’ conversion. The ignition limit point bifurcation is where the ‘low’ and the ‘intermediate’ steady-state conversion branches coalesce. The extinction limit point bifurcation is where the ‘intermediate’ and
the ‘high’ steady-state conversion branches coalesce.

![Steady-state diagram with two limit points.](image)

Fig. 1.1: Steady-state diagram with two limit points.

The cusp curve is the set of points that satisfy the equations:

\[
G = G_X = G_{XX} = 0, \quad (1.11)
\]

\[
G_{XXX} \neq 0, G_\lambda \neq 0.
\]
1.7 **Software**

In this thesis we used a range of mathematical software to analyze different model configurations. We used software Xpp [20] to integrate the governing equations and also to find the bifurcation diagrams. We also used Maple to plot all figures in this thesis.

1.8 **Thesis structure**

In this thesis we investigate different reactor configurations. In Chapter 2 we consider the adiabatic case when there is no heat transfer between the system and its surroundings. In Chapter 3 we consider the diabatic case. This model relaxes the assumption considered in Chapter 2. In Chapter 4 we extend the diabatic model considered in Chapter 3 by increasing the number of reactors. In Chapters 5 and 6 we examine reactor configuration where the reactor is surrounded by a jacket. In this case we relax the assumption of taking the temperature of the reactor walls to be constant.
2. ADIABATIC REACTOR

In an adiabatic reactor heat-transfer across the walls of the reactor is assumed to be negligible. This means that the process occurs without transfer of heat between the system and its surroundings; such a system is said to be adiabatically isolated. The assumption that the process is adiabatic is useful when it is combined with other systems to make the calculation of the system’s behaviour possible. Furthermore, the assumption of perfect behaviour gives an initial approximation of how the real world works. When the system operates adiabatically the temperature of the reacting mixture in the reactor will rise (exothermic reaction) or fall (endothermic reaction) as the reaction proceeds. Adiabatic operation is preferred for design simplicity due to the heat released by the reaction.

2.1 Adiabatic reactor configuration

Figure 2.1: Prototype reactor configuration. \( A_0 \) is the feed concentration, \( T_0 \) is the feed temperature needed to start the reaction in the first reactor and \( q \) is the flow rate.

Figure 2.1 shows the processes that occur in reactor one and reactor two. The concentration of the reactant \( A \) flowing into reactor one is \( A_0 \). The concentrations of the reactant \( A \) and the intermediate \( B \) leaving reactor one are \( A_1 \) and \( B_1 \) respectively. Recall the reaction (1.7) does not happen in the first reactor. The concentrations of the reactant...
2. Adiabatic Reactor

A and the intermediate B and the concentration C leaving reactor two are \( A_2, B_2 \) and \( C_2 \) respectively. \( T_1 \) and \( T_2 \) are the temperatures of the reacting mixture in reactor one and reactor two respectively.

We are particularly interested in identifying the choice of catalysts and reactor operation conditions that will ensure a minimum of 90% conversion of reactant \( A \) to product \( C \).

2.2 Model equations

In section 2.2.1 we give the model equations for the reaction schemes (1.6) and (1.7). In section 2.2.2 new variables are introduced to non-dimensionalise the system equations.

2.2.1 Dimensional equations

The system of equations in the first reactor is given by equations (2.1)–(2.7):

The rate of change of the concentration of the reactant \( A \).

\[
V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1. \tag{2.1}
\]

The left hand side of the equation represents the rate of change of mass of reactant \( A \) inside the reactor. On the right hand side there are two terms. The first term represents the flow of the material into the reactor at a concentration \( A_0 \) and the flow of the material leaving the reactor at a concentration \( A_1 \). The second term represents the rate at which the reactant \( A \) is converted into the intermediate \( B \). The negative sign indicates that the reactant species has been removed.

The rate of change of the concentration of the intermediate \( B \).

\[
V_1 \frac{dB_1}{dt} = q(B_0 - B_1) + V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1. \tag{2.2}
\]
The left hand side of the equation represents the rate of change of mass of intermediate $B$ inside the reactor. On the right hand side there are two terms. The first term represents the flow of the material into the reactor at a concentration $B_0$ and the flow of the material leaving the reactor at a concentration $B_1$. The second term represents the rate at which the reactant $A$ is converted into the intermediate $B$. The plus sign indicates that the intermediate species has been added.

The rate of change of the concentration of the product $C$.

$$V_1 \frac{dC_1}{dt} = q(C_0 - C_1). \tag{2.3}$$

The left hand side of the equation represents the rate of change of mass of product $C$ inside the reactor. On the right hand side there is only one term. It represents the flow of the material into the reactor at a concentration $C_0$ and the flow of the material leaving the reactor at a concentration $C_1$. There is no reaction term in this equation because this reaction only happens in the second reactor. There is no product $C$ in the first reactor, however the equation is included here for completeness.

The rate of change of the temperature inside the reactor.

$$c_p \rho g V_1 \frac{dT_1}{dt} = q c_p \rho g (T_0 - T_1) - Q_1 V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{a,1}). \tag{2.4}$$
The left hand side of the equation represents the rate of change of thermal energy having units Js$^{-1}$. On the right hand side there are three terms. The first term represents the change in the heat content due to the flow of the material through the reactor. The second term represents the energy that is taken away from the reactor due to the conversion of reactant $A$ into intermediate $B$. The negative sign indicates that the reaction is endothermic. The third term represents the heat transfer coefficient. It has been written as the product $J_1 \chi_1$ rather than the usual form of $\chi_1$. We have done this so that we can nondimensionalise time using a Newtonian-cooling time-scale whilst retaining the ability to consider adiabatic operation by taking $J_1 = 0$. This avoids the use of different dimensionless schemes for the cases of adiabatic and diabatic behaviour.

The definition of the pre-exponential factor $a_1$ in terms of the characteristic temperature $T_{c1}$ (see chapter 1.5.1):

$$a_1 = \frac{E_1 \alpha}{RT_{c1}^2} \exp \left[ \frac{E_1}{RT_{c1}} \right]. \tag{2.5}$$

The initial conditions are given by equation (2.6). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

$$A_1(0) = B_1(0) = C_1(0) = 0, \quad T_1(0) = \frac{q c_p g \rho g T_0 + J_1 \chi_1 S_1 T_{a,1}}{q c_p g \rho g + J_1 \chi_1 S_1}. \tag{2.6}$$

The residence time is the average time spent inside a reactor by the species in the fluid

$$\tau_1 = \frac{V_1}{q}. \tag{2.7}$$

The system of equations in the second reactor is given by equations (2.8)–(2.14). The physical meaning of many of the terms in these equations is identical to those in the first reactor. These have not been repeated.
The rate of change of the concentration of reactant $A$.

$$V_2 \frac{dA_2}{dt} = q(A_1 - A_2).$$ \hspace{1cm} (2.8)

There is no reaction term in this equation as the catalyst for this process is not found in reactor two.

The rate of change of the concentration of reactant $B$.

$$V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2.$$ \hspace{1cm} (2.9)

The second term on the right hand side represents the conversion of the intermediate species $B$ into the product $C$. The negative sign indicates that the intermediate species has been removed.

The rate of change of the concentration of reactant $C$.

$$V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2.$$ \hspace{1cm} (2.10)

The plus sign indicates that the product species has been increased.

The rate of change of the temperature inside the reactor is given by the following equation (the positive sign in the second term indicates that the reaction is exothermic)

$$c_{pg}\rho_g V_2 \frac{dT_2}{dt} = q c_{pg} \rho_g (T_1 - T_2) + Q_2 V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2 - J_2 \chi_2 S_2 (T_2 - T_{a,2}).$$ \hspace{1cm} (2.11)
The definition of the pre-exponential factor $a_2$ in terms of the characteristic temperature $T_{c,2}$ (see chapter 1.5.1):

$$a_2 = \frac{E_2 \alpha}{RT_{c,2}^2} \exp \left[ \frac{E_2}{RT_{c,2}} \right]. \tag{2.12}$$

The initial conditions are given by equation (2.13). As described previously, before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

$$A_2(0) = B_2(0) = C_2(0) = 0, \quad T_2(0) = \frac{q c_{pg} \rho_g T_1 + J_2 \chi_2 S_2 T_{a,2}}{q c_{pg} \rho_g + J_2 \chi_2 S_2}. \tag{2.13}$$

The residence time is

$$\tau_2 = \frac{V_2}{q}. \tag{2.14}$$

Note that the concentrations flowing into reactor two are the concentrations exiting from reactor one. Similarly the temperature of the fluid entering reactor two is equal to that from reactor one. Normally for the two reactor model, we take the residence time in each reactor to be equal, i.e. $\tau_1 = \tau_2$. Therefore, the total residence time for this system is $\tau_r = 2\tau_1$. This means that $\tau_1 = \frac{\tau_r}{2}$ and $\tau_2 = \frac{\tau_r}{2}$.

The terms appearing in equations (2.1)-(2.14) are defined in Table 2.1.

### 2.2.2 Dimensionless equations

In non-dimensionalising equations (2.1)-(2.14) we introduce dimensionless concentrations ($A_i^*, B_i^*, C_i^*$), dimensionless temperatures ($\theta_i$), where ($i = 1, 2$), and dimensionless time ($t^*$). These are defined in Appendix.1.
2. Adiabatic Reactor

Tab. 2.1: The definition of terms that appeared in the model equations (2.1)-(2.14). An index \(i\) can take values 1 and 2, referring to a property in either reactor one or reactor two.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_i, B_i, C_i) (molm(^{-3}))</td>
<td>The concentration of the reactant (A), intermediate (B) and product (C).</td>
</tr>
<tr>
<td>(A_0) (molm(^{-3}))</td>
<td>The concentration of the reactant (A) in the feed.</td>
</tr>
<tr>
<td>(T_i) (K)</td>
<td>The temperature inside the reactors.</td>
</tr>
<tr>
<td>(T_0) (K)</td>
<td>The feed temperature.</td>
</tr>
<tr>
<td>(T_{a,i}) (K)</td>
<td>The temperature of the reactor walls.</td>
</tr>
<tr>
<td>(E_i) (Jmol(^{-1}))</td>
<td>The activation energy.</td>
</tr>
<tr>
<td>(Q_i) (Jmol(^{-1}))</td>
<td>The modulus of a heat of reaction.</td>
</tr>
<tr>
<td>(S_i) (m(^2))</td>
<td>The internal surface area.</td>
</tr>
<tr>
<td>(V_i) (m(^3))</td>
<td>The reactor volume.</td>
</tr>
<tr>
<td>(R) (JK(^{-1})mol(^{-1}))</td>
<td>The ideal gas constant.</td>
</tr>
<tr>
<td>(a_i) (s(^{-1}))</td>
<td>The pre-exponential factor.</td>
</tr>
<tr>
<td>(J_i) (–)</td>
<td>A constant, when (J_i = 0) is adiabatic case and when (J_i = 1) is diabatic case.</td>
</tr>
<tr>
<td>(q) (m(^3)s(^{-1}))</td>
<td>The flow-rate.</td>
</tr>
<tr>
<td>(t) (s)</td>
<td>The time.</td>
</tr>
<tr>
<td>(\chi_i) (Js(^{-1})m(^{-2})K(^{-1}))</td>
<td>The heat transfer coefficient between the reaction mixture and the reactor walls.</td>
</tr>
<tr>
<td>(c_{p_g}) (JK(^{-1})kg(^{-1}))</td>
<td>The heat capacity of the reaction mixture.</td>
</tr>
<tr>
<td>(\rho_g) (kg m(^{-3}))</td>
<td>The density of the reaction mixture.</td>
</tr>
<tr>
<td>(\tau_i) (s)</td>
<td>The residence time.</td>
</tr>
</tbody>
</table>

The system of non-dimensional equations in the first reactor is:

\[
\frac{dA^*_1}{dt^*} = \frac{1 - A^*_1}{\tau^*_1} - a^*_1 \exp\left[\frac{-E^*_1}{\theta^*_1}\right] A^*_1, \tag{2.15}
\]

\[
\frac{dB^*_1}{dt^*} = \frac{B^*_0 - B^*_1}{\tau^*_1} + a^*_1 \exp\left[\frac{-E^*_1}{\theta^*_1}\right] A^*_1, \tag{2.16}
\]

\[
\frac{dC^*_1}{dt^*} = \frac{C^*_0 - C^*_1}{\tau^*_1}, \tag{2.17}
\]

\[
\frac{d\theta^*_1}{dt^*} = \frac{\theta_0 - \theta^*_1}{\tau^*_1} - Q^*_1 a^*_1 \exp\left[\frac{-E^*_1}{\theta^*_1}\right] A^*_1 - J_1 \chi^*_1 \left(\theta^*_1 - \theta_{a,1}\right), \tag{2.18}
\]

\[
a^*_1 = \frac{\alpha^* V^* E^*_1}{T^*_c l^2} \exp\left[\frac{E^*_1}{T^*_c}\right]. \tag{2.19}
\]

Dimensionless initial conditions are

\[
A^*_1(0) = B^*_1(0) = C^*_1(0) = 0, \quad \theta^*_1(0) = \frac{\theta_0 + J_1 \chi^*_1 \tau^*_1 \theta_{a,1}}{1 + J_1 \chi^*_1 \tau^*_1}. \tag{2.20}
\]
The system of non-dimensional equations in the second reactor is:

\[
\frac{dA^*_2}{dt^*} = \frac{A^*_1 - A^*_2}{\tau^*_2}, \quad (2.21)
\]

\[
\frac{dB^*_2}{dt^*} = \frac{B^*_1 - B^*_2}{\tau^*_2} - a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2, \quad (2.22)
\]

\[
\frac{dC^*_2}{dt^*} = \frac{C^*_1 - C^*_2}{\tau^*_2} + a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2, \quad (2.23)
\]

\[
\frac{d\theta^*_2}{dt^*} = \frac{\theta^*_1 - \theta^*_2}{\tau^*_2} + Q^*_2 a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2 - J_2 (\theta^*_2 - \theta^*_a,2), \quad (2.24)
\]

\[
a^*_2 = \frac{\alpha^*}{T^*_{c1}} \exp \left[ \frac{1}{T^*_{c1}} \right]. \quad (2.25)
\]

Dimensionless initial conditions are

\[
A^*_2(0) = B^*_2(0) = C^*_2(0) = 0, \quad \theta^*_2(0) = \frac{\theta^*_1 + J_2 \tau^*_2 \theta^*_a,2}{1 + J_2 \tau^*_2}. \quad (2.26)
\]

From now on we assume that there is no intermediate or product feed in the stream, i.e. \( B_0 = B^*_0 = 0 \) and \( C_0 = C^*_0 = 0 \). It is worth noting that in studying the system (2.15)–(2.24) we are interested in long-time behaviour.

Normally for our two model systems, the residence times in the first and second reactor are \( \tau_1 = \tau_2 = 8 \) (s).

### 2.3 Model reduction

In section 2.3.1 we show that the model equations for the general non-adiabatic reactor can be reduced from eight to five. In section 2.3.2 we show that the model equation systems for an adiabatic reaction can be reduced to two equations (one for each reactor).

#### 2.3.1 The general case

For non-adiabatic operation the system of eight equations, (2.15)–(2.18) and (2.21)-(2.24) can be reduced to a system of five equations.
2. Adiabatic Reactor

2.3.1.1 Reactor one

As we assume that the feed concentration of the product is zero \((C_0^* = 0)\) and the initial condition of the product is zero \((C^*(0) = 0)\), we can immediately ignore equation (2.17). We now show that there is a relationship between the concentration of the reactant \(A_1^*\) and the concentration of the intermediate \(B_1^*\).

Let \(Z_1^* = A_1^* + B_1^*\). By differentiating \(Z_1\) with respect to \(t\) we have

\[
\frac{dZ_1^*}{dt} = \frac{dA_1^*}{dt} + \frac{dB_1^*}{dt}.
\]

From equations (2.15) and (2.16), and using the fact that \(B_0^* = 0\) we have

\[
\tau_1^* \frac{dZ_1^*}{dt} = 1 - Z_1^*.
\] (2.27)

Integrating equation (2.27) we find that at large values for time we have \(Z_1^* = 1\). Thus

\[
A_1^* + B_1^* = 1.
\]

Hence for large values of time we obtain a reduced model for reactor one.

\[
\frac{dA_1^*}{dt} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1^*} \right] A_1^*,
\] (2.28)

\[
\frac{d\theta_1}{dt} = \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[ \frac{-E_1^*}{\theta_1^*} \right] A_1^* - J_{1\chi_{T,1}}(\theta_1 - \theta_{a,1}),
\] (2.29)

\[
B_1^*(t^*) = 1 - A_1^*(t^*),
\] (2.30)

\[
C_1^*(t^*) = 0.
\] (2.31)

2.3.1.2 Reactor two

We now show that there is a concentration relationship between the concentrations \(A_2^*\), \(B_2^*\) and \(C_2^*\) inside reactor two.

Let \(Z_2^* = A_2^* + B_2^* + C_2^*\). By differentiating \(Z_2^*\) with respect to \((t^*)\), using equations (2.21)–(2.23), and then integrating and using the fact that \(C_1^* = 0\) we find that at large values
for time we have $Z_2^* = 1$. Hence

$$A_2^* + B_2^* + C_2^* = 1.$$  \hspace{1cm} (2.32)

Note that this reaction is a unimolecular reaction. Thus it makes sense physically. As one unit of the reactants enters reactor one, the sum of reactants and products leaving the second reactor must also sum to one. Equation (2.32) shows that only two concentrations need to be measured.

Therefore, the model equations for reactor two at large values of time are:

\[
\begin{align*}
\frac{dA_2^*}{dt^*} &= \frac{A_1^* - A_2^*}{\tau_2^*}, \\
\frac{dB_2^*}{dt^*} &= 1 - A_1^* - B_2^* a_2^* \exp \left[ -\frac{1}{\theta_2} \right] B_2^*, \\
\frac{d\theta_2}{dt^*} &= \theta_1 - \theta_2 \tau_2^* + Q_2^* a_2^* \exp \left[ -\frac{1}{\theta_2} \right] B_2^* - J_2(\theta_2 - \theta_a, 2), \\
C_2^* &= 1 - A_2^* - B_2^*.
\end{align*}
\]  \hspace{1cm} (2.33-2.36)

2.3.2 The adiabatic case

The model equations for an adiabatic system can be reduced to a two equation model, one in each reactor, such as two concentration equations or two temperature equations.

2.3.2.1 Reactor one

We now show that for the adiabatic case, i.e. $J_1 = 0$, there is an invariant relationship between the concentration $A_1^*(t^*)$ and the temperature $\theta_1(t^*)$.

Let $Z_3^* = Q_1^* A_1^* - \theta_1$. By differentiating $Z_3^*$ with respect to $t^*$, using equations (2.15)–(2.18), and integrating we find that at large values for time we have $Z_3^* = Q_1^* - \theta_0$. Hence

$$Z_3^* = Q_1^* A_1^* - \theta_1 = Q_1^* - \theta_0,$$  \hspace{1cm} (2.37)

$$\Rightarrow A_1^* = \frac{(\theta_1 - \theta_0)}{Q_1^*} + 1.$$  \hspace{1cm} (2.38)

Thus under the assumption of adiabatic operation and using equation (2.37) it is possible to reduce the model equations for reactor one to either a scalar equation for the
concentration $A_1^*$

\[
\frac{dA_1^*}{dt^*} = 1 - A_1^* \frac{a_1^*}{\tau_1^*} \exp \left[ -\frac{E_1^*}{Q_1^* A_1^* - (Q_1^* - \theta_0)} \right] A_1^* \tag{2.39}
\]

or to a scalar equation for the temperature $\theta_1$

\[
\frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] (Q_1^* - \theta_0 + \theta_1). \tag{2.40}
\]

### 2.3.2.2 Reactor two

For the adiabatic case, i.e. $J_2 = 0$. It is straightforward to show that the value of $A_2^*$ converges to the same steady-state as $A_1^*$.

Let

\[
A_1^* = A_{1\text{steady state}} + \delta \exp \left[ -\lambda t^* \right], \tag{2.41}
\]

where $\lambda > 0$ is the eigenvalue of the first reactor. Substituting (2.41) into (2.33) we obtain

\[
\frac{dA_2^*}{dt^*} + A_2^* \frac{\tau_2^*}{\tau_2^*} = A_{1\text{steady state}} \frac{\tau_2^*}{\tau_2^*} + \frac{\delta}{\tau_2^*} \exp \left[ -\lambda t^* \right].
\]

Integrating we obtain

\[
A_2^* = A_{1\text{steady state}} + \frac{\delta}{1 - \lambda \tau_2^*} \exp \left[ -\lambda t^* \right]; \quad (1 - \lambda \tau_2^* \neq 0).
\]

At large values of time ($t^* \gg 1$) we have

\[
A_2 = A_{1\text{steady state}},
\]

regardless of the initial size of the disturbance $\delta$.

Therefore, equation (2.36) can be written as

\[
C_2^* = 1 - A_1^* - B_2^*; \quad 1 - \lambda \tau_2^* \neq 0.
\]

(The case $1 - \lambda \tau_2^* = 0$ is non-generic and is therefore not considered. However the same conclusion holds.)
We now show that for the adiabatic case there is an invariant relationship between the concentration $B_2^*$ and the reactor temperature $\theta_2$. This will allow a further reduction of the adiabatic model in the second reactor to a one-variable model.

Let $Z_4^* = Q_2^* B_2^* + \theta_2$. By differentiating $Z_4^*$ with respect to $t^*$ and integrating we find that at large values for time we have $Z_4^* = Q_2^* (1 - A_1^*) + \theta_1$. Hence

\[
Z_4^* = Q_2^* B_2^* + \theta_2 = Q_2^* (1 - A_1^*) + \theta_1, \quad (2.42)
\]

\[\Rightarrow B_2^* = \frac{1}{Q_2^*} (Q_2^* (1 - A_1^*) + \theta_1 - \theta_2).\]

or

\[\Rightarrow \theta_2 = Q_2^* (1 - A_1^* - B_2^*) + \theta_1.\]

We assume that $B_0^* = C_0^* = 0$. Therefore, in unit time the dimensionless concentration of chemicals entering the first reactor is one. In unit time the dimensionless concentration of chemicals leaving the second reactor is $A_2^* + B_2^* + C_2^*$. For large values of time we have $A_1^* = A_2^*$. Hence, the dimensionless concentration of chemicals leaving the second reactor is $A_1^* + B_2^* + C_2^*$. On a physical grounds we must have

\[A_1^* + B_2^* + C_2^* = 1.\]

As all the concentrations are positive we have

\[0 \leq 1 - A_1^* - B_2^* \leq 1.\]

This is because the reaction $B \rightarrow C$ decreases the concentration of $B_2^*$ by the same amount that it increases the concentration of $C_2^*$. Hence

\[\theta_1 \leq \theta_2 \leq \theta_1 + Q_2^*\]

Thus, it is possible to reduce the model for reactor two to either a scalar equation for
the concentration $B_2^*$

$$\frac{dB_2^*}{dt^*} = \frac{1 - A_1^* - B_2^*}{\tau_2^*} - a_2^* \exp \left( - \frac{1}{Q_2^* (1 - A_1^* - B_2^*) + \theta_1} \right) B_2^*, \tag{2.43}$$

or to a scalar equation for the temperature $\theta_2$

$$\frac{d\theta_2}{dt^*} = \frac{\theta_1 - \theta_2}{\tau_2^*} + a_2^* \exp \left( - \frac{1}{\theta_2} \right) (Q_2^* (1 - A_1^*) + \theta_1 - \theta_2). \tag{2.44}$$

### 2.3.3 Final adiabatic reactor

The model equations for both reactors can be reduced to either a two equation model for two concentrations or a two equation model for the temperature of each reactor. We can also construct a mixed model, $(\theta_1$ and $B_2^*)$ or $(\theta_2$ and $A_1^*)$ however, chemical engineering researchers are more interested in either the concentration model or the temperature model.

#### 2.3.3.1 Concentration model

Using the ideas from the previous section the system can be reduced to two equations, one for each reactor. In this section, the model is reduced to a concentration equation for the reactant $A_1^*$ and the intermediate $B_2^*$. The remaining variables are found from invariant relationships (2.47)–(2.52).

$$\frac{dA_1^*}{dt^*} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left( - \frac{E_1^*}{Q_1^* A_1^* - (Q_1^* - \theta_0)} \right) A_1^*, \tag{2.45}$$

$$\frac{dB_2^*}{dt^*} = \frac{1 - A_1^* - B_2^*}{\tau_2^*} - a_2^* \exp \left( - \frac{1}{Q_2^* (1 - A_1^* - B_2^*) + \theta_1} \right) B_2^*, \tag{2.46}$$

$$B_1^* = 1 - A_1^*, \tag{2.47}$$

$$C_1^* = 0, \tag{2.48}$$

$$\theta_1 = \theta_0 - Q_1^* (1 - A_1^*), \tag{2.49}$$

$$A_2^* = A_1^*, \tag{2.50}$$

$$C_2^* = 1 - A_1^* - B_2^*, \tag{2.51}$$

$$\theta_2 = Q_2^* (1 - A_1^* - B_2^*) + \theta_1. \tag{2.52}$$
2.3.3.2 Temperature model

Using the ideas from section (2.3.2) the system can be reduced to two equations, one for each reactor. In this section, the model is reduced to a temperature equation for the first reactor and a temperature equation for the second reactor. The remaining variables are found from invariant relationships (2.55)–(2.60).

\[ \frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] (Q_1^* - \theta_0 + \theta_1), \]  
\[ \frac{d\theta_2}{dt^*} = \frac{\theta_1 - \theta_2}{\tau_2^*} + a_2^* \exp \left[ \frac{-1}{\theta_2} \right] (Q_2^*(1 - A_1^*) + \theta_1 - \theta_2), \]  
\[ A_1^* = \frac{\theta_1 - \theta_0 + Q_1^*}{Q_1^*}, \]  
\[ B_1^* = 1 - A_1^*, \]  
\[ C_1^* = 0, \]  
\[ A_2^* = A_1^*, \]  
\[ B_2^* = \frac{Q_2^*(1 - A_1^*) + \theta_1 - \theta_2}{Q_2^*}, \]  
\[ C_2^* = 1 - A_1^* - B_2^*. \]  

2.3.4 Analysis of the reduced adiabatic model (R1)

We investigate the uniqueness and stability of the steady-state solution of (2.40). We have:

\[ H(\theta_1) = \frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] (Q_1^* - \theta_0 + \theta_1) = 0. \]  

From equation (2.20) note that for an adiabatic reactor the initial conditions is \( \theta_1(t^* = 0) = \theta_0 \), since \( J_1 = 0 \). We now show that the solution \( \theta_1(t^*) \) is bounded by

\[ 0 \leq \theta_1(t^*) \leq \theta_0. \]

We have

\[ H(0) = \lim_{\theta_1 \to 0} \frac{d\theta_1}{dt^*} = \frac{\theta_0}{\tau_1^*} > 0, \]
and

\[ H(\theta_0) = \frac{d\theta_1}{dt^*} \bigg|_{(\theta_1=\theta_0)} = -a^*_1 \exp \left[ \frac{-E^*_1}{\theta_0} \right] Q^*_1 < 0. \]

As \( \theta_1(t^* = 0) = \theta_0 \) we have shown that \( 0 \leq \theta_1(t^*) \leq \theta_0 \).

We now show that equation (2.61) has only one physically meaningful solution. Differentiating equation (2.61) we have

\[ \frac{dH}{d\theta_1} = \frac{-1}{\tau^*_1} - a^*_1 \exp \left[ \frac{-E^*_1}{\theta_1} \right] - \frac{a^*_1 E^*_1}{\theta^*_1} (Q^*_1 - \theta_0 + \theta_1) \exp \left[ \frac{-E^*_1}{\theta_1} \right] < 0, \]

as by equation (2.38)

\[ Q^*_1 - \theta_0 + \theta_1 = Q^*_1 A^*_1 > 0. \]

As \( H(\theta_1 = 0) > 0, H(\theta_1 = \theta_0) < 0 \) and \( dH/d\theta_1 < 0 \) it now follows that the function \( H(\theta_1) \) has a single steady-state solution. It also follows immediately that the unique steady-state solution is locally stable.

### 2.4 Results

In order to maximize the yield of the product \( C \) in the second reaction we need to increase the yield of the intermediate \( B \) in the first reaction. Therefore if we do not obtain high conversion in the first reactor it is impossible to achieve high conversion to product.

All calculations performed in this chapter use the the parameter values stated in Appendix.1, unless otherwise stated.

#### 2.4.1 Achieving 90\% conversion in reactor one

We investigate how the value for the inflow temperature \( T_0 \) required to achieve a conversion of 90\% varies as one of three parameters is changed: the activation energy \( E_1 \), the characteristic temperature \( T_{c1} \) or the modulus of the heat of reaction \( Q_1 \).

From equation (2.39) we have at steady-state that

\[ \theta_0 = \frac{-E^*_1}{\ln \left( \frac{1-A^*_1}{a^*_1 A^*_1 \gamma^*_1} \right)} - Q^*_1 A^*_1 + Q^*_1. \]  

(2.62)
Recall that the parameter $\alpha^*_1$ depends upon $E^*_1$; see equation (2.19). Differentiating (2.62), using (2.19), with respect to $E^*_1$ we obtain

$$\frac{d\theta_0}{dE^*_1} = -\left( \frac{E^*_1 + T^*_c + T^*_c \ln \left[ \frac{1 - A^*_1}{\alpha^*_1 A^*_1} \right]}{T^*_c \left( \ln \left[ \frac{1 - A^*_1}{\alpha^*_1 A^*_1} \right] \right)^2} \right) < 0,$$

(2.63)

for

$$\tau^*_1 < \frac{1 - A^*_1}{\alpha^*_1 A^*_1} \exp \left[ 1 + \frac{E^*_1}{T^*_c} \right].$$

(2.64)

(This holds for the parameter values in Appendix.1). Equations (2.63) shows that, when equation (2.64) holds, the required inflow temperature is a decreasing function of the activation energy parameter $E_1$, i.e. a lower activation energy requires a higher inflow temperature to achieve a specified conversion.

Recall that $\alpha^*_1$ depends upon $T^*_c$; see equation (2.19). Differentiating (2.62), using (2.19), with respect to $T^*_c$ we obtain

$$\frac{d\theta_0}{dT^*_c} = \frac{E^*_1 (2T^*_c + E^*_1)}{T^*_c^2 \left( \ln \left[ \frac{1 - A^*_1}{\alpha^*_1 A^*_1} \right] \right)^2} > 0.$$ 

(2.65)

Equation (2.65) shows that the required inflow temperature is an increasing function of the parameter $T_c$, i.e. a higher characteristic temperature requires a higher inflow temperature to achieve a specified conversion.

Differentiating (2.62) with respect to $Q^*_1$ we obtain

$$\frac{d\theta_0}{dQ^*_1} = -A^*_1 + 1 > 0,$$

(2.66)

as $0 < A^*_1 < 1$.

Equation (2.66) shows that the required feed temperature is an increasing function of the endothermicity parameter $Q_1$, i.e. a more endothermic reaction requires a higher feed temperature to achieve a specified conversion.

The value for the feed temperature $T_0$ to obtain a conversion of 90% of the reactant $A_1$ as a function of the rate parameters $E_1$ and $T_c$ and the heat of endothermicity $Q_1$ is shown in Tables 2.2 and 2.3. We find that, for a high value of the endothermicity...
$Q_1 = 205.8 \text{ kJ mol}^{-1}$, the required feed temperature $T_0$ is always unrealistic for the lab scale model; Table 2.2. The required feed temperature values $T_0$ to achieve 90% conversion in the industrial model are almost always unrealistic.

The required feed temperature $T_0$ values to achieve 90% conversion in the lab scale model are dramatically higher than those in the industrial model (approximately twice). Thus, it is easier to obtain 90% conversion of the reactant $A$ within the limit of the realistic feed temperature $T_0$ in the industrial model.

Tables 2.4 and 2.5 show the feed temperature required to achieve 90% as a function of the heat of endothermicity $Q_1$ for a fixed characteristic temperature $T_{c1} = 342 \text{ K}$ and for four values of activation energy $E_1$. We see that for smaller values of the heat of endothermicity parameter $Q_1$ and for larger values of the activation energy $E_1$, the required feed temperature is more realistic. The values in the industrial model are smaller than those in the lab scale model.

Based on these results, we will only use the industrial model parameter values in the rest of this section to investigate the parameter regions to obtain the required conversion with a realistic feed temperature.

**Tab. 2.2:** The inflow temperature $T_0$ required to achieve 90% conversion in the first reactor $A_1^* = 0.1$ for different values of the activation energy $E_1$ and the characteristic temperature $T_{c1}$. $Q_1 = 205.8 \text{ kJ mol}^{-1}$. (Lab scale model.)

<table>
<thead>
<tr>
<th>$T_{c1}$</th>
<th>$T_0(E_1 = 50)$</th>
<th>$T_0(E_1 = 80)$</th>
<th>$T_0(E_1 = 120)$</th>
<th>$T_0(E_1 = 180)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>342</td>
<td>2034.2</td>
<td>1979.4</td>
<td>1956.5</td>
<td>1943.9</td>
</tr>
<tr>
<td>442</td>
<td>2260.5</td>
<td>2133.9</td>
<td>2086</td>
<td>2060.6</td>
</tr>
<tr>
<td>642</td>
<td>3118.2</td>
<td>2546.3</td>
<td>2391.2</td>
<td>2317.8</td>
</tr>
<tr>
<td>842</td>
<td>6787.8</td>
<td>3213.8</td>
<td>2785.1</td>
<td>2616</td>
</tr>
<tr>
<td>942</td>
<td>36285.1</td>
<td>3736.2</td>
<td>3030.7</td>
<td>2784.7</td>
</tr>
</tbody>
</table>

**Tab. 2.3:** The inflow temperature $T_0$ required to achieve 90% conversion in the first reactor $A_1^* = 0.1$ for different values of the activation energy $E_1$ and the characteristic temperature $T_{c1}$. $Q_1 = 205.8 \text{ kJ mol}^{-1}$. (Industrial model.)

<table>
<thead>
<tr>
<th>$T_{c1}$</th>
<th>$T_0(E_1 = 50)$</th>
<th>$T_0(E_1 = 80)$</th>
<th>$T_0(E_1 = 120)$</th>
<th>$T_0(E_1 = 180)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>342</td>
<td>1038.1</td>
<td>983.4</td>
<td>960.4</td>
<td>947.8</td>
</tr>
<tr>
<td>442</td>
<td>1264.4</td>
<td>1137.9</td>
<td>1089.9</td>
<td>1064.5</td>
</tr>
<tr>
<td>642</td>
<td>2122.2</td>
<td>1550.2</td>
<td>1395.1</td>
<td>1321.8</td>
</tr>
<tr>
<td>842</td>
<td>5791.7</td>
<td>2217.1</td>
<td>1789.0</td>
<td>1619.9</td>
</tr>
<tr>
<td>942</td>
<td>35289.1</td>
<td>2740.1</td>
<td>2034.6</td>
<td>1788.6</td>
</tr>
</tbody>
</table>
Tab. 2.4: The inflow temperature required $T_0$ to achieve a steady-state $A^*_1 = 0.1$ for different values of the endothermacity parameter $Q_1$ when the characteristic temperature $T_{c1} = 342$ K. (Lab scale model.)

<table>
<thead>
<tr>
<th>$Q_1$</th>
<th>$T_0(E_1 = 50)$</th>
<th>$T_0(E_1 = 80)$</th>
<th>$T_0(E_1 = 120)$</th>
<th>$T_0(E_1 = 180)$</th>
</tr>
</thead>
<tbody>
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<td>175</td>
<td>1796.9</td>
<td>1742.2</td>
<td>1719.2</td>
<td>1706.6</td>
</tr>
<tr>
<td>200</td>
<td>1989.5</td>
<td>1934.8</td>
<td>1911.8</td>
<td>1899.2</td>
</tr>
<tr>
<td>205.8</td>
<td>2034.2</td>
<td>1979.4</td>
<td>1956.5</td>
<td>1943.9</td>
</tr>
</tbody>
</table>

Tab. 2.5: The inflow temperature required $T_0$ to achieve a steady-state $A^*_1 = 0.1$ for different values of the endothermacity parameter $Q_1$ when the characteristic temperature $T_{c1} = 342$ K. (Industrial model.)

<table>
<thead>
<tr>
<th>$Q_1$</th>
<th>$T_0(E_1 = 50)$</th>
<th>$T_0(E_1 = 80)$</th>
<th>$T_0(E_1 = 120)$</th>
<th>$T_0(E_1 = 180)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>592.0</td>
<td>537.2</td>
<td>514.3</td>
<td>501.6</td>
</tr>
<tr>
<td>100</td>
<td>735.2</td>
<td>680.4</td>
<td>657.5</td>
<td>644.8</td>
</tr>
<tr>
<td>125</td>
<td>806.8</td>
<td>752.0</td>
<td>729.1</td>
<td>716.4</td>
</tr>
<tr>
<td>150</td>
<td>878.3</td>
<td>823.6</td>
<td>800.6</td>
<td>788.0</td>
</tr>
<tr>
<td>175</td>
<td>949.9</td>
<td>895.2</td>
<td>872.2</td>
<td>859.6</td>
</tr>
<tr>
<td>200</td>
<td>1021.5</td>
<td>966.7</td>
<td>943.8</td>
<td>931.2</td>
</tr>
<tr>
<td>205.8</td>
<td>1038.1</td>
<td>983.4</td>
<td>960.4</td>
<td>947.8</td>
</tr>
</tbody>
</table>

Figure 2.2 shows how the parameter regions where the conversion is either lower or higher than 90% depend upon the reaction kinetics. The feed temperature is 1000 K. This figure therefore represents a “worst case”. If a catalyst is unable to achieve the desired 90% conversion at the maximum allowed feed temperature it will not achieve it at a lower feed temperature. This is obviously “physical”. To see that rewrite equation (2.62) as

$$A^*_1 = \left[ -\frac{E^*_1}{\ln \left( \frac{1-A^*_1}{\sigma A^*_1\theta_0} \right)} + Q^*_1 \right] \frac{1}{Q^*_1} - \frac{\theta_0}{Q^*_1},$$

(2.67)

Differentiating equation (2.67) with respect to the feed temperature $\theta_0$ we obtain

$$\frac{dA^*_1}{d\theta_0} = -\frac{1}{Q^*_1}.$$

Thus the value of the reactant concentration $A^*_1$ is a decreasing function of the feed temperature, i.e. as the feed temperature increases the reactant concentration decreases.

Figure 2.2 confirms that for a weakly endothermic reaction there is a wide range of
Fig. 2.2: The parameter values required to achieve 90% conversion in the first reactor as a function of the activation energy $E_1$ and the characteristic temperature $T_{c1}$ where the feed temperature $T_0 = 1000$ K. (Industrial model.)

(a) $Q_1 = 50$ kJ mol$^{-1}$.

(b) $Q_1 = 100$ kJ mol$^{-1}$.

Fig. 2.3: The feed temperature $T_0$ required to achieve 90% conversion in the first reactor as a function of the activation energy $E_1$. The characteristic temperature $T_{c1} = 342$ K, 442 K and 542 K. (Industrial model.)

Figures 2.3a and 2.3b show the feed temperature required to achieve 90% conversion.
of the reactant $A_1^*$ in the first reactor as a function of the activation energy in the first reactor $E_1$ for different values of the characteristic temperature $T_{c1}$ and the heat of endothermicity $Q_1$. These figures show that lower feed temperatures require lower values for the heat of endothermicity $Q_1$ and lower values of the characteristic temperature $T_{c1}$. Feed temperatures higher than 1000 K are considered to be unachievable inside these reactors. These figures confirm that it is more difficult to find a suitable catalyst for a highly endothermic reaction. When the reaction is weakly endothermic there is a larger range of catalysts that can be used.

Figure 2.3 shows that under adiabatic operation it is challenging to achieve the desired conversion of the reactant for a highly endothermic reaction with a realistic feed temperature. With a good combination of the parameter values it is possible to achieve high conversion in a weakly endothermic reaction.

In conclusion, equations (2.65) and (2.66) in conjunction with Figures 2.2 and 2.3 show that in order to achieve 90% conversion of the reactant $A$ in the first reactor at a realistic feed temperature, a weakly endothermic reaction is required. Also, the characteristic temperature $T_{c1}$ is required to be small whereas the activation energy $E_1$ should be large.

It should be realized that for a given process it is not possible to change the value of the endothermicity $Q_1$. Our results should be interpreted as identifying which process would be possible for adiabatic reaction.

### 2.4.2 Achieving 90% conversion in reactor two

We now investigate the steady-state product concentration $C_2^*$ for the four different values of the pre-exponential factor $a_2$ and the activation energy $E_2$ given in Table 2.6. Initially, in Section 2.4.2.1, we investigate how the use of a catalyst combined with a large value for the characteristic temperature in the first reactor $T_{c1} = 942$ K affects the product concentration $C_2^*$ for the specified conditions. In Section 2.4.2.2 the product concentration $C_2^*$ is examined for a lower values of the characteristic temperature $T_{c1} = 342$ K. Based on the results obtained, we conclude that only the fourth catalyst in the second reactor gives satisfactory conversion.

The results shown in Tables 2.7–2.10 were obtained by integrating the governing equations of the reduced system (2.28)–(2.36).
Tab. 2.6: The four parameter values for $a_2, T_{c2}$ and $E_2$.

<table>
<thead>
<tr>
<th>$T_{c2}$ K</th>
<th>$a_2$ s$^{-1}$</th>
<th>$E_2$ kJ mol$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>98</td>
<td>50</td>
<td>from [33]</td>
</tr>
<tr>
<td>613</td>
<td>exp (12.6)</td>
<td>88</td>
<td>from [43]</td>
</tr>
<tr>
<td>571</td>
<td>$10^{12}$</td>
<td>150</td>
<td>from [41]</td>
</tr>
<tr>
<td>383</td>
<td>$0.2 \times 10^{22}$</td>
<td>166</td>
<td>from [24]</td>
</tr>
</tbody>
</table>

2.4.2.1 **Scenario one**

We fix the characteristic temperature in the first reactor $T_{c1} = 942$ K and investigate the performance of each of the four catalysts in the second reactor. We can already say that for high endothermicity $Q_1$, high conversion levels, especially $C_2^* > 0.90$, are impossible in the adiabatic reactor. From our results in Section 2.4 we know that 90% conversion of the reactant concentration $A_1$ to the intermediate $B_1$ cannot be achieved for large endothermicity $Q_1$ and high characteristic temperature $T_{c1}$.

Table 2.7 investigates the effects of a lower value for the heat of endothermicity $Q_1$ on the steady-state product concentration $C_2^*$. It shows that at lower values of the heat of endothermicity $Q_1$, the steady-state product concentrations are still below a conversion efficiency of 90% conversion. The table shows that at the specified conditions we do not get 90% concentration of the reactant $A$ in reactor one. The second column of this table illustrates that the wrong choice of the catalysts in the first reactor leads to process failure.
Tab. 2.7: The steady-state values of the product \( C_2^* \) when \( Q_1 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, a_1 = 98 \text{ s}^{-1}, Q_2 = 41.2 \text{ kJ mol}^{-1} \) and \( T_{c1} = 942 \text{ K} \). The results shown were obtained by integrating the governing equations of the reduced system (2.28)–(2.36). (Industrial model)

<table>
<thead>
<tr>
<th>( T_0 )</th>
<th>( A_1^* )</th>
<th>( a_2 = 98 \text{ s}^{-1} )</th>
<th>( a_2 = 10^{12} \text{ s}^{-1} )</th>
<th>( a_2 = \exp(12.6) \text{ s}^{-1} )</th>
<th>( a_2 = 0.2 \times 10^{22} \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>1</td>
<td>0.3 \times 10^{-7}</td>
<td>0.97 \times 10^{-11}</td>
<td>0.3 \times 10^{-7}</td>
<td>0.1 \times 10^{-13}</td>
</tr>
<tr>
<td>603</td>
<td>0.9999</td>
<td>0.00009</td>
<td>0.3 \times 10^{-5}</td>
<td>0.00005</td>
<td>0.00004</td>
</tr>
<tr>
<td>803</td>
<td>0.995</td>
<td>0.003</td>
<td>0.001</td>
<td>0.4 \times 10^{-5}</td>
<td>0.005</td>
</tr>
<tr>
<td>1000</td>
<td>0.963</td>
<td>0.014</td>
<td>0.023</td>
<td>0.5 \times 10^{-6}</td>
<td>0.037</td>
</tr>
</tbody>
</table>
2.4.2.2 Scenario two

In this section we reduce the characteristic temperature in the first reactor $T_{c1} = 342$ K and set the value of the feed temperature $T_0$ to that required to achieve 90% conversion of the reactant $A_1^*$, as shown in Table 2.5. We investigate the steady-state product concentration $C_2^*$ for the case $E_1 = 80$ kJ mol$^{-1}$ and $T_0 = 983.4$ K (Section 2.4.2.2.1) for the highest value of the heat of endothermicity $Q_1 = 205.8$ kJ mol$^{-1}$. We conclude from this section that when the reaction is highly endothermic the fourth catalyst is the only catalyst that gives an excellent conversion.

We then reduce the heat of endothermicity $Q_1$ to the lower values of 100 kJ mol$^{-1}$ (Section 2.4.2.2.2) and 50 kJ mol$^{-1}$ (Section 2.4.2.2.3) and investigate the change in the steady-state behaviour of the product concentration $C_2^*$. We conclude from these sections that the fourth catalyst is the best catalyst among the four catalysts under all applied conditions.

2.4.2.2.1 Case one

We fix the activation energy in the first reactor $E_1 = 80$ kJ mol$^{-1}$ and the feed temperature $T_0 = 983.4$ K. We fix the feed temperature to ensure 90% conversion of the reactant $A$ in the first reactor. In Table 2.8 we see that, although we have a conversion of 90% in the first reactor, only the fourth catalyst in the second reactor gives a satisfactory conversion (nearly 90%).

An obvious conclusion is that selecting a good catalyst for the first reactor does not guarantee 90% conversion into product. By the end of this chapter we will identify how to select appropriate catalysts for both reactors.

Table 2.8: The steady-state values of the product $C_2^*$ when $E_1 = 80$ kJ mol$^{-1}$, $Q_1 = 205.8$ kJ mol$^{-1}$, $Q_2 = 41.2$ kJ mol$^{-1}$, $T_{c1} = 342$ K and $T_0 = 983.4$ K. The results shown were obtained by integrating the governing equations of the reduced system (2.28)–(2.36). (Industrial model.)

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>$a_2$</th>
<th>$E_2$</th>
<th>$A_1^*$</th>
<th>$B_2^*$</th>
<th>$C_2^*$</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>exp(12.6)</td>
<td>50</td>
<td>0.1</td>
<td>0.900</td>
<td>0.0002</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>613</td>
<td>98</td>
<td>88</td>
<td>0.1</td>
<td>0.900</td>
<td>$5 \times 10^{-5}$</td>
<td>0.037</td>
<td>0.037</td>
</tr>
<tr>
<td>571</td>
<td>$10^{12}$</td>
<td>150</td>
<td>0.1</td>
<td>0.900</td>
<td>$9 \times 10^{-7}$</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>383</td>
<td>$2 \times 10^{22}$</td>
<td>166</td>
<td>0.1</td>
<td>$5 \times 10^{-5}$</td>
<td>0.900</td>
<td>0.020</td>
<td>0.026</td>
</tr>
</tbody>
</table>
2.4.2.2.2 Case two

In this section we use the same reactor parameters in the first reactor as in Table 2.8, but reduce the feed temperature to $T_0 = 680.4$ K and the heat of endothermicity to $Q_1 = 100$ kJ mol$^{-1}$. These choices are to ensure that we obtain a conversion of 90% in the first reactor $A_1^* = 0.1$, see Table 2.3. Table 2.9 shows the steady-state of the product concentration $C_2^*$. It shows that only the fourth catalyst in the second reactor gives a satisfactory conversion.

Tab. 2.9: The steady-state values of the product $C_2^*$ when $E_1 = 80$ kJ mol$^{-1}$, $Q_1 = 100$ kJ mol$^{-1}$, $Q_2 = 41.2$ kJ mol$^{-1}$, $T_{c1} = 342$ K and $T_0 = 680.4$ K. The results shown were obtained by integrating the governing equations of the reduced system (2.28)–(2.36). (Industrial model)

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>$a_2$</th>
<th>$E_2$</th>
<th>$A_1^*$</th>
<th>$B_2^*$</th>
<th>$C_2^*$</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>98</td>
<td>50</td>
<td>0.1</td>
<td>0.900</td>
<td>0.0002</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>613</td>
<td>$\exp(12.6)$</td>
<td>88</td>
<td>0.1</td>
<td>0.900</td>
<td>$0.5 \times 10^{-5}$</td>
<td>0.037</td>
<td>0.037</td>
</tr>
<tr>
<td>571</td>
<td>$10^{12}$</td>
<td>150</td>
<td>0.1</td>
<td>0.900</td>
<td>$0.9 \times 10^{-7}$</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>383</td>
<td>$0.2 \times 10^{22}$</td>
<td>166</td>
<td>0.1</td>
<td>$0.5 \times 10^{-5}$</td>
<td>0.900</td>
<td>0.020</td>
<td>0.026</td>
</tr>
</tbody>
</table>

2.4.2.2.3 Case three

In this section the heat of endothermicity $Q_1$ is reduced to 50 kJ mol$^{-1}$. We investigate the steady-state product concentration $C_2^*$ for the case $E_1 = 80$ kJ mol$^{-1}$. In Table 2.10, where the inflow temperature is reduced to $T_0 = 537.2$ K, only the fourth catalyst gives a satisfactory conversion (nearly 90%).

Tab. 2.10: The steady-state values values of the product $C_2^*$ when $E_1 = 80$ kJ mol$^{-1}$, $Q_1 = 50$ kJ mol$^{-1}$, $Q_2 = 41.2$ kJ mol$^{-1}$, $T_{c1} = 342$ K and $T_0 = 537.2$ K. The results shown were obtained by integrating the governing equations of the reduced system (2.28)–(2.36). (Industrial model)

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>$a_2$</th>
<th>$E_2$</th>
<th>$A_1^*$</th>
<th>$B_2^*$</th>
<th>$C_2^*$</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>98</td>
<td>50</td>
<td>0.1</td>
<td>0.900</td>
<td>0.0002</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>613</td>
<td>$\exp(12.6)$</td>
<td>88</td>
<td>0.1</td>
<td>0.900</td>
<td>$0.5 \times 10^{-5}$</td>
<td>0.037</td>
<td>0.037</td>
</tr>
<tr>
<td>571</td>
<td>$10^{12}$</td>
<td>150</td>
<td>0.1</td>
<td>0.900</td>
<td>$0.9 \times 10^{-7}$</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>383</td>
<td>$0.2 \times 10^{22}$</td>
<td>166</td>
<td>0.1</td>
<td>$0.5 \times 10^{-5}$</td>
<td>0.900</td>
<td>0.020</td>
<td>0.026</td>
</tr>
</tbody>
</table>
2.4.2.3 Summary

In this section we mimicked an experimental investigation into the performance of different catalysts to identify which one performed best. We varied parameters to investigate when we can obtain a high conversion of the product \( C_2^* \). We showed that obtaining 90% conversion in the first reactor does not mean that we will obtain 90% conversion in the second reactor.

We now wonder “is there a better way to do this investigation rather than trial and error”? Is there a more mathematical way to identify good catalysts?”

2.5 Applications of singularity theory

At steady-state, we have from equation (2.59) that

\[
    B_2^* = \frac{Q_2^*(1 - A_1^*) + \theta_1 - \theta_2}{Q_2^*}.
\]

Substituting this value into the steady-state version of equation (2.35) we obtain the singularity function for the temperature in the second reactor

\[
    G(\theta_2) = \frac{\theta_1 - \theta_2}{\tau_2^*} + a_2^* \exp \left[ \frac{-1}{\theta_2} \right] \left[ Q_2^*(1 - A_1^*) + \theta_1 - \theta_2 \right].
\]

(2.68)

The feed temperature \( \theta_0 \) does not appear explicitly in equation (2.68), but it appears implicitly as it determines the values of \( A_1^* \) and \( \theta_1 \). The value for \( A_1^* \) is given by

\[
    A_1^* = \frac{\theta_1 - \theta_0 + Q_1^*}{Q_1^*},
\]

(2.69)

and the parameter \( \theta_1 \) solves the equation

\[
    \frac{\theta_0 - \theta_1}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] (Q_1^* - \theta_0 + \theta_1) = 0.
\]

(2.70)

In this analysis we view the steady-state solutions in the first reactor (\( \theta_1 \) and \( A_1^* \)) as free-parameters.
2.5.1 Limit point bifurcation

The defining and non-degeneracy conditions for limit point bifurcations [2, chapter 2] are

\[ G = G_{\theta_2} = 0, \]  
\[ G_{\theta_2 \theta_2} \neq 0, G_{\lambda} \neq 0, \]  

where \( \lambda \) is the selected bifurcation parameter, one of \((\tau^*_2, a^*_2, \theta_0)\), and the subscripts denote the \( n \)th-order partial derivatives. After some manipulation the following equations for the limit points can be derived from conditions (2.71)

\[ a^*_2 \exp \left( \frac{-1}{\theta_2} \right) = \frac{\theta_1 - \theta_2}{\tau^*_2 [Q^*_2(1 - A^*_1) + \theta_1 - \theta_2]}, \]  

and

\[ (1 + D)\theta_2^2 - (2\theta_1 + D)\theta_2 + \theta_1(D + \theta_1) = 0, \]

where \( D = Q^*_2(1 - A^*_1) \).

Thus the temperature at which limit point(s) occur is given by

\[ \theta_2 = \frac{(2\theta_1 + D) \pm \sqrt{(2\theta_1 + D)^2 - 4\theta_1(D + \theta_1)(1 + D)}}{2(1 + D)}. \]

This equation has no real solutions when

\[ (2\theta_1 + D)^2 - 4\theta_1(D + \theta_1)(1 + D) < 0. \]

The cusp curve is defined as the solutions satisfying

\[ (2\theta_1 + D)^2 - 4\theta_1(D + \theta_1)(1 + D) = 0. \]

2.5.1.1 Lab scale model

In this section we investigate the steady-state behaviour in the lab scale model by looking at the cusp curve and the limit points. In the next section we repeat this analysis using the industrial parameters.
The region in parameter space in which limit points are found, underneath the limit point curve, is shown in Figure 2.4.

It is important to note that although $\theta_1$ and $A_1^*$ are treated as independent parameters, in the two-reactor system their value is determined by the choice of the feed temperature $T_0$. We now investigate how the value of $\theta_1$ and $A_1^*$ are parameterized by the feed temperature $T_0$. For fixed feed temperature $T_0$, the values of $\theta_1$ and $A_1^*$ are the steady-state values in reactor one given by equations (2.69) and (2.70).

![Graph showing limit points](image)

**Fig. 2.4:** The region in parameter space in which two limit points are found. They are under the cusp curve in the lab scale model. They are under the cusp curve in the lab scale model. $S_2 = 2 \times 10^{-3} \text{m}^2, A_0 = 4.68 \text{mol mol}^{-3}, R = 8.31441 (\text{JK}^{-1}\text{mol}^{-1}), Q_2 = 41.2 \text{kJmol}^{-1}, c_{pg} = 1.35 \text{kJkg}^{-1}\text{K}^{-1}, \rho_g = 0.405 \text{kg m}^{-3}, V_2 = 5.1 \times 10^{-6} \text{m}^3$ and $\chi_2 = 25 \text{Js}^{-1}\text{m}^{-2}\text{K}^{-1}$. (Lab scale model.)

Figure 2.5 contains two lines: the solid line is the cusp curve and the dashed line is the parameterisation of the steady-state in the first reactor as a function of the feed temperature $T_0$. For fixed feed temperature $T_0$, the values of $\theta_1$ and $A_1^*$ are the steady-state values in reactor one given by equations (2.69) and (2.70).
temperature. The right hand end (left hand end) of the dashed line corresponds to a feed temperature of 403 K (1203 K) respectively. The parameterisation is found numerically, by solving for the parameters $A_1^*$ and $\theta_1$ as a function of the feed temperature $\theta_0$, as explained in the following example.

**Example:**
Consider Figure 2.5a. When the feed temperature is fixed to be $T_0 = 403$ K we solve for the parameters $A_1^*$ and $\theta_1$ and obtain $A_1^* = 0.9166$ and $\theta_1 = 0.0551$. This point is outside the region of static multiplicity, i.e. there are no limit points. When we increase the value of the feed temperature to $T_0 = 703$ K and solve for the parameters $A_1^*$ and $\theta_1$ we obtain $A_1^* = 0.5950$ and $\theta_1 = 0.0593$. This point is inside the region of static multiplicity, i.e. there are two limit points.

When the dashed line for the steady-state values in reactor one is inside the cusp curve it is assured that the steady-state diagram for reactor two will contain two limit points. It might be expected that this will lead to high product conversions under the given inflow temperature. We will demonstrate that this very reasonable expectation is not always true.

Figure 2.6 shows steady-state diagrams for reactor two for particular values of $T_0$, $E_2$ and $T_{c2}$. For each value for the activation energy $E_2$, two steady-state diagrams are shown. The figure on the left hand side shows the steady-state reactor temperature whereas the figure on the right hand side shows the steady-state product concentration. The steady-state diagrams shown in Figure 2.6 exhibit bistability; that is, there are parameter regions over which there are multiple stable steady-state solutions. In all cases the ignition limit point and the extinction limit point are for the value of the residence time in the second reactor $\tau_2^*$. Bistability is a common phenomenon in open chemically reacting systems with non-linear kinetics [24, 51]. In systems featuring exothermic reactions bistability typically comprises stable steady-state solutions with ‘low’ and ‘high’ values.

In simplified systems the phenomenon of bistability is easily demonstrated by plotting “heat loss” and “heat-generation” on the same figure [24, Figure 7.2]. The essence of the situation is that whilst heat-loss is a linear function of the reactor temperature heat generation is a sigmoidal function of reactor temperature. Depending upon parameter values there are generically either one or three intersection points for the two plots.
The procedure of separating out heat-loss and heat-generation and plotting them as functions of the reactor temperature was carried out in one of the pioneering studies into the behaviour of such systems over sixty years ago [6, Figure 2]. The presence of bistability is a consequence of the non-linearity of the heat-generation curve.

We consider the residence time in the second reactor \( \tau_2 \) to be the primary bifurcation parameter. For any value of the bifurcation parameter the steady-state solutions contain two limit points when it is inside the cusp curve. There will be a high temperature solution branch and a low temperature solution branch. A high conversion will be achieved when the system operates on the high temperature solution branch. Therefore, our first expectation is that we will have a high conversion branch when the steady-state solution is inside the cusp curve. For example, in Figure 2.6b we see that on the upper branch we have a conversion of nearly 80%. However, this is not the ‘whole picture’. The residence times of the two limit points in Figure 2.6b are \( \tau_{Lp1}^* = 5747.1 \) and \( \tau_{Lp2}^* = 20759.5 \). If \( \tau_2^* > \tau_{Lp2}^* \) the conversion will be nearly 80%. If \( \tau_{Lp1}^* < \tau_2^* < \tau_{Lp2}^* \) the conversion will either be nearly 70 – 80% or negligible depending on the reaction conditions. If \( \tau_2^* < \tau_{Lp1}^* \) the conversion will be negligible. Normally for our reactor system \( \tau_2^* = 143.45 \ll \tau_{Lp1}^* \). Hence, although Figures 2.6a and 2.6b suggest that we should have high conversion, in practice we are on the low conversion branch. It is not enough to be inside the cusp curve.

Similarly, in Figures 2.6c-2.6f the practical residence time \( \tau_2^* \) is less than the value of the residence time at the ignition limit point \( \tau_2^* < \tau_{Lp1}^* \). Consequently, the system cannot achieve the desired conversion for these catalysts. In Figures 2.6g and 2.6h, the system always operates on the high conversion branch because the residence time is higher than the residence time at the extinction limit point \( \tau_2^* > \tau_{Lp2}^* \). Thus, in practice Figures 2.6g and 2.6h suggest that we should have high conversion as we are on the high conversion branch at our residence time.

In Figures 2.7-2.8 the values of \( Q_1 \) is reduced to 50 kJ mol\(^{-1}\). The figures are to be compared against Figures 2.5 and 2.6. Figure 2.7 shows the cusp curves whereas Figure 2.8 shows typical steady-state diagrams. In Figure 2.7a the dashed line is outside-inside-outside the cusp curve. In Figures 2.7b-2.7d the dashed line is always inside the cusp curve. This means that the steady-state will have two limit points. Whether or not high conversion is achieved depends on the relationship between our typical residence time
2. Adiabatic Reactor

(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 88 \text{ kJ mol}^{-1}$.

(c) $E_2 = 150 \text{ kJ mol}^{-1}$.

(d) $E_2 = 166 \text{ kJ mol}^{-1}$.

Fig. 2.5: The cusp curve and steady-state curve in the first reactor when $Q_1 = 100 \text{ kJ mol}^{-1}$, $Q_2 = 41.2 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$ and $T_{c2}$ is given in Table 2.6 where the inflow temperature $T_0$ ranges from 403(K) to 1203(K). (Lab scale model.)

$\tau^*_2$ and the residence time at the limit points $\tau^*_{Lp1}$ and $\tau^*_{Lp2}$. The only difference between Figures 2.5 and 2.7 is that in the latter the steady-state curves move to the left. Similar to Figure 2.6, Figure 2.8 exhibits bistability. Figure 2.8 shows that the system always achieves a high conversion and the difference is in the amount of conversion we obtain. An important practical difference between Figures 2.6 and 2.8 is that in the latter the limit point bifurcations occur at significantly lower values of the residence time $\tau^*_2$.

The catalytic system shown in Figures 2.8a and 2.8b is not useful as there are no limit points. This conclusion can be drawn from Figure 2.7a. However, for the catalytic system
shown in Figures 2.8c-2.8d, 2.8e-2.8f and 2.8g-2.8h we have that our typical residence time is higher that that at the ignition limit point $\tau^*_2 > \tau^*_{Lp2}$. Note that in Figures 2.8g-2.8h the extinction limit point occurs for an exceedingly small value (approximately $10^{-11}$). Thus for our typical residence time the system will give 90% conversion. This system may be useful. Figures 2.8c-2.8d show that the system evolves to the high conversion branch; however, only 70% conversion is achieved. Even if we are inside the cusp curve and even if our typical residence time is higher than that at the ignition limit point $\tau^*_{Lp2} < \tau^*_2$ we are not guaranteed to obtain 90% conversion. Figure 2.8 shows that the system always achieves a high conversion for higher values of the activation energy $E_2 = 88, 150, 166 \text{ kJ mol}^{-1}$. The difference between these catalysts is the amount of conversion achieved. This is an important result: just because we are on the high conversion branch does not mean that we obtain 90% conversion.
Fig. 2.6: The steady-state structure in the adiabatic reactor when $Q_1 = 100$ kJ mol$^{-1}$, $Q_2 = 41.2$ kJ mol$^{-1}$, $E_1 = 80$ kJ mol$^{-1}$, $T_{c1} = 342$ K, $T_0 = 1203$ K and $T_{c2}$ is given in Table 2.6. The typical residence time in the second reactor is $\tau_{2}^* = 143.45$. (Lab scale model.)
(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 88 \text{ kJ mol}^{-1}$.

(c) $E_2 = 150 \text{ kJ mol}^{-1}$.

(d) $E_2 = 166 \text{ kJ mol}^{-1}$.

*Fig. 2.7: The cusp curve and steady-state curve in the first reactor when $Q_1 = 50 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$ and $T_{c2}$ is given in Table 2.6 where the inflow temperature $T_0$ from 403 K to 1203 K. (Lab scale model.)*
2. Adiabatic Reactor

(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 50 \text{ kJ mol}^{-1}$.

(c) $E_2 = 88 \text{ kJ mol}^{-1}$.

(d) $E_2 = 88 \text{ kJ mol}^{-1}$.

(e) $E_2 = 150 \text{ kJ mol}^{-1}$.

(f) $E_2 = 150 \text{ kJ mol}^{-1}$.

(g) $E_2 = 166 \text{ kJ mol}^{-1}$.

(h) $E_2 = 166 \text{ kJ mol}^{-1}$.

Fig. 2.8: The steady-state structure in the adiabatic reactor when $Q_1 = 50 \text{ kJ mol}^{-1}$, $Q_2 = 41.2 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$, $T_0 = 1203 \text{ K}$ and $T_{c2}$ is given in Table 2.6. The typical residence time in the second reactor is $\tau^*_1 = 143.45$. (Lab scale model.)
2.5.1.2 *Industrial model*

The region in parameter space in which limit points are found underneath the limit curve is shown in Figure 2.9 for different values of the activation energy $E_2$. Whether or not the steady-state diagram contains limit points depends upon the steady-state values in the first reactor ($A_1^*, \theta_1$). In turn these values depend upon the feed temperature $T_0$. We investigate this dependency in Figures 2.10 and 2.12.

![Graph showing the region in parameter space with limit points](image)

*Fig. 2.9:* The region in parameter space in which two limit points are found under the cusp curve. $Q_2 = 41.2$ kJmol$^{-1}$. (Industrial model.)

Each graph in Figure 2.10 contains two lines: the solid line is the cusp curve and the dashed line is the parameterisation of the steady-state in the first reactor as a function of the feed temperature. The feed temperature ranges from 294.4 K, which is at the right hand end of the dashed line, to 894.4 K, which is at the left hand end of the dashed line. In Figure 2.10a the steady-state curve is always outside the region of static multiplicity. Thus in the steady-state diagram there is always a unique solution for any value of the
bifurcation parameter. In Figures 2.10b, 2.10c and 2.10d the right hand side of the steady-state curve, when $T_0 = 294.4$ K, is initially outside the region of static multiplicity. This means that for any value of the bifurcation parameter the steady-state has a unique solution. As the inflow temperature increases the steady-state curve enters the region of static multiplicity. Thus for sufficiently high feed temperature the steady-state diagram contains two limit points. There will be a high temperature solution branch and a low temperature solution branch. It might be that there will be a high conversion on the high temperature branch. However, it is seen in Figures 2.11a–2.11f that this is not true. In Figure 2.10b the steady-state curve goes outside the multiplicity region when the feed temperature is higher than $794.4$ K. This leads to the steady-state curve following an outside-inside-outside pattern.

We might anticipate that when the dashed line is always above the cusp curve that the corresponding catalyst gives a low conversion (this is the case for catalyst one in Table 2.6). We might also anticipate that high conversion levels can be achieved when the dashed line is underneath the cusp curve because the corresponding steady-state diagram will exhibit multiplicity. It will contain a “low” temperature branch and a “high” temperature branch. Higher conversion should be associated with the latter. Based upon our conclusion in the previous section we know that the situation is more complicated than this.

Figure 2.11 shows the steady-state diagram for reactor two for particular values of $T_0$, $E_2$ and $T_{c2}$. As mentioned previously, the steady-state diagrams shown in Figure 2.11h exhibit bistability. We fixed the value of the residence time in the first reactor $\tau_1$ and allowed the residence time in the second reactor $\tau_2$ to vary Figure 2.11. From Figure 2.10a we know that the steady-state diagram for the first catalyst is single-valued. Figures 2.11a and 2.11b show that low product conversions are achieved for this catalyst.

Figures 2.11c and 2.11d show that for higher feed temperature the conversion is around 50%. However, the normal residence time in the second reactor ($\tau_2^* = 0.046$) is less than the value of the residence time at the extinction limit point. Therefore, it is impossible to achieve a conversion of 50% at our typical residence time because it is lower than that at the extinction limit point ($\tau_2^* < \tau_{L_p2}$).

Figures 2.11e–2.11h show the steady-state diagram for reactor two for the third and fourth catalysts. These steady-state diagrams exhibit steady-state multiplicity.
By looking at Figure 2.11b, we predict that the first catalyst in the second reactor is not good. Figures 2.11d, 2.11f and 2.11h show that it is impossible to obtain high conversion at low feed temperature values at our typical residence time \( \tau_2^* = 0.046 \).

Fig. 2.10: The cusp curve (solid line) and steady-state curve in the first reactor (dashed line) when \( Q_1 = 100 \text{ kJ mol}^{-1} \), \( E_1 = 80 \text{ kJ mol}^{-1} \), \( T_{c1} = 342 \text{ K} \) and \( T_{c2} \) is given in Table 2.6 where the feed temperature \( T_0 \) from 294.4 K to 894.4 K. (Industrial model.)

In Figures 2.12 and 2.13 the value of the heat of endothermicity \( Q_1 \) is reduced to 50 kJ mol\(^{-1}\). Figure 2.12 shows the cusp and steady-state curves whereas Figure 2.13 shows typical steady-state diagrams. In Figure 2.12a the dashed line is outside the cusp curve. The steady-state diagram will contain a unique solution. In Figures 2.12b and 2.12c the dashed line follows the outside-inside-outside pattern. In Figure 2.12d the dashed line is initially outside the cusp and it enters the cusp curve as the feed temperature increases. Figure 2.13 shows a similar behaviour to that shown in Figure 2.11 with the
same conclusion. The conversion shown in Figure 2.13h is slightly improved compared to 2.11h. Even though the system is always operating on the high conversion branch for our choice of the initial conditions we only obtain nearly 50% product concentration. This confirms the result we have obtained earlier: being on the high conversion branch does not guarantee achieving 90% conversion.

From Figures 2.6, 2.8, 2.11 and 2.13 the product conversion depends on the relationship between the residence time in the second reactor $\tau_2^*$ and the residence time at the two limit points ($\tau_{Lp1}^*, \tau_{Lp2}^*$). Again, it is not enough to be inside the region of static multiplicity to obtain high conversion. In order to achieve “high” conversion, the value for the normal residence time in the second reactor needs to be larger than the values of the residence times at the ignition limit point ($\tau_2^* > \tau_{Lp2}^*$). However, even when these conditions hold, the concentration of product $C_2^*$ leaving the reactor is limited by the amount of intermediate $B_1^*$ leaving reactor one.

Thus the condition that the residence time in the second reactor is higher that the residence time at the ignition limit point $\tau_2^* > \tau_{Lp2}^*$, produces a “high” product concentration. This will give a high yield, i.e. the ratio of the product concentration to the concentration of the intermediate entering reactor two. However, if the intermediate concentration entering the second reactor is small the overall conversion will be small. For example, in Figure 2.11d we obtain only 50% conversion. This means that even if the condition is available, maximizing the overall conversion depends on the conversion achieved in the first reactor.
Fig. 2.11: The steady-state structure in the adiabatic industrial reactor when $Q_1 = 100 \, \text{kJ mol}^{-1}, Q_2 = 41.2 \, \text{kJ mol}^{-1}, E_1 = 80 \, \text{kJ mol}^{-1}, T_{c1} = 342 \, \text{K}, T_0 = 444.4 \, \text{K}$ and $T_{c2}$ is given in Table 2.6. The typical residence time in the second reactor is $\tau_2^* = 0.046$. (Industrial model.)
Fig. 2.12: The cusp curve (solid line) and steady-state curve in the first reactor (dashed line) when $Q_1 = 50 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$ and $T_{c2}$ is given in Table 2.6 where the feed temperature $T_0$ from 294.4 K to 894.4 K. (Industrial model.)
(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 50 \text{ kJ mol}^{-1}$.

(c) $E_2 = 88 \text{ kJ mol}^{-1}$.

(d) $E_2 = 88 \text{ kJ mol}^{-1}$.

(e) $E_2 = 150 \text{ kJ mol}^{-1}$.

(f) $E_2 = 150 \text{ kJ mol}^{-1}$.

(g) $E_2 = 166 \text{ kJ mol}^{-1}$.

(h) $E_2 = 166 \text{ kJ mol}^{-1}$.

Fig. 2.13: The steady-state structure in the adiabatic industrial reactor when $Q_1 = 50 \text{ kJ mol}^{-1}, Q_2 = 41.2 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, T_{cl} = 342 \text{ K}$ and $T_{c2}$ is given in Table 2.6. The typical residence time in the second reactor is $\tau_2^{*} = 0.046$. (Industrial model.)
2.6 Discussion

2.6.1 Values of the feed temperature required to achieve 90% conversion ($C_2^* = 0.9$ in the industrial model)

In this section we work backwards and ask “what is the required feed temperature ($T_0$) to obtain 90% product conversion ($C_2^* = 0.9$)?”

We fix the product conversion $C_2^*$ to 0.9. Using the algebraic relationships (2.59)–(2.60), we find

$$\theta_2 = 0.9Q_2^* + \theta_1$$

(2.77)

Substituting the expression for $A_1^*$, equation (2.49),

$$A_1^* = (Q_1^* - \theta_0 + \theta_1)/Q_1^*$$

and the expression for $\theta_2$, equation (2.49),

$$\theta_2 = 0.9Q_2^* + \theta_1$$

into the steady-state equation for the temperature in the second reactor, equation (2.54),

$$-0.9Q_2^*/\tau_2^* + a_2^* \left[ \exp \frac{-1}{0.9Q_2^* + \theta_1} \right] [(Q_2^*/Q_1^*)(\theta_0 - \theta_1) - 0.9Q_2^*] = 0.$$  

Solving the latter equation we have the value of $\theta_1$.

Then the value of the feed temperature is found by substituting the values of $\theta_1$ into the steady-state equation (2.53).

Tables 2.11 and 2.12 show the required feed temperature to achieve 90% conversion of the product concentration $C_2^*$. For the feed temperature to not be too high $T_0 \leq 1000$K, low values of the heat of endothermicity $Q_1$ and characteristic temperature $T_{c1}$ are required whereas high values of the activation energy $E_1$ are required. We have also calculated the eigenvalue for reactor two to show that the required steady-state is stable.

Table 2.11 shows the required values of the feed temperature when $T_{c1} = 942$ K and $E_1 = 80$ kJ mol$^{-1}$. Table 2.12 shows the required values of the feed temperature
when $T_{c1} = 342$ K and $E_1 = 80$ kJ mol$^{-1}$. The final column in each table indicates the eigenvalues associated with the second reactor. This case confirms that the steady-state solution is stable.

Looking at Table 2.11 we see that for three different endothermic reactions, $Q_1 = 205.8$, 100 and 50 kJ mol$^{-1}$, the feed temperature values are unrealistic for all four catalysts in the second reactor. Thus it is impossible to obtain the desired conversion for the highest value of the characteristic temperature $T_{c1} = 942$ K.

In Table 2.12 the characteristic temperature in the first reactor is reduced from 942 K to 342 K. Looking at this table, when $Q_1 = 205.8$ kJ mol$^{-1}$ the feed temperature values are unrealistic for the first, second and third catalysts in the second reactor. When $Q_1 = 100$ kJ mol$^{-1}$ the feed temperature values are only unrealistic for the first and second catalysts. When $Q_1 = 50$ kJ mol$^{-1}$ the feed temperature value is only unrealistic for the first catalyst.

We conclude that even with reducing the characteristic temperature $T_{c1}$ it is difficult to achieve 90% conversion in the second reactor for a highly endothermic reaction in the range of realistic feed temperature $T_0 \leq 1000$ K.

**Tab. 2.11:** The feed temperature required to achieve 90% conversion to the product $C^*_2 = 0.9$ for different values of the heat of endothermicity $Q_1$ kJ mol$^{-1}$ and the activation energy $E_2$ kJ mol$^{-1}$. $T_{c1} = 942$ K and $E_1 = 80$ kJ mol$^{-1}$. (Industrial model.)

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Tab. 2.12: The feed temperature required to achieve 90% conversion to the product $C_2^* = 0.9$ for different values of the heat of endothermicity $Q_1$ kJ mol$^{-1}$ and the activation energy $E_2$ kJ mol$^{-1}$. $T_{cl} = 342$ K and $E_1 = 80$ kJ mol$^{-1}$. (Industrial model.)

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2.6.2 Values of residence time ($\tau_2$) and its influence on conversion in the industrial model

In this section we investigate the influence of the residence time in the second reactor on the conversion. We show how the system behaviour changes for some values of the residence time when we increase the value of the feed temperature.

Normally for our model, the residence time in the second reactor is $\tau_2^* = 0.046$. Figure 2.14a shows the dimensionless product concentration as a function of the dimensionless residence time for a fixed value of the feed temperature. Figure 2.14b adds the dimensionless intermediate concentration. It shows that the standard value for the residence time $\tau_2^*$ is on the lower branch of the steady-state curve, being lower than the values of the residence time at extinction limit point $\tau_{ext} \sim 0.6$. For the the parameter values used in this figure the steady-state reactant concentration in reactor one is $A_1^* = 0.7$. Hence, there is not enough intermediate $B_1^*$ to achieve high conversion Figure 2.14b. For this system it follows that it is impossible to have 90% conversion to the product concentration $C_2$.

In Figure 2.15 the kinetics parameters are identical to that in Figure 2.14 except that the feed temperature $T_0$ is increased to 654.4 K. In this case there is a significant jump in the conversion to nearly 90%. In this case the typical value of the residence time is on the upper branch of the steady-state curve.
2. Adiabatic Reactor

(a) $C_2^*$ steady-state.  
(b) A combination of $B_2^*$ and $C_2^*$ steady-state.

Fig. 2.14: The position of the our typical residence time curve on the steady-state diagram and the dimensionless concentration of the intermediate $B_2$ and the product $C_2$ when $A_1^* = 0.7$, $T_0 = 444.4$ K, $T_{c1} = 342$ K, $E_1 = 80$ kJ mol$^{-1}$, $E_2 = 166$ kJ mol$^{-1}$ and $Q_1 = 100$ kJ mol$^{-1}$. (Industrial model.)

2.7 Conclusion

We wrote the model for a cascade reaction occurring in two reactors where there is an endothermic process in the first reactor and an exothermic process in the second reactor. In the general case it is shown that the system of eight equations can be reduced to five equations. Moreover, in the adiabatic case there is a further reduction to two equations.

In the first reactor there is always a unique stable steady-state which is locally stable. In the second reactor there are two steady-state diagrams: one where there is always a unique steady-state solution and one when there are two limit points. We examined how changing the inflow temperature in the first reactor can determine which steady-state diagrams we have. We investigated the performance of the catalyst in the first reactor and the second reactor. We have shown that in adiabatic operation it is very difficult to obtain 90% conversion of the reactant unless the inflow temperature $T_0$ is very high and there is a good combination of the parameters in the first reactor. Namely, this requires the activation energy $E_1$ to be high and the heat of endothermicity $Q_1$ and the characteristic temperature $T_{c1}$ to be low.
Fig. 2.15: The position of the our typical residence time curve on the steady-state diagram when the feed temperature $T_0$ increased to 654.4 K. $T_{c1} = 342$ K, $E_1 = 80$ kJ mol$^{-1}$, $E_2 = 166$ kJ mol$^{-1}$ and $Q_1 = 100$ kJ mol$^{-1}$. (Industrial model)

To achieve the desired conversion of 90% in the second reactor we need to obtain at least 90% conversion of the reactant. If we ensure high conversion in the first reactor we can then examine the conditions to obtain the preferable conversion in the second reactor. Using singularity theory we can predict whether a given catalyst will have two limit points or no limit points on the steady state diagram. Having two limit points is not sufficient to achieve 90% conversion under two circumstances:

- If the reference value of the residence time in the second reactor $\tau^*_2$ is lower than the value of the residence time at the extinction limit point $\tau^*_{ext}$ it is impossible to obtain high product conversion.

- If the reference value of the residence time in the second reactor $\tau^*_2$ is higher than the
value of the residence time at the ignition limit point $\tau_{ign}^*$ and there is not enough conversion in the first reactor it is impossible to obtain high product conversion.

Namely, our typical residence time in the second reactor must be higher than the residence time in the ignition limit point and obtaining at least 90% conversion in the first reactor to achieve the desired product conversion.

Also, we can distinguish whether the catalyst in the second reactor is “good” or “bad” depending on how much of the intermediate $B$ is converted into the product $C$. To facilitate the choice of the appropriate catalyst we work backwards by fixing the product concentration in the second reactor $C_2$ to 90% to find the required feed temperature for each chosen catalyst. This technique can assist us to choose the appropriate catalyst that will give the desired conversion.
3. DIABATIC REACTOR

In this chapter we develop a mathematical model describing the operation of a diabatic reactor. This model relaxes the adiabatic assumption that the heat-transfer through the walls of the reactor is negligible. However, it is assumed that the reactor walls are held at a constant temperature. The reaction mechanism investigated is $A \rightarrow B \rightarrow C$, where the reactions occur in a two reactor cascade. Specific features of coupled endothermic and exothermic reactions are taken into account. Particular considerations are presented and discussed for different catalysts to obtain 90% conversion into product.

3.1 Diabatic reactor configuration

Figure 3.1 shows the processes that occur in the reactor cascade. The concentrations of the reactant $A$ and the intermediate $B$ leaving reactor one are $A_1$ and $B_1$, respectively. The concentrations of the reactant $A$ and the intermediate $B$ and the product $C$ leaving reactor two are $A_2$, $B_2$ and $C_2$, respectively. The coolant temperatures for the two reactors are $T_{a,1}$ and $T_{a,2}$, respectively. The temperatures of the reacting mixtures in reactor one and two are $T_1$ and $T_2$, respectively.

We are particularly interested in identifying catalysts and reactor operation conditions that ensure a minimum of 90% conversion of reactant $A$ to product $C$.

\[ \begin{array}{c}
q, T_0, A_0 & \xrightarrow{T_{a,1}} & T_1, \text{Catalyst 1} & \xrightarrow{A_1, B_1} & T_{a,2} & \xrightarrow{T_2, \text{Catalyst 2}} & A_2, B_2, C_2
\end{array} \]

Fig. 3.1: Prototype reactor configuration. $A_0$ is the feed concentration, $T_0$ is the feed temperature and $q$ is the flow rate.
3.2 Model equations

In Section 3.2.1 we introduce the assumption for the reaction occurring in each reactor (1.6) and (1.7). In Section 3.2.2 we give the model equations for each reaction (1.6) and (1.7). In Section 3.2.3 new variables are introduced to non-dimensionalise the system equations. In Section 3.2.4 we show how the model equation systems for a diabatic reaction can be reduced from eight equations to five equations.

For an overview of the model equations for the classic chemical engineering problem of a non-isothermal continuously stirred tank reactor we refer to Gray and Scott [24, Chapter 7]. Recall that our reactor configuration consists of a cascade of two reactors. The effluent stream from reactor one provides the feed stream for reactor two. Consequently, our model equations are obtained by straightforwardly adapting the model for a single reactor. The model equations for a similar system, in which an exothermic reaction occurs in both reactors, has been studied [17].

3.2.1 Model assumptions

It is assumed that the reactor vessels are well stirred. We consider a feed temperature to be realistic if $T_0 \leq 1000K$. It is often useful to characterize a chemical reaction in terms of a “characteristic temperature” [44]. We write the pre-exponential factor $a_i$ in terms of a characteristic temperature $T_{ci}$ [44]

$$a_i = \frac{E_i \alpha}{RT_{ci}^2} \exp \left[ \frac{E_i}{RT_{ci}} \right],$$

for $i = 1, 2$ referring to the reactor number, $E_i$ Jmol$^{-1}$ is the activation energy, $R$ JK$^{-1}$mol$^{-1}$ the ideal gas constant and $\alpha$ Ks$^{-1}$ is a constant heating rate.

The residence time in each reactor is defined by

$$\tau_i = \frac{V_i}{q},$$

for $i = 1, 2$, $V_i$ m$^3$ is the reactor volume and $q$ m$^3$s$^{-1}$ is the flow-rate.
3.2.2 Dimensional equations

The system of equations in the first reactor is given by equations (3.1)–(3.7):

The rate of change of the concentration of the reactant $A$

$$V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1.$$  \hfill (3.1)

The rate of change of the concentration of the intermediate $B$

$$V_1 \frac{dB_1}{dt} = q(B_0 - B_1) + V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1.$$  \hfill (3.2)

The rate of change of the concentration of the product $C$

$$V_1 \frac{dC_1}{dt} = q(C_0 - C_1).$$  \hfill (3.3)

The rate of change of the temperature inside the reactor

$$c_{pg} \rho_g V_1 \frac{dT_1}{dt} = q c_{pg} \rho_g (T_0 - T_1) - Q_1 V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{a,1}).$$  \hfill (3.4)

The definition of the pre-exponential factor $a_1$ in terms of the characteristic temperature $T_{c1}$ (see chapter 1.5.1)

$$a_1 = \frac{E_1 \alpha}{RT_{c1}^2} \exp \left[ \frac{E_1}{RT_{c1}} \right].$$  \hfill (3.5)

The initial conditions are given by equation (3.6). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

$$A_1(0) = B_1(0) = C_1(0) = 0, \quad T_1(0) = \frac{qc_{pg} \rho_g T_0 + J_1 \chi_1 S_1 T_{a,1}}{qc_{pg} \rho_g + J_1 \chi_1 S_1}.$$  \hfill (3.6)
The residence time is

\[ \tau_1 = \frac{V_1}{q}. \]  

(3.7)

The system of equations in the second reactor is given by equations (3.8)–(3.14):

The rate of change of the concentration of reactant \( A \)

\[ V_2 \frac{dA_2}{dt} = q(A_1 - A_2). \]  

(3.8)

The rate of change of the concentration of reactant \( B \)

\[ V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \]  

(3.9)

The rate of change of the concentration of reactant \( C \)

\[ V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \]  

(3.10)

The rate of change of the temperature inside the reactor

\[ c_{pg}\rho_gV_2 \frac{dT_2}{dt} = q c_{pg}\rho_g(T_1 - T_2) + Q_2V_2a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2 - J_2\chi_2S_2(T_2 - T_{a,2}). \]  

(3.11)

The definition of the pre-exponential factor \( a_2 \) in terms of the characteristic temperature \( T_{c,2} \) (see chapter 1.5.1)

\[ a_2 = \frac{E_2\alpha}{RT_{c,2}^2} \exp \left[ \frac{E_2}{RT_{c,2}} \right]. \]  

(3.12)
The initial conditions are given by equation (3.13). As described previously, before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

\[
A_2(0) = B_2(0) = C_2(0) = 0, \quad T_2(0) = \frac{qc_{pg}T_1 + J_2\chi_2S_2T_{a.2}}{qc_{pg} + J_2\chi_2S_2}. \tag{3.13}
\]

The residence time is

\[
\tau_2 = \frac{V_2}{q}. \tag{3.14}
\]

The concentrations flowing into reactor two are the concentrations exiting from reactor one. Similarly the temperature of the fluid entering reactor two is equal to that from reactor one.

The terms appearing in equations (3.1)-(3.14) are defined in Appendix.1.

### 3.2.3 Dimensionless equations

In nondimensionalising equations (3.1)-(3.14) we introduce dimensionless concentrations \((A_i^*, B_i^*, C_i^*)\), dimensionless temperatures \((\theta_i)\), where \((i = 1, 2)\), and dimensionless time \((t^*)\). These are defined in Appendix.1.

The system of non-dimensional equations in the first reactor is given by equations (3.15)–(3.20):

\[
\frac{dA_1^*}{dt^*} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^*, \tag{3.15}
\]

\[
\frac{dB_1^*}{dt^*} = \frac{B_0^* - B_1^*}{\tau_1^*} + a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^*, \tag{3.16}
\]

\[
\frac{dC_1^*}{dt^*} = \frac{C_0^* - C_1^*}{\tau_1^*}, \tag{3.17}
\]

\[
\frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^* - J_1\chi_{T,1}(\theta_1 - \theta_{a,1}), \tag{3.18}
\]

\[
a_1^* = \frac{\alpha^* V^* E_1^*}{T_{c1}^2} \exp \left[ \frac{E_1^*}{T_{c1}} \right]. \tag{3.19}
\]
Dimensionless initial conditions are

\[ A_1^*(0) = B_1^*(0) = C_1^*(0) = 0, \quad \theta_1(0) = \theta_0 + J_1 \chi_{1,T} \tau_1^* \theta_{a,1}, \] (3.20)

The system of non-dimensional equations in the second reactor is given by equations (3.21)–(3.26):

\[
\frac{dA_2^*}{dt^*} = \frac{A_1^* - A_2^*}{\tau_2^*}, \quad (3.21)
\]
\[
\frac{dB_2^*}{dt^*} = \frac{B_1^* - B_2^*}{\tau_2^*} - a_2^* \exp\left[-\frac{1}{\theta_2}\right] B_2^*, \quad (3.22)
\]
\[
\frac{dC_2^*}{dt^*} = \frac{C_1^* - C_2^*}{\tau_2^*} + a_2^* \exp\left[-\frac{1}{\theta_2}\right] B_2^*, \quad (3.23)
\]
\[
\frac{d\theta_2}{dt^*} = \frac{\theta_1 - \theta_2}{\tau_2^*} + Q_2^* a_2^* \exp\left[-\frac{1}{\theta_2}\right] B_2^* - J_2(\theta_2 - \theta_{a,2}), \quad (3.24)
\]
\[
a_2^* = \frac{\alpha_2^*}{T_{c1}^*} \exp\left[\frac{1}{T_{c1}^*}\right]. \quad (3.25)
\]

Dimensionless initial conditions are

\[ A_2^*(0) = B_2^*(0) = C_2^*(0) = 0, \quad \theta_2(0) = \frac{\theta_1 + J_2 \tau_2^* \theta_{a,2}}{1 + J_2 \tau_2^*}. \] (3.26)

From now on we assume that there is no intermediate or product in the feed stream, i.e. \( B_0 = B_0^* = 0 \) and \( C_0 = C_0^* = 0 \). In Chapter 2 we showed that the the system of eight equations can be reduced to a system of five equations – equations for the chemical species \( B_1^*, C_1^* \) and \( C_2^* \) are not required. As we are interested in the long-time behaviour we study the steady-state solutions of our model.

### 3.2.4 Reduced model

For non-adiabatic operation the system of eight equations, (3.15)-(3.18) and (3.21)-(3.24) can be reduced to a system of five equations. The reduced system of non-dimensional
The reduced system of non-dimensional equations in the second reactor is:

\[
\begin{align*}
\frac{dA_2^*}{dt^*} &= \frac{A_1^* - A_2^*}{\tau_2^*}, \\
\frac{dB_2^*}{dt^*} &= \frac{1 - A_1^* - B_2^*}{\tau_2^*} - a_2^* \exp\left[\frac{-1}{\theta_2}\right] B_2^*, \\
\frac{d\theta_2^*}{dt^*} &= \frac{\theta_1 - \theta_2^*}{\tau_2^*} + Q_2^* a_2^* \exp\left[\frac{-1}{\theta_2}\right] B_2^* - J_2(\theta_2 - \theta_{a,2}), \\
C_2^* &= 1 - A_2^* - B_2^*.
\end{align*}
\]  

3.3 Results and discussion

All calculations performed in this thesis use the industrial parameter values stated in Appendix.1, unless otherwise stated.

3.3.1 Achieving 90% conversion in reactor one

To achieve 90% conversion of the reactant \( A \) into the product \( C \) we must achieve at least 90% conversion of the reactant into the intermediate species \( B \) in the first reactor. In order to find the steady-state solutions we set the derivatives of the reactant \( A_1^* \) and the temperature \( \theta_1 \) equal to zero. By taking a suitable linear combination of equations (3.27) and (3.28) we find an equation giving the feed temperature required to achieve a specified steady-state value of the reactant concentration:

\[
\theta_0 = \frac{-(1 + J_1 \tau_1^* \chi_1^*) E_1^*}{\ln\left[(1 - A_1^*)/(a_1^* A_1^* \tau_1^*)\right]} + Q_1^* (1 - A_1^*) - J_1 \chi_1^* \theta_{a,1}.
\]  

Differentiating (3.35) with respect to the heat transfer coefficient between the reaction
mixture and the reactor walls $J_1\chi_1^*$ we obtain

$$
\frac{d\theta_0}{dJ_1\chi_1^*} = - \left[ \frac{\tau_1^* E_1^*}{\ln \left[ \frac{1 - A_1^*}{a_1^* A_1^* \tau_1^*} \right]} + \tau_1^* \theta_{a,1} \right] < 0,
$$

(3.36)

for $\tau_1^* < \left[ \frac{1 - A_1^*}{a_1^* A_1^*} \right] \exp \left[ -\frac{E_1^*}{\theta_1} \right]$. (This inequality holds for the parameter values in Appendix.1).

Equation (3.36) shows that as the heat transfer coefficient $J_1\chi_1$ increases the required feed temperature to achieve the specified conversion decreases.

Recall that the pre-exponential factor ($a_1^*$) depends on the activation energy ($E_1^*$). Differentiating (3.35) with respect to the activation energy $E_1^*$ and using equation (3.19) where appropriate, we obtain

$$
\frac{d\theta_0}{dE_1^*} = -(1 + J_1\tau_1^* \chi_1^*) \left( \frac{E_1^* + T_{c1}^* + T_{c1}^* \ln \left[ \frac{(1 - A_1^*)/(a_1^* A_1^* \tau_1^*)}{2} \right]}{T_{c1}^* \left( \ln \left[ \frac{(1 - A_1^*)/(a_1^* A_1^* \tau_1^*)}{2} \right] \right)^2} \right) < 0,
$$

(3.37)

for $\tau_1^* < \left[ \frac{1 - A_1^*}{a_1^* A_1^*} \right] \exp \left[ 1 + \frac{E_1^*}{T_{c1}^*} \right]$. (This inequality holds for the parameter values in Appendix.1).

When $J_1 = 0$, i.e. adiabatic operation, we recover equation (2.63).

Equation (3.37) shows that the required inflow temperature is a decreasing function of $E_1^*$; that is, a lower activation energy requires a higher inflow temperature to achieve a specified conversion.

Differentiating (3.35) with respect to the characteristic temperature $T_{c1}^*$ and using equation (3.19) where appropriate, we obtain

$$
\frac{d\theta_0}{dT_{c1}^*} = \frac{E_1^*(1 + J_1\tau_1^* \chi_1^*)(2T_{c1}^* + E_1^*)}{T_{c1}^*(\ln \left[ \frac{(1 - A_1^*)/(a_1^* A_1^* \tau_1^*)}{2} \right]^2)} > 0.
$$

(3.38)

When $J_1 = 0$, i.e. adiabatic operation, we recover equation (2.65). Equation (3.38) shows that the required inflow temperature is an increasing function of $T_{c1}$; that is, a higher characteristic temperature requires a higher inflow temperature to achieve a specified conversion.

Equations (3.37) and (3.38) show that the ideal catalyst for reactor one has a high activation energy $E_1^*$ and a low characteristic temperature $T_{c1}^*$. Returning to dimensional values, the value for the feed temperature $T_0$ to obtain a conversion of 90% of the reactant $A_1$ as a function of the catalyst parameters $E_1$ and $T_{c1}$ is shown in Table 3.1. This table
shows that for a high value of the endothermicity $Q_1$, the required feed temperature $T_0$ is almost always unrealistic; that is, higher than 1000K.

Differentiating (3.35) with respect to the endothermicity parameter $Q_1^*$ we obtain

$$\frac{dT_0}{dQ_1^*} = -A_1^* + 1 > 0,$$

as $0 < A_1^* < 1$. Equation (3.39) shows that the required feed temperature is an increasing function of $Q_1^*$. That is, more endothermic reactions require a higher feed temperature to achieve a specified conversion.

Figure 3.2 shows the characteristic temperature $T_{c1}$ required to achieve 90% conversion of the reactant $A_1$ as a function of the activation energy $E_1$ when the inflow temperature $T_0$ is fixed to its maximum value 1000 K for different values of the heat of endothermicity $Q_1$. This figure confirms that there is a reduced range of values for the activation energy $E_1$ and the characteristic temperature $T_{c1}$ for which we obtain 90% conversion as the heat of endothermicity $Q_1$ increases. For example, compare lines (a) and (d). This means that it is more challenging to find a potential catalyst.

Tab. 3.1: The inflow temperature $T_0$ required to achieve 90% conversion in the first reactor, $A_1^* = 0.1$, as a function of the activation energy $E_1$ kJ mol$^{-1}$ and the characteristic temperature $T_{c1}$ K. The heat of endothermicity is $Q_1 = 205.8$ kJ mol$^{-1}$ and the coolant temperature is $T_{a,1} = 800$ K.

<table>
<thead>
<tr>
<th>$T_{c1}$</th>
<th>$T_0(E_1 = 50)$</th>
<th>$T_0(E_1 = 80)$</th>
<th>$T_0(E_1 = 120)$</th>
<th>$T_0(E_1 = 180)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>342</td>
<td>1021.9</td>
<td>964.6</td>
<td>940.6</td>
<td>927.4</td>
</tr>
<tr>
<td>442</td>
<td>1258.6</td>
<td>1126.2</td>
<td>1076.1</td>
<td>1049.5</td>
</tr>
<tr>
<td>542</td>
<td>1602.7</td>
<td>1319.8</td>
<td>1226.5</td>
<td>1179.4</td>
</tr>
</tbody>
</table>

The effect of changing the heat of endothermicity $Q_1$ is shown in Figures 3.3b and 3.3a. These figures show the inflow temperature required to achieve 90% conversion of the reactant $A_1$ in the first reactor as a function of the activation energy $E_1$ for different values of the characteristic temperature $T_{c1}$ and the heat of endothermicity $Q_1$. The horizontal lines represent a feed temperature of 1000 K. Feed temperatures higher than this are considered to be unachievable. These figures confirm that it is more difficult to find a suitable catalyst for a highly endothermic reaction. When the reaction is weakly endothermic there is a larger range of catalysts that can be used.

Differentiating equation (3.35) with respect to the coolant temperature $\theta_{a,1}$ we obtain
Fig. 3.2: The parameters values required to achieve 90% conversion in the first reactor as a function of the activation energy $E_1$ and the characteristic temperature $T_{c1}$. The feed temperature $T_0 = 1000$ K and the coolant temperature $T_{a,1} = 800$ K. The heat of endothermicity $Q_1$ is (a) 50 kJ mol$^{-1}$, (b) 100 kJ mol$^{-1}$, (c) 150 kJ mol$^{-1}$ and (d) 205.8 kJ mol$^{-1}$. All other parameters are given in Appendix.1.

\[
\frac{d\theta_0}{d\theta_{a,1}} = -J_1 r_1^* \chi_1^* < 0. \tag{3.40}
\]

Equation (3.40) shows that the required inflow temperature is a decreasing function of $\theta_{a,1}$; that is, a higher coolant temperature allows a lower inflow temperature to achieve a specified conversion. Figure 3.4 shows the feed temperature $T_0$ required to achieve 90% conversion as a function of the coolant temperature. Note that a very low characteristic temperature is required to obtain this figure. This figure confirms that the feed temperature is always realistic for any value of the coolant temperature $T_{a,1}$.

In conclusion, in order to achieve 90% conversion in the first reactor at a realistic feed temperature $T_0 < 1000$ K, the characteristic temperature $T_{c1}$ and the heat of endother-
3. Diabatic Reactor

3.3 Diabatic Reactor

3.3.1 Achieving 90% conversion in reactor one

In this section we fix the catalyst in the first reactor to ensure slightly more than 90% conversion of the reactant $A_1^*$. We investigate how the choice of the catalyst in the second reactor affects the steady-state concentration of the product, $C_2^*$. We consider the case $E_2 = 50 \text{ kJ mol}^{-1}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$ and examine how the steady-state diagram changes as the characteristic temperature $T_{c2}$ is raised. The red and black branches in the steady-state diagrams shown in Figure 3.5 are stable and unstable, respectively.

The high branch is called the high conversion branch and the low branch is called the...
Fig. 3.4: The feed temperature $T_0$ required to achieve 90% conversion in the first reactor as a function of the coolant temperature $T_{a,1}$. The characteristic temperature $T_{c,1} = 342$ K, the activation energy $E_1 = 80$ kJ mol$^{-1}$. The heat of endothermicity $Q_1$ is $(a) 50$ kJ mol$^{-1}$, $(b) 100$ kJ mol$^{-1}$, $(c) 150$ kJ mol$^{-1}$ and $(d) 205.8$ kJ mol$^{-1}$. All other parameters are given in Appendix.1.

Fig. 3.5a shows the steady-state concentration diagram when $T_{c,2} = 405$ (K). In this figure both the extinction and the ignition limit point bifurcations occur at unphysical values (negative!) of the coolant temperature $T_{a,2}$. The practical consequence of this is that the system always evolves to the high conversion branch. Consequently, this

3.3.2.1 Scenario one $T_{c,1} < 408$ K

Figure 3.5a shows the steady-state concentration diagram when $T_{c,2} = 405$ (K). In this figure both the extinction and the ignition limit point bifurcations occur at unphysical values (negative!) of the coolant temperature $T_{a,2}$. The practical consequence of this is that the system always evolves to the high conversion branch. Consequently, this
steady-state diagram is the best possible case as there is at least 90% conversion for all realistic values of the coolant temperature of reactor two: a high coolant temperature is not required to ensure high product concentration. We consider the reaction in scenario one to be autothermal because it does not require heat to be supplied in order to obtain high conversion.

3.3.2.2 Scenario two \( 408 \, K \leq T_{c1} < 441 \, K \)

In Figure 3.5b the value of the characteristic temperature has been increased to \( T_{c2} = 435 \, K \). The stable solution branches are physically disjoint. By “physically disjoint” it is meant that if the solutions corresponding to a negative coolant temperature are removed the remaining solution branches are not connected. This is because the extinction limit point occurs for a negative value of the coolant temperature.

The value of the coolant temperature at the ignition limit point is now positive. High conversion can be achieved by temporarily increasing the value of the coolant temperature past that of the ignition limit point. It is then possible to decrease the coolant temperature to a lower value, in theory any other value, without the system “falling” off the high conversion branch. This case is good in practice, provided that the coolant temperature at the ignition limit point is not too high. If the critical value of the coolant temperature is lower than 298 K, i.e room temperature, then in practice this case is indistinguishable from the first scenario.

3.3.2.3 Scenario three \( 441 \, K \leq T_{c1} < 444 \, K \)

As the value of the characteristic temperature is further increased the next transition occurs when the value of the coolant temperature at the extinction limit point moves into the right half plane. The steady-state diagram following this transition is shown in Figure 3.5c. The steady-state diagram is now “physically” connected.

As in the previous scenario the system can be moved to the high conversion branch by increasing the coolant temperature. However, there is now a minimum value of the coolant temperature that is required in order to operate on the high conversion branch. If the coolant temperature is decreased through this value then the system will “fall off” the high conversion branch onto the low conversion branch. This case is good in practice,
provided that the values of the coolant temperature at both the extinction and ignition limit points are not too high. In particular, if the critical value of the coolant temperatures at the extinction limit point is below 298 K the system can operate at a normal room temperature of 298 K. This means that additional heat need not be supplied to reactor two.

3.3.2.4 Scenario four $444 \leq T_{c1} < 462 \text{ K}$

The next transition to occur is when the value of the coolant temperature at the ignition limit point moves through the maximum value of the coolant temperature $T_{a,2} = 1000 \text{ K}$. A steady-state diagram for this case is shown in Figure 3.5d. It is no longer possible to reach the high conversion branch by increasing the coolant temperature while staying below the maximum allowable temperature. Instead, a temporary perturbation of some kind must be imposed onto the system to “kick” it from the low conversion branch onto the high conversion branch. For example, it is possible to achieve this by either increasing the value of the feed temperature temporarily or increasing the concentration of the reactant entering the first reactor.

3.3.2.5 Scenario five $462 \leq T_{c1} < 511 \text{ K}$

Figure 3.5e shows the steady-state when both the ignition and extinction limit points have moved through the maximum value of the coolant temperature. It is now impossible to reach the high product conversion branch by either increasing the coolant temperature while staying below the practical limit of 1000 K or by imposing a “kick”. From a practical perspective, catalysts falling into this category are of no interest because it is impossible to operate on the high conversion branch.

3.3.2.6 Scenario six $T_{c1} \geq 511 \text{ K}$

The final transition to occur is a cusp singularity, at which the two limit points disappear. The steady-state diagram after this transition is shown in Figure 3.5f. For realistic values of the coolant temperature only a low conversion is achieved. From a practical perspective, catalysts falling into this category are impractical.
Fig. 3.5: The steady-state structure in the diabatic reactor when $Q_1 = 100$ kJ mol$^{-1}$, $Q_2 = 100$ kJ mol$^{-1}$, $E_1 = 80$ kJ mol$^{-1}$, $E_2 = 50$ kJ mol$^{-1}$, $T_{c1} = 342$ K, $T_0 = 680$ K and $T_{a,1} = 800$ K. All other parameters are given in Appendix.1.


3.3.3 Limit point unfolding diagram

In the previous section we discussed how the steady-state diagram changes as the characteristic temperature of the catalyst in the second reactor is increased. These transitions were identified by determining the steady-state diagram for many values of the characteristic temperature and characterizing how they differed. In this section we show that there is a less labour intensive way to identify these changes.

Figure 3.6 shows a limit point unfolding diagram. The red branches are the ignition (IGLp) and extinction (EXLp) limit points as a function of the characteristic temperature. The horizontal lines denote the different transitions between steady-state diagrams. For example, the line at $T_{c1} = 441$ (K) separates the steady-state diagram, Figure 3.5b, from the steady-state diagram, Figure 3.5c. The values of the characteristic temperature at all the transitions described earlier can be identified from Figure 3.6. The importance of this figure is that it displays the behaviour more concisely allowing the location of all transitions to be determined from the unfolding diagram.

In Figure 3.6, region (a) is the most desirable region as the system always evolves to the high conversion branch for all values of the coolant temperature. We consider this region to be the autothermal region because no external heat is required to be supplied. Region (b) is also of interest since high conversion can be achieved by temporarily increasing the value of the coolant temperature. The other regions are of less interest because they exhibit “bad” steady-state behaviour.

3.3.4 The influence of the activation energy and the exothermicity in the second reactor on the steady-state transitions

After constructing the unfolding diagram in Figure 3.6 we can easily determine all the locations of the steady-state transitions. We extended this idea to investigate the influence of the activation energy $E_2$ and the heat of exothermicity $Q_2$ on the position of each transition. This is shown in Figures 3.7a, 3.7b and 3.7c. These figures show the critical values of the characteristic temperature for each transition when the heat of exothermicity $Q_2$ values are 50, 100 and 200 (kJ mol$^{-1}$), respectively. The red and blue branches in Figure 3.7 show the ignition and the extinction limit points, respectively. The solid and
Fig. 3.6: The limit point unfolding diagram in the characteristic temperature and coolant temperature plane. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$, $T_0 = 680 \text{ K}$, $T_{a,1} = 800 \text{ K}$, $E_2 = 50 \text{ kJ mol}^{-1}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$. The legends a-f related to the steady-state diagrams shown in Figures 3.5a-3.5f. All other parameters are given in Appendix 1. The ignition limit point (IGLp) is the red branch and extinction limit point (EXLp) is the blue branch.

Dashed branches shown in Figure 3.7 are when the ambient temperature values $T_{a,2}$ are 0 K and 1000 K, respectively. Parameter values below the solid red line are the most desirable. Parameter values above the dashed blue line are “worthless”. The green line is the cusp curve.

Figure 3.7a shows the regions where all the transitions (a,b,c,cc,d,e,f) between the steady state diagrams occur. The transitions (a,b,c,d,e,f) are those described earlier in Figure 3.6 when $E_2 = 50 \text{ kJ mol}^{-1}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$; see Figure 3.7b. The region (a) is the desired autothermal region where the system always evolves to the high conversion branch for all values of the coolant temperature. The region (c) is where the extinction and ignition limit point are both positive and less than the critical value of the ambient
temperature, i.e. \( T_{a,2} = 1000 \text{ K} \) is smaller, Figure 3.7b, when the heat of exothermicity is increased to \( Q_2 = 100 \text{ kJ mol}^{-1} \). In Figure 3.7c, when the heat of exothermicity is increased to \( Q_2 = 200 \text{ kJ mol}^{-1} \), the region (c) disappears.

The new region (cc) can be investigated by constructing an unfolding limit point diagram when the activation energy is \( E_2 = 60 \text{ kJ mol}^{-1} \), Figure 3.8. In this figure the transition between region (a) and region (b) is of particular interest since region (a) has the best possible steady-state diagram. In region (cc) the extinction limit point occurs at a negative value of the coolant temperature. However, the ignition limit point has moved through the maximum value of the coolant temperature. Thus, achieving high conversion in region (cc) depends on a good choice of catalysts and the initial conditions.

For a fixed value of the heat of exothermicity \( Q_2 \) the curve where the (a-b) transition occurs has two features. If the activation energy \( E_2 \) is sufficiently low, then the characteristic temperature \( T_{c,2} \) at the transition point is an increasing function of the activation energy \( E_2 \). If the activation energy \( E_2 \) is sufficiently high, then the characteristic temperature \( T_{c,2} \) is a decreasing function of the activation energy \( E_2 \). Thus, in order to achieve the required conversion of the product \( C_2 \) at the autothermal region (a), the heat of exothermicity \( Q_2 \) is required to be large and the characteristic temperature \( T_{c,2} \) to be lower than the maximum value of the characteristic temperature in each transition. Finding the maximum value of the characteristic temperature \( T_{c,2} \) for each fixed value of the heat of exothermicity \( Q_2 \) will be helpful to find the parameter values that in region (a).
Fig. 3.7: The region in parameter space in which the transitions occur. The parameter values are \( E_1 = 80 \text{ kJ mol}^{-1} \), \( Q_1 = 100 \text{ kJ mol}^{-1} \), \( T_{c1} = 342 \text{ K} \), \( T_0 = 680 \text{ K} \) and \( T_{a,1} = 800 \text{ K} \). The solid lines when \( T_{a,2} = 0 \text{ K} \) and the dashed lines when \( T_{a,2} = 1000 \text{ K} \).
3. Diabatic Reactor

Fig. 3.8: The limit point unfolding diagram in the characteristic temperature and coolant temperature plane. The parameter values are $E_2 = 60 \text{ kJ mol}^{-1}$, $Q_2 = 100 \text{ kJ mol}^{-1}$, $Q_1 = 100 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$, $T_0 = 680 \text{ K}$ and $T_{a,1} = 800 \text{ K}$. The legends a-f related to the steady-state diagrams shown in figure 3.7b. All other parameters are given in Appendix.1.
Fig. 3.9: The steady-state structure in the diabatic reactor following region (cc). The parameter values are $E_1 = 80 \text{ kJ mol}^{-1}$, $Q_1 = 100 \text{ kJ mol}^{-1}$, $T_{c1} = 342 \text{ K}$, $T_{c2} = 453 \text{ K}$, $T_0 = 680 \text{ K}$, $T_{a,1} = 800 \text{ K}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$.
Fig. 3.10: The region in parameter space in which the transitions occur when $T_{a,2} = 0$ K. The parameter values are $E_1 = 80$ kJ mol$^{-1}$, $Q_1 = 100$ kJ mol$^{-1}$, $T_{c1} = 342$ K, $T_0 = 680$ K, $T_{a,1} = 800$ K and $Q_2 = 50(a), 100(b)$ and 200(c) kJ mol$^{-1}$. 
3.4 Applications of Singularity Theory

In this section we show how to determine the important features of particular interest on the steady-state diagrams using the singularity theory.

At steady-state we find by rearranging equation (3.32) that

$$B_2^* = \frac{1 - A_1^*}{1 + a_2^* \tau_2^* \exp \left[ \frac{-1}{\theta_2} \right]}.$$ 

Substituting this value into equation (3.33) we obtain the singularity function for the temperature in the second reactor:

$$G(\theta_2) = \frac{\theta_1 - \theta_2}{\tau_2^*} + a_2^* Q_2^* \exp \left[ \frac{-1}{\theta_2} \right] \left[ \frac{1 - A_1^*}{1 + a_2^* \tau_2^* \exp \left[ \frac{-1}{\theta_2} \right]} \right] - J_2(\theta_2 - \theta_{a,2}).$$

With some mathematical manipulation, the latter equation can be written as

$$G_1(\theta_2) = a_2^* \exp \left[ \frac{-1}{\theta_2} \right] \left[ \theta_1 - (1 + J_2 \tau_2^*) \theta_2 + J_2 \tau_2^* \theta_{a,2} + Q_2^*(1 - A_1^*) \right] + \theta_1 - (1 + J_2 \tau_2^*) \theta_2 + J_2 \tau_2^* \theta_{a,2}.$$  

(3.41)

The feed temperature \( \theta_0 \) does not appear explicitly in equation (3.41), but it appears implicitly as it determines the values \( A_1^* \) and \( \theta_1 \). The value for \( A_1^* \) is given by

$$A_1^* = \frac{1}{1 + a_1^* \exp \left[ \frac{-E_1^*}{\theta_1^*} \right] \tau_1^*},$$

and \( \theta_1 \) solves the equation

$$\frac{\theta_0 - \theta_1}{\tau_1^*} - \frac{a_1^* \exp \left[ \frac{-E_1^*}{\theta_1^*} \right]}{1 + a_1^* \exp \left[ \frac{-E_1^*}{\theta_1^*} \right] \tau_1^*} = 0.$$ 

In this analysis we view the steady-state solutions in the first reactor (\( \theta_1 \) and \( A_1^* \)) as free-parameters.
3.4.1 Limit Point

The defining and non-degeneracy conditions for limit points [2, chapter 2] are

\[ G = G_{\theta_2} = 0, \quad (3.42) \]
\[ G_{\theta_2 \theta_2} \neq 0, G_{\lambda} \neq 0, \quad (3.43) \]

where \( \lambda \) is the selected bifurcation parameter, one of \((\theta_{a,2}, T_{c,2}, \theta_0)\), and the subscripts denote the \( n \)th-order partial derivatives. Differentiating equation (3.41) with respect to \( \theta_2 \) we obtain

\[ G_{\theta_2} = -(1 + J_{2 \tau_2^*})\theta_2^2 + a_{2}^*\tau_2^* \exp \left[ \frac{-1}{\theta_2} \right] \left( \theta_1 - (1 + J_{2 \tau_2^*})(1 + \theta_2)\theta_2 + J_{2 \tau_2^*}\theta_{a,2} + Q_{2}^*(1 - A_1^*) \right). \quad (3.44) \]

Substituting

\[ \tau_2^*a_{2}^* \exp \left[ \frac{-1}{\theta_2} \right] = \frac{\theta_1 - (1 + J_{2 \tau_2^*})\theta_2 + J_{2 \tau_2^*}\theta_{a,2}}{1 - (1 + J_{2 \tau_2^*})\theta_2 + J_{2 \tau_2^*}\theta_{a,2} + Q_{2}^*(1 - A_1^*)}, \]

in equation (3.44) we obtain equation (3.45).

After some manipulation we derive the limit points from the conditions (3.42):

\[ D_3(1 + D_1)\theta_2^2 - D_3[2(D_2 + \theta_1) + D_1]\theta_2 + \theta_1(D_1 + \theta_1) + D_2(D_1 + D_2 + 2) = 0, \quad (3.45) \]

where

\[ D_1 = Q_{2}^*(1 - A_1^*), \quad (3.46) \]
\[ D_2 = J_{2 \tau_2^*}\theta_{a,2}, \]
\[ D_3 = 1 + J_{2 \tau_2^*}, \]

Thus the temperature at which limit point(s) occur is given by

\[ \theta_{2\pm} = \frac{D_3[2(D_2 + \theta_1) + D_1] \pm \sqrt{D_4}}{2D_3(1 + D_1)}, \quad (3.47) \]
where $D_4 = D_3^2[2(D_2 + \theta_1) + D_1]^2 - 4D_3(1 + D_1)[\theta_1(D_1 + \theta_1) + D_2(D_1 + D_2 + 2)]$.

Note that all $D_i > 0$, thus

$$\theta_{2+} > \theta_{2-}$$

where $\theta_{2+}$ is the extinction limit point and $\theta_{2-}$ is the ignition limit point. This equation has no solutions when

$$D_4 < 0,$$ (3.48)

where $D_4 = D_3^2[2(D_2 + \theta_1) + D_1]^2 - 4D_3(1 + D_1)[\theta_1(D_1 + \theta_1) + D_2(D_1 + D_2 + 2)]$.

The region in parameter space for different values of the activation energy $E_2$ and the heat of exothermicity $Q_2$ in which limit points are found underneath the limit points curve.

### 3.5 Conclusion

In this chapter we considered a cascade model consisting of two sequential reactions; the first reaction is endothermic whilst the second reaction is exothermic. It is assumed that the reaction takes place in a reactor cascade in which catalysts for the first and second reactions are placed in the first and second reactors, respectively. As there is no recycling, the steady-state behaviour in the first reactor is independent of that in the second reactor.

In the previous chapter we considered adiabatic operation. In this chapter we considered diabatic operation. We first examined the operating conditions required in the first reactor to obtain a minimum of 90% conversion. Realistic feed temperatures, i.e. a feed temperature lower than 1000 K, require a high activation energy, a high coolant temperature and a low characteristic temperature in the first reactor. To achieve high conversion weakly endothermic reaction is more preferable. The required value of the feed temperature is a decreasing function of both the coolant temperature and the heat transfer parameter.

We then fixed the catalyst in the first reactor and examined how the choice of the catalyst and coolant temperature in the second reactor affected the product concentration.
leaving the reactor. We found that there are seven characteristic steady-state diagrams for the chosen parameters. The best possible catalysts, which produce autothermal behavior, have the ignition limit point occurring at an unphysical value (negative!) of the coolant temperature. We carried out time consuming calculations to investigate how the steady-state diagram changes as the value of the characteristic temperature in the second reactor is varied. We then showed the importance of constructing the limit point unfolding diagram to find all the transitions between the steady-state diagrams. We also used insights from this calculation to find the desired autothermal region and the conditions required to achieve the desired behaviour. Using this calculation we found that the characteristic temperature in the second reactor must be lower than the maximum value between the transition (a) and (b) in Figure 3.10.
4. FOUR REACTORS SYSTEM

Among new reactor concepts proposed in recent years, new lines of research have been continued in relation to improving safety, sustainability, efficiency and cost.

At the NSW ANZIAM conference (6-9/12/2015) I was asked whether it would be better to have a cascade of four reactors rather than a cascade of two reactors. From this point, interesting questions arise: What are the advantages of constructing a four reactor system? What will happen to the steady-state diagrams when we have a four reactor series? In order to answer these questions, we compare in this chapter the conversion in such a system to the conversion in a cascade of two reactors.

4.1 Model chemistry and reactor configuration

The reaction is assumed to take place in a cascade of four reactors. The catalyst for the first reaction is placed in reactors one and three whilst the catalyst for second reaction is placed in reactors two and four. Consequently the first (second) reaction only occurs in the first (second) and third (fourth) reactors.

Figure 4.1 shows the processes that occur in the reactor cascade. The concentrations of the reactant $A$ and the intermediate $B$ leaving reactor one are $A_1$ and $B_1$ respectively. The concentrations of the reactant $A$, the intermediate $B$ and the concentration $C$ leaving reactor $i$ are $A_i$, $B_i$ and $C_i$ ($i = 2, 3, 4$) respectively. The coolant temperatures for the four reactors are $T_{a,i}$ ($i = 1, 2, 3, 4$). The temperatures of the reacting mixture in each reactor are $T_i$ ($i = 1, 2, 3, 4$).

We are particularly interested in identifying the choice of catalysts and reactor operation conditions that ensure a minimum of 90% conversion of reactant $A$ to product $C$. It is assumed that the reactor vessels are well stirred. We consider a feed temperature to be realistic if $T_0 \leq 1000$K.
4. Four Reactors System

4.1 Prototype reactor configuration. \( A_0 \) is the feed concentration, \( T_0 \) is the feed temperature and \( q \) is the flow rate.

4.2 Model equations

In section 4.2.1 we give the model equations. In section 4.2.2 we non-dimensionalise the model.

4.2.1 Dimensional equations

The system of equations in the first reactor is given by equations (4.1)–(4.7):

The rate of change of the concentration of the reactant \( A \)

\[
V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp \left( -\frac{E_1}{RT_1} \right) A_1. 
\]  
(4.1)

The rate of change of the concentration of the intermediate \( B \)

\[
V_1 \frac{dB_1}{dt} = q(B_0 - B_1) + V_1 a_1 \exp \left( -\frac{E_1}{RT_1} \right) A_1. 
\]  
(4.2)

The rate of change of the concentration of the product \( C \)

\[
V_1 \frac{dC_1}{dt} = q(C_0 - C_1). 
\]  
(4.3)
The rate of change of the temperature inside the reactor

\[ c_{pg} \rho_g V_1 \frac{dT_1}{dt} = q c_{pg} \rho_g (T_0 - T_1) - Q_1 V_1 a_1 \exp \left[ -\frac{E_1}{RT_1} \right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{a,1}). \] (4.4)

The definition of the pre-exponential factor \( a_1 \) in terms of the characteristic temperature \( T_{c1} \) (see chapter 1.5.1)

\[ a_1 = \frac{E_1 \alpha}{RT_{c1}^2} \exp \left[ \frac{E_1}{RT_{c1}} \right]. \] (4.5)

The initial conditions are given by equation (4.6). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

\[ A_1(0) = B_1(0) = C_1(0) = 0, \quad T_1(0) = \frac{q c_{pg} \rho_g T_0 + J_1 \chi_1 S_1 T_{a,1}}{q c_{pg} \rho_g + J_1 \chi_1 S_1}. \] (4.6)

The residence time is

\[ \tau_1 = \frac{V_1}{q}. \] (4.7)

Note that there is no reaction term in equation (4.3) because there is no catalyst for the second reaction in the first reactor.

The system of equations in the second reactor is given by equations (4.8)–(4.14):

The rate of change of the concentration of reactant \( A \)

\[ V_2 \frac{dA_2}{dt} = q(A_1 - A_2). \] (4.8)

The rate of change of the concentration of reactant \( B \)

\[ V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2 a_2 \exp \left[ -\frac{E_2}{RT_2} \right] B_2. \] (4.9)
The rate of change of the concentration of reactant $C$

$$V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2 a_2 \exp \left[ -\frac{E_2}{RT_2} \right] B_2. \quad (4.10)$$

The rate of change of the temperature inside the reactor

$$c_{pg} \rho_g V_2 \frac{dT_2}{dt} = q c_{pg} \rho_g (T_1 - T_2) + Q_2 V_2 a_2 \exp \left[ -\frac{E_2}{RT_2} \right] B_2 - J_2 \chi_2 S_2 (T_2 - T_{a,2}). \quad (4.11)$$

The definition of the pre-exponential factor $a_2$ in terms of the characteristic temperature $T_{c,2}$ (see chapter 1.5.1)

$$a_2 = \frac{E_2 \alpha}{RT_{c,2}^2} \exp \left[ \frac{E_2}{RT_{c,2}} \right]. \quad (4.12)$$

The initial conditions are given by equation $(4.13)$. Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

$$A_2(0) = B_2(0) = C_2(0) = 0, \quad T_2(0) = \frac{q c_{pg} \rho_g T_1 + J_2 \chi_2 S_2 T_{a,2}}{q c_{pg} \rho_g + J_2 \chi_2 S_2}. \quad (4.13)$$

The residence time is

$$\tau_2 = \frac{V_2}{q}. \quad (4.14)$$

Note that the concentrations flowing into reactor two are the concentrations exiting from reactor one. Similarly the temperature of the fluid entering reactor two is equal to that from reactor one. There is no reaction term in equation $(4.8)$ because there is no catalyst for the first reaction in the second reactor.

The system of equations in the third reactor is given by equations $(4.15)$–$(4.20)$:
The rate of change of the concentration of the reactant \( A \)

\[
V_3 \frac{dA_3}{dt} = q(A_2 - A_3) - V_3 a_1 \exp \left[ \frac{-E_1}{RT_3} \right] A_3. \tag{4.15}
\]

The rate of change of the concentration of the intermediate \( B \)

\[
V_3 \frac{dB_3}{dt} = q(B_2 - B_3) + V_3 a_1 \exp \left[ \frac{-E_1}{RT_3} \right] A_3. \tag{4.16}
\]

The rate of change of the concentration of the product \( C \)

\[
V_3 \frac{dC_3}{dt} = q(C_2 - C_3). \tag{4.17}
\]

The rate of change of the temperature inside the reactor

\[
c_{pg}\rho_g V_3 \frac{dT_3}{dt} = q c_{pg}\rho_g (T_2 - T_3) - Q_1 V_3 a_1 \exp \left[ \frac{-E_1}{RT_3} \right] A_3 - J_3 \chi_3 S_3 (T_3 - T_{a,3}). \tag{4.18}
\]

The initial conditions are given by equation (4.19). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

\[
A_3(0) = B_3(0) = C_3(0) = 0, \quad T_3(0) = \frac{q c_{pg}\rho_g T_2 + J_3 \chi_3 S_3 T_{a,3}}{q c_{pg}\rho_g + J_3 \chi_3 S_3}. \tag{4.19}
\]

The residence time is

\[
\tau_3 = \frac{V_3}{q}. \tag{4.20}
\]

Note that the concentrations flowing into reactor three are the concentrations exiting from reactor two. Similarly the temperature of the fluid entering reactor three is equal to that from reactor two. As in the first reactor there is no reaction happening in equation (4.17) because there is no catalyst for the second reaction in the third reactor.
The system of equations in the fourth reactor is given by equations (4.21)–(4.26):

The rate of change of the concentration of reactant \( A \)

\[
V_4 \frac{dA_4}{dt} = q(A_3 - A_4). \tag{4.21}
\]

The rate of change of the concentration of reactant \( B \)

\[
V_4 \frac{dB_4}{dt} = q(B_3 - B_4) - V_4 a_2 \exp \left[ \frac{-E_2}{RT_4} \right] B_4. \tag{4.22}
\]

The rate of change of the concentration of reactant \( C \)

\[
V_4 \frac{dC_4}{dt} = q(C_3 - C_4) + V_4 a_2 \exp \left[ \frac{-E_2}{RT_4} \right] B_4. \tag{4.23}
\]

The rate of change of the temperature inside the reactor

\[
c_{pg}\rho_g V_4 \frac{dT_4}{dt} = q c_{pg}\rho_g(T_3 - T_4) + Q_2 V_4 a_2 \exp \left[ \frac{-E_2}{RT_4} \right] B_4 - J_4 \chi_4 S_4(T_4 - T_{a,4}). \tag{4.24}
\]

The initial conditions are given by equation (4.25). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

\[
A_4(0) = B_4(0) = C_4(0) = 0, \quad T_4(0) = \frac{q c_{pg}\rho_g T_3 + J_4 \chi_4 S_4 T_{a,4}}{q c_{pg} \rho_g + J_4 \chi_4 S_4}. \tag{4.25}
\]

The residence time is

\[
\tau_4 = \frac{V_4}{q}. \tag{4.26}
\]

Note that the concentrations flowing into reactor four are the concentrations exiting from reactor three. Similarly the temperature of the fluid entering reactor four is equal to
that from reactor three. Similarly to the second reactor there is no reaction term in
equation (4.21) because there is no catalyst for the third reaction in the fourth reactor.

The terms appearing in equations (4.1)–(4.26) are defined in Appendix.1.

The heat transfer coefficients in equations (4.4), (4.11), (4.18) and (4.24) have been
written as the product \( J_i \chi_i \) rather than the usual form of \( (\chi_i) \), where \( i = 1, 2, 3, 4 \).
We have done this so that we can nondimensionalise time using a Newtonian-cooling
time-scale.

4.2.2 Dimensionless equations

In nondimensionalising equations (4.1)-(4.26) we introduce dimensionless concentrations
\( A_1^*, B_1^* and C_1^* \), dimensionless temperatures \( \theta_i \), where \( i = 1, 2, 3, 4 \), and dimensionless time
\( t^* \). These are defined in Appendix.1.

The system of non-dimensional equations in the first reactor is:

\[
\frac{dA_1^*}{dt^*} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^*, \quad (4.27)
\]

\[
\frac{dB_1^*}{dt^*} = \frac{B_0^* - B_1^*}{\tau_1^*} + a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^*, \quad (4.28)
\]

\[
\frac{dC_1^*}{dt^*} = \frac{C_0^* - C_1^*}{\tau_1^*}, \quad (4.29)
\]

\[
\frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[ -\frac{E_1^*}{\theta_1} \right] A_1^* - J_1 \chi_1 \theta_a, \quad (4.30)
\]

\[
a_1^* = \frac{\alpha^* V^* E_1^*}{T_c^*} \exp \left[ \frac{E_1^*}{T_c^*} \right]. \quad (4.31)
\]

Dimensionless initial conditions are:

\[
A_1^*(0) = B_1^*(0) = C_1^*(0) = 0, \quad \theta_1(0) = \frac{\theta_0 + J_1 \chi T \theta_a}{1 + J_1 \chi T \theta_a}. \quad (4.32)
\]
The system of non-dimensional equations in the second reactor is:

\[
\begin{align*}
\frac{dA_2^*}{dt^*} &= \frac{A_1^* - A_2^*}{\tau_2^*}, \\
\frac{dB_2^*}{dt^*} &= \frac{B_1^* - B_2^*}{\tau_2^*} - a_2^* \exp \left[ -\frac{1}{\theta_2} \right] B_2^*, \\
\frac{dC_2^*}{dt^*} &= \frac{C_1^* - C_2^*}{\tau_2^*} + a_2^* \exp \left[ -\frac{1}{\theta_2} \right] B_2^*, \\
\frac{d\theta_2}{dt^*} &= \frac{\theta_1 - \theta_2}{\tau_2^*} + Q_2^* a_2^* \exp \left[ -\frac{1}{\theta_2} \right] B_2^* - J_2 (\theta_2 - \theta_{a,2}). \\
a_2^* &= \frac{\alpha^*}{T_{c1}^*} \exp \left[ \frac{1}{T_{c1}^*} \right].
\end{align*}
\]

Dimensionless initial conditions are:

\[
A_2^*(0) = B_2^*(0) = C_2^*(0) = 0, \quad \theta_2(0) = \frac{\theta_1 + J_2 \tau_2^* \theta_{a,2}}{1 + J_2 \tau_2^*}. \tag{4.38}
\]

The system of non-dimensional equations in the third reactor is:

\[
\begin{align*}
\frac{dA_3^*}{dt^*} &= \frac{A_2^* - A_3^*}{\tau_3^*} - a_1^* \exp \left[ -\frac{E_1^*}{\theta_3} \right] A_3^*, \\
\frac{dB_3^*}{dt^*} &= \frac{B_2^* - B_3^*}{\tau_3^*} + a_1^* \exp \left[ -\frac{E_1^*}{\theta_3} \right] A_3^*, \\
\frac{dC_3^*}{dt^*} &= \frac{C_2^* - C_3^*}{\tau_3^*}, \\
\frac{d\theta_3}{dt^*} &= \frac{\theta_2 - \theta_3}{\tau_3^*} - Q_1^* a_1^* \exp \left[ -\frac{E_1^*}{\theta_3} \right] A_3^* - J_3 \chi_{T,3}^* (\theta_3 - \theta_{a,3}).
\end{align*}
\]

Dimensionless initial conditions are:

\[
A_3^*(0) = B_3^*(0) = C_3^*(0) = 0, \quad \theta_3(0) = \frac{\theta_2 + J_3 \chi_{T,3} \tau_3^* \theta_{a,1}}{1 + J_3 \chi_{T,3} \tau_3^*}. \tag{4.43}
\]
The system of non-dimensional equations in the fourth reactor is:

\[
\begin{align*}
\frac{dA^*_4}{dt^*} &= \frac{A^*_3 - A^*_4}{\tau^*_4}, \\
\frac{dB^*_4}{dt^*} &= \frac{B^*_3 - B^*_4}{\tau^*_4} - a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4, \\
\frac{dC^*_4}{dt^*} &= \frac{C^*_3 - C^*_4}{\tau^*_4} + a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4, \\
\frac{d\theta^*_4}{dt^*} &= \frac{\theta^*_3 - \theta^*_4}{\tau^*_4} + Q^*_2 a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4 - J^*_4 \chi^*_T \frac{\theta^*_4}{\tau^*_4} \left( \theta^*_4 - \theta^*_a,4 \right). 
\end{align*}
\] (4.44) 

\begin{align*}
\frac{dA^*_4}{dt^*} &= \frac{A^*_3 - A^*_4}{\tau^*_4}, \\
\frac{dB^*_4}{dt^*} &= \frac{B^*_3 - B^*_4}{\tau^*_4} - a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4, \\
\frac{dC^*_4}{dt^*} &= \frac{C^*_3 - C^*_4}{\tau^*_4} + a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4, \\
\frac{d\theta^*_4}{dt^*} &= \frac{\theta^*_3 - \theta^*_4}{\tau^*_4} + Q^*_2 a^*_2 \exp \left[ \frac{-1}{\theta^*_4} \right] B^*_4 - J^*_4 \chi^*_T \frac{\theta^*_4}{\tau^*_4} \left( \theta^*_4 - \theta^*_a,4 \right). 
\end{align*}
(4.45) 

Dimensionless initial conditions are:

\[
A^*_4(0) = B^*_4(0) = C^*_4(0) = 0, \quad \theta^*_4(0) = \frac{\theta^*_3 + J^*_4 \chi^*_T \tau^*_4 \theta^*_a,4}{1 + J^*_4 \chi^*_T \tau^*_4}. 
\] (4.48)

It is worth noting that in studying the system (4.27)-(4.47) we are interested in the long-time behaviour.

Normally for the four reactor model, we take the residence time in each of the first, second, third and fourth reactors to be equal, i.e. \( \tau_1 = \tau_2 = \tau_3 = \tau_4 \). Consequently, the total residence time for this system is \( \tau_r = 4\tau_1 \). This means that \( \tau_i = \frac{\tau_r}{4} \), where \( i = 1, 2, 3, 4 \). Similarly for the two reactor model the total residence time for this system is \( \tau_r = 2\tau_1 \). This means that \( \tau_1 = \frac{\tau_r}{2} \) and \( \tau_2 = \frac{\tau_r}{2} \).

We compare the product conversion in the four reactor configuration \( (C^*_4) \) to the product conversion in the two reactor system \( (C^*_2) \). In making this comparison we fix the total residence time \( (\tau_r) \) in the four reactor cascade to be equal to the total residence time in the two reactor cascade.

### 4.3 Results and discussion

All calculations performed in this thesis use the industrial parameter values stated in Appendix.1, unless otherwise stated. The first reaction occurs in the first and third reactors, and the second reaction occurs in the second and fourth reactors. Thus, the same catalyst is used in the first and third reactors and the same catalyst is used in the second and fourth reactors.

In Chapter 2 and Chapter 3, in order to achieve 90% conversion of the reactant \( A \) into
the product $C$ in the **two reactor cascade** we must achieve at least 90% conversion of the reactant $A$ into the intermediate $B$ in the **first** reactor. However, this is not true for the **four reactor cascade**. In the four reactor cascade, the reactant $A$ is converted into the intermediate $B$ in both the **first and third** reactors. Thus the overall conversion of the reactor cascade can be 90% even though the conversion in the first reactor is less than 90%.

We carry out two investigations. In the first case we fix the the catalyst in the first reactor for both the two and four reactor cascades to ensure 90% conversion of the reactant $A^\ast_1$. We investigate how the choice of the catalyst in the second reactor affects the steady-state concentrations in both systems $C^\ast_2$ and $C^\ast_4$ and analyze which configuration is preferable. In the second case we investigate how the feed temperature $T_0$ influences the conversion in both reactor systems. In this case the conversion of the reactant $A$ in the first reactor is a function of the feed temperature $T_0$.

### 4.3.1 Scenario one: fixed feed temperature

We fix the inflow temperature $T_0 = 680$ K and the coolant temperature in the first, third and fourth reactors $T_{a,1} = T_{a,3} = T_{a,4} = 800$ K and investigate how the conversion in both configurations varies as one of two parameters is changed: the activation energy for the exothermic reaction $E_2$ or the coolant temperature of the second reactor $T_{a,2}$. Tables 4.1 and 4.2 show the values for the product concentration in the two reactor cascade $C^\ast_2$ and the product concentration in the four reactor cascade $C^\ast_4$ respectively, as a function of the rate parameters $E_2$ and $T_{a,2}$.

The first thing to note in Table 4.1 is that we have a conversion greater than 90% of the reactant $A$ in reactor one $A^\ast_1 = 0.066$. Note for all the values of the activation energy $E_2$ the product concentration $C^\ast_2$ increases by either a small amount, when $E_2 = 50$ and 80 kJ mol$^{-1}$, or by negligible amount when $E_2 = 120$ kJ mol$^{-1}$ as the coolant temperature $T_{a,2}$ increases. In practice it is satisfactory to set the coolant temperature to $T_{a,2} = 400$ K. Table 4.1 shows that the conversion in the two reactor cascade $C^\ast_2$ is good for all sets of parameter values. However, when the activation energy in the second reactor is at its lowest value; $E_2 = 50$ kJ mol$^{-1}$, the product conversion $C^\ast_2$ is always less than 90%. When the activation energy in the second reactor is higher; $E_2 = 80$ or 120 kJ mol$^{-1}$, the
product conversion is more than 90% for any value of the coolant temperature $T_{a,2}$.

In Table 4.2 we present the data from the four reactor cascade. We first note that the conversion of the reactant $A$ in the first reactor is almost 90% ($A_1^* = 0.105$). Note that as the total residence time is fixed, the total residence time in the first reactor of the two reactor cascade is higher than that in the first reactor of the four reactor cascade.

We also note for all the values of the activation energy $E_2$ the product concentration $C_4^*$ increases as the coolant temperature $T_{a,2}$ increases (although only a small amount when the activation energy $E_2 = 80$ and 120 kJ mol$^{-1}$). The product conversion in the four reactor cascade $C_4^*$ is a mixture of “good” and “bad”. When the activation energy in the second reactor is at its lowest value, $E_2 = 50$ (kJ mol$^{-1}$), and the coolant temperature is comparatively small, $T_{a,2} = 400, 600$ and 800 K, the product conversion $C_4^*$ is feeble, while it is around 77% when the coolant temperature is $T_{a,2} = 1000$ K. However, for higher values of the activation energy, $E_2 = 80$ and 120 (kJ mol$^{-1}$), the product conversion is significantly higher than 90% for any value of the coolant temperature $T_{a,2}$. This is a strong contrast to the behaviour exhibited in Table 4.1 for the two reactor cascade. For the two highest values of the activation energy $E_2$ high product conversion is predictable. The concentration of the reactant $A$ leaving the third reactor is $10^{-6}$. This means that there has been almost complete conversion of the reactant $A$ into the intermediate $B$. Therefore, we predict that we will obtain a high conversion. The concentration of the reactant $A$ entering the third reactor is reduced to 0.1.

Comparing Tables 4.1 and 4.2 we find that for the two highest values of the activation energy $E_2$ the four reactor cascade is superior to the two reactor cascade. We obtain almost full conversion of the product in the four reactor cascade, whereas it is just slightly higher than 90% in the two reactor cascade. However, the conversion in the two reactor system is significantly superior to the four reactor system at the lowest value of the activation energy $E_2 = 50$ kJ mol$^{-1}$.

An obvious question arises “why is the two reactor cascade is significantly superior for a low activation energy catalyst and why is the four reactor cascade superior for a high activation energy catalyst?” We investigate this question in subsequent sections.
4. Four Reactors System

Tab. 4.1: The product conversion $C_2^*$ in a two reactor cascade as a function of the activation energy $E_2$ kJ mol$^{-1}$ and the coolant temperature in the second reactor $T_{a,2}$ K. Parameter values $Q_2 = 100$ kJ mol$^{-1}$, $T_{c,2} = 435$ K, $T_{a,1} = 800$ K, $T_0 = 680$ K and the total residence time $\tau_r = 16$ s.

<table>
<thead>
<tr>
<th>$T_{a,2}$</th>
<th>$A_1^*$</th>
<th>$C_2^*$ ($E_2 = 50$)</th>
<th>$C_2^*$ ($E_2 = 80$)</th>
<th>$C_2^*$ ($E_2 = 120$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.066</td>
<td>0.841</td>
<td>0.9315</td>
<td>0.9336</td>
</tr>
<tr>
<td>600</td>
<td>0.066</td>
<td>0.855</td>
<td>0.9318</td>
<td>0.9336</td>
</tr>
<tr>
<td>800</td>
<td>0.066</td>
<td>0.865</td>
<td>0.9321</td>
<td>0.9336</td>
</tr>
<tr>
<td>1000</td>
<td>0.066</td>
<td>0.874</td>
<td>0.9324</td>
<td>0.9336</td>
</tr>
</tbody>
</table>

Tab. 4.2: The product conversion $C_4^*$ in a four reactor cascade as a function of the activation energy $E_2$ kJ mol$^{-1}$ and the coolant temperature in the second reactor $T_{a,2}$ K. Parameter values $Q_2 = 100$ kJ mol$^{-1}$, $T_{c,2} = 435$ K, $T_{a,1} = T_{a,3} = T_{a,4} = 800$ K, $T_0 = 680$ K and the total residence time $\tau_r = 16$ s.

<table>
<thead>
<tr>
<th>$T_{a,2}$</th>
<th>$A_1^*$</th>
<th>$E_2 = 50$</th>
<th>$E_2 = 80$</th>
<th>$E_2 = 120$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A_3^*$</td>
<td>$C_3^*$</td>
<td>$C_4^*$</td>
</tr>
<tr>
<td>400</td>
<td>0.105</td>
<td>0.021</td>
<td>0.027</td>
<td>0.2 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>600</td>
<td>0.105</td>
<td>0.017</td>
<td>0.032</td>
<td>0.2 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>800</td>
<td>0.105</td>
<td>0.014</td>
<td>0.038</td>
<td>0.2 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>1000</td>
<td>0.105</td>
<td>0.8 $\times$ 10$^{-5}$</td>
<td>0.776</td>
<td>0.1 $\times$ 10$^{-5}$</td>
</tr>
</tbody>
</table>

4.3.1.1 The conversion when $E_2 = 50$ kJ mol$^{-1}$

Figures 4.2a-4.2b show the steady-state diagram for the two reactor cascade and four reactor cascade respectively as a function of the total residence time $\tau_r$ when the activation energy is $E_2 = 50$ kJ mol$^{-1}$. These figures shed light on the behaviour at our reference residence time of 16 s. The red branches in the S-shape diagram are stable and the black branch is unstable. The high branch is called the high conversion branch and the low branch is called the low conversion branch. The middle branch is called the intermediate branch.

In Figure 4.2a the extinction and the ignition limit point bifurcations occur at a residence time of 8.508 s and 15.346 s respectively. These values are lower than our total residence time $\tau_r$, which is 16 s. The practical consequence of this is that the system must evolve to the high conversion branch when the total residence time is $\tau_r = 16$ s. However, in Figure 4.2b the extinction and the ignition limit point bifurcations occur at residence times of 17.016 s and 30.69 s respectively. These values are higher than the experimental value of total residence time $\tau_r = 16$ s. Consequently, when the total residence time is $\tau_r = 16$ s the latter system must operate on the low conversion branch.
It is now obvious why the conversion in the two reactor cascade is superior to that in the four reactor cascade at the lowest value of the activation energy $E_2 = 50 \text{ kJ mol}^{-1}$.

We can say that if the total residence time at the ignition limit point for the two reactor cascade is less than 16 s and the total residence time at the extinction limit point for the four reactor cascade more than 16 s, then the product conversion in the two reactor cascade is greater than the product conversion in the four reactor cascade.

![Graph](image)

*Fig. 4.2:* The steady-state conversion of the product concentration $C$ in both 2-reactor and 4-reactor systems as a function of the total residence time $\tau$. The vertical lines are the total residence time $\tau = 16$ s. Parameter values $E_2 = 50 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, T_{c,2} = 435 \text{ K}, T_0 = 680 \text{ K}$ and $T_{a,2} = 800 \text{ K}$.

More investigations have been carried out to clarify the total residence time $\tau$ needed to obtain 90% conversion for the parameter values used in Figures 4.2a-4.2b. Table 4.3 shows the required total residence time to obtain the desired conversion in the two reactor cascade and the four reactor cascade respectively, as a function of the coolant temperature in the second reactor $T_{a,2}$ when the activation energy is $E_2 = 50 \text{ kJ mol}^{-1}$. In Table 4.3 we first note that the required total residence time $\tau$ decreases as the coolant temperature $T_{a,2}$ increases. Furthermore, the total residence time in a four reactor cascade to obtain the desired conversion is slightly less than the total residence time in a two reactor cascade. We conclude that for the smallest value of the activation energy $E_2 = 50 \text{ kJ mol}^{-1}$, if the total residence time is fixed to our reference value $\tau = 16$ s, then the two reactor cascade is significantly superior to the four reactor cascade. However, the required total residence
time to achieve 90% conversion in the two reactor cascade is greater than in the four reactor cascade. Thus at higher values for the total residence time the performance of the four reactor cascade will be superior to that of the two reactor cascade.

Tab. 4.3: The required total residence time \( \tau \) in order to obtain 90% conversion in a two reactor cascade for different values of the coolant temperature in the second reactor \( T_{a,2} \). Parameter values \( E_2 = 50 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, T_{c,2} = 435 \text{ K} \) and \( T_0 = 680 \text{ K} \). In the two reactors cascade the coolant temperature for the first reactor is \( T_{a,1} = 800 \text{ K} \). In the four reactors cascade the coolant temperature for the first, third and four reactors are \( T_{a,1} = T_{a,3} = T_{a,4} = 800 \text{ K} \).

<table>
<thead>
<tr>
<th>( T_{a,2} )</th>
<th>( \tau ) (two reactors)</th>
<th>( \tau ) (four reactors)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>24.54664176</td>
<td>23.58158242</td>
</tr>
<tr>
<td>400</td>
<td>23.38850975</td>
<td>22.56615618</td>
</tr>
<tr>
<td>600</td>
<td>21.62528940</td>
<td>20.92098168</td>
</tr>
<tr>
<td>800</td>
<td>20.29197337</td>
<td>19.5994332</td>
</tr>
<tr>
<td>1000</td>
<td>19.54072307</td>
<td>18.5031916</td>
</tr>
</tbody>
</table>

4.3.1.2 The conversion when \( E_2 = 80 \text{ kJ mol}^{-1} \)

Figures 4.3a-4.3b show the steady-state diagram for the two reactor cascade and the four reactor cascade respectively as a function of the total residence time \( \tau \) when the activation energy is \( E_2 = 80 \text{ kJ mol}^{-1} \). In Figure 4.3a the extinction and the ignition limit point bifurcations occur at 0.473 s and 9.588 s respectively, which are lower than the total residence time \( \tau = 16 \text{ s} \). Consequently, at a total residence time of 16 s the system evolves to the high conversion branch. In Figure 4.3b the extinction and the ignition limit point bifurcations occur at 0.946 s and 19.176 s. As the extinction limit point is less than 16 s and the ignition limit point is greater than 16 s it is possible to operate on either the low conversion branch or the high conversion branch depending on how the reactor is started up.

An important feature of these figures is that in Figure 4.3a the typical experimental value of the total residence time is greater than the total residence time at the ignition limit point. However, in Figure 4.3b it is smaller than the total residence time at the ignition limit point.

Figure 4.4 shows the combination of the steady-state diagram shown in Figures 4.3a (the red line) and 4.3b (the blue line). This figure confirms that the product conversion in the four reactor cascade \( C_4^* \) is higher than the conversion in the two reactor cascade.
4. Four Reactors System

4.3. The conversion when $E_2 = 120 \text{ kJ mol}^{-1}$

Figures 4.5a-4.5b show the steady-state diagram for the two reactor cascade and four reactor cascade respectively as a function of the total residence time $\tau_r$ when $E_2 = 120 \text{ kJ mol}^{-1}$. In both Figures 4.5a-4.5b the extinction and the ignition limit point bifurcations occur at 0.0059 s and 7.549 s, and 0.0118 s and 15.098 s for the two reactor and
The combination of Figures 4.3a and Figure 4.3b. The product concentration in the two reactor cascade $C_2$ (red branch) and the product concentration in the four reactor cascade $C_4$ (blue branch).

Fig. 4.4: The combination of Figures 4.3a and Figure 4.3b. The product concentration in the two reactor cascade $C_2$ (red branch) and the product concentration in the four reactor cascade $C_4$ (blue branch).

four reactor cascades respectively. All these values are lower than the total residence time 16 s. The practical consequence of this is that both systems always evolve to the high conversion branch when the total residence time is 16 s.

Figure 4.6 shows the combination of the steady-state diagram shown in Figures 4.5a-4.5b. This figure shows that the range of the total residence time that ensures the system is operating on the high conversion branch in the two reactor cascade is wider than in the four reactor cascade. However, for our choice of the initial conditions the four reactor cascade always operates on the high conversion branch for any value of the total residence time greater than that of the extinction limit point.

This figure confirms that the product conversion in the four reactor cascade ($C^*_4$) is higher than the conversion in the two reactor cascade $C^*_2$ when both systems operate at our experimental total residence time $\tau_r = 16$ s. Also, this figure shows that the range
between the ignition limit point and our experimental total residence time $\tau_r = 16$ s to operate to the high conversion branch is wider in the two reactor cascade than in the four reactor cascade. When either of the reactor cascades is operated at a value of the total residence time that is lower than that at the ignition limit point but is higher than that at the extinction limit point there are two stable steady-state solutions. One of these corresponds to a low conversion and the other corresponds to a high conversion. Numerical integration shows that the system evolves to the high conversion branch with a good choice of the initial conditions. Figure 4.6 shows that in these circumstances the conversion achieved in the four reactor cascade is higher than that in the two reactor cascade.

### 4.3.2 Scenario two: fixed coolant temperature

From our results in section 4.3.1, we know that the activation energy $E_2$ has a significant influence on the product conversion. In this section we fix the coolant temperature $T_{a,1} = T_{a,2} = T_{a,3} = T_{a,4} = 800$ K and investigate how the steady-state product concentration in both systems varies as one of two parameters is changed: the activation energy $E_2$ or the feed temperature $T_0$. Tables 4.4 and 4.5 show that the product conversion in both

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**Fig. 4.5:** The steady-state conversion of the product concentration $C$ in both 2-reactor and 4-reactor systems as a function of the total residence time $\tau_r$. The vertical lines are the total residence time $\tau_r = 16$ s. Parameter values $E_2 = 120$ kJ mol$^{-1}$, $Q_2 = 100$ kJ mol$^{-1}$, $T_{e,2} = 435$ K, $T_0 = 680$ K and $T_{a,2} = 800$ K.
the two reactor cascade $C_2^*$ and the four reactor cascade $C_4^*$ is a mixture of “good” and “bad”.

In Table 4.4 we note that the conversion of the reactant $A_1^*$ is increasing as the feed temperature $T_0$ increases and thus the product conversion increases. We find that the product conversion is less than 90% when the feed temperature is sufficiently small $T_0 < 700$ and 680 K when the activation energy is $E_2 = 50$ and 80 and 120 kJ mol$^{-1}$ respectively.

Similarly in Table 4.5 we note that the conversion of the reactant $A$ in the first and third reactors increases while the product conversion is increasing as the feed temperature increases. We find that when the feed temperature is $T_0 < 700$ and 680 K and the activation energy is $E_2 = 50$ and 80 and 120 kJ mol$^{-1}$ respectively the product conversion is less than 90%.

Tables 4.4 and 4.5 show that for the same specified feed temperature the product
conversion in the four reactor cascade is generally higher than that in the two reactor cascade. Therefore, the four reactor cascade is superior to the two reactor cascade. The required feed temperature is almost identical in both reactor cascades for the lowest value of the activation energy $E_2$. However, for a lower value of the feed temperature and the lowest value of the activation energy $E_2 = 50$ (kJ mol$^{-1}$) the product conversion (written in bold) in the two reactor cascade $C^*_2$ is higher than the conversion in the four reactor cascade $C^*_4$.

Tab. 4.4: The product conversion $C_2$ in the two reactor system for different values of the activation energy $E_2$ and feed temperature $T_0$. Parameter values $Q_2 = 100$ kJ mol$^{-1}, T_{c2} = 435$ K and $T_{a,2} = 800$ K. The temperature in bold indicates when the two reactor cascade is superior to the four reactor cascade.

$$\begin{array}{|c|c|c|c|c|}
\hline
T_0 & A_1 & C^*_2 (E_2 = 50) & C^*_2 (E_2 = 80) & C^*_2 (E_2 = 120) \\
\hline
500 & 0.501 & 0.006 & 0.003 & 0.493 \\
600 & 0.240 & 0.021 & 0.753 & 0.759 \\
680 & 0.066 & 0.865 & 0.9321 & 0.936 \\
700 & 0.037 & 0.909 & 0.961 & 0.962 \\
800 & 0.001 & 0.980 & 0.999 & 0.999 \\
900 & 0.00003 & 0.991 & 0.9999 & \sim 1 \\
\hline
\end{array}$$

Tab. 4.5: The product conversion $C_4$ in the four reactor system for different values of the activation energy $E_2$ and the feed temperature $T_0$. Parameter values $Q_2 = 100$ kJ mol$^{-1}, T_{c2} = 435$ K and $T_{a,2} = 800$ K. The temperature in bold indicates when the two reactor cascade is superior to the four reactor cascade.

$$\begin{array}{|c|c|c|c|c|c|}
\hline
T_0 & A_1 & E_2 = 50 & E_2 = 80 & E_2 = 120 \\
\hline
 & & A_3^* & C^*_3 & A_4^* & C^*_4 \\
500 & 0.554 & 0.440 & 0.004 & 0.441 & 0.002 \\
600 & 0.292 & 0.168 & 0.011 & 0.0002 & 0.820 \\
680 & 0.105 & 0.014 & 0.038 & 0.1 \times 10^{-5} & 0.9983 \\
700 & 0.069 & 0.1 \times 10^{-5} & 0.923 & 0.4 \times 10^{-6} & 0.9996 \\
800 & 0.002 & 0.2 \times 10^{-8} & 0.998 & 0.2 \times 10^{-8} & \sim 1 \\
900 & 0.0001 & 0.2 \times 10^{-10} & 0.9996 & 0.2 \times 10^{-10} & \sim 1 \\
\hline
\end{array}$$

4.3.2.1 The conversion when $E_2 = 50$ kJ mol$^{-1}$

Figures 4.7a-4.7b show the steady-state diagrams for the two reactor cascade and four reactor cascade respectively as a function of the feed temperature $T_0$ at the lowest value of the activation energy $E_2 = 50$ kJ mol$^{-1}$. In Figure 4.7a the extinction and the ignition limit point bifurcations occur at 619.8 K and 675.6 K respectively. These values are lower than our reference value of the feed temperature ($T_0 = 680$ (K)). The practical
consequence of this is that the system must evolve to the high conversion branch when the feed temperature is $T_0 = 680$ K. In Figure 4.7b the extinction and the ignition limit point bifurcations occur at 685.5 K and 732.7 K respectively which are higher than our reference value of feed temperature $T_0 = 680$ K. Consequently, when the feed temperature is $T_0 = 680$ K the latter system operates at the low conversion branch. It is now obvious why the conversion in the two reactor cascade is better than that in the four reactor cascade for the lowest value of the activation energy $E_2 = 50$ KJ mol$^{-1}$ when the feed temperature is $T_0 = 680$ K.

4.3.2.2 The conversion when $E_2 = 80$ kJ mol$^{-1}$

Figures 4.8a-4.8b show the steady-state diagram for the two reactor cascade and four reactor cascade respectively as a function of the feed temperature $T_0$ when the activation energy is $E_2 = 80$ kJ mol$^{-1}$. In Figure 4.8a the extinction and the ignition limit point bifurcations occur at 514.3 K and 640.5 K which are lower than our reference value of the feed temperature $T_0 = 680$ K. Consequently, at the reference value of the feed temperature the system operates on the high conversion branch. In Figure 4.8b the extinction and the ignition limit point bifurcations occur at 550 K and 690 K. The ignition limit point is
higher than the reference value of the feed temperature. This figure shows that at the default value of the feed temperature it is possible to operate on either the low conversion branch or the high conversion branch depending on the initial conditions used to start up the reactor.

![Diagram showing steady-state conversion of product concentration](image)

\[(a)\ 2\text{-reactor system}\hspace{1cm}(b)\ 4\text{-reactor system}\]

**Fig. 4.8:** The steady-state conversion of the product concentration \( C \) in both 2-reactor and 4-reactor cascade as a function of the inflow temperature \( T_0 \). The vertical lines are the reference value of the feed temperature \( T_0 = 680 \) K. Parameter values \( E_2 = 80 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, \tau = 16 \text{ s}, T_{c2} = 435 \text{ K} \) and \( T_{a,2} = 800 \text{ K} \).

Figure 4.9 shows the combination of the steady-state diagram shown in Figures 4.8a-4.8b. This figure shows that the range of the feed temperature that ensures the two reactor cascade operates at the high conversion branch is wider than for the four reactor cascade. In the four reactor cascade, as the ignition limit point is higher than the reference value of the feed temperature, a temporary perturbation of some kind must be imposed onto the system to “kick” it from the low conversion branch onto the high conversion branch. With a good choice of the initial conditions to start up the system it is possible to reach the high conversion branch in each system. When the feed temperature is smaller than some critical value \( T_0 \) around 555.46 K, the conversion in the two reactor system is higher than the conversion in the four reactor system.
Fig. 4.9: The combination of Figure 4.3a and Figure 4.3b. The product concentration in the two reactor cascade $C_2$ (red branch) and the product concentration in the four reactor cascade $C_4$ (blue branch).

4.3.2.3 The conversion when $E_2 = 120$ (kJ mol$^{-1}$)

Figures 4.10a-4.10b show the steady-state diagrams for the two reactor cascade and four reactor cascade respectively as a function of the feed temperature $T_0$ when the activation energy is $E_2 = 120$ kJ mol$^{-1}$. In both Figures 4.10a-4.10b both the extinction and the ignition limit point bifurcations occur at a value lower than our reference value of the feed temperature (468.1 K and 638.3 K) and (499.1 K and 677.8 K), respectively. The practical consequence of this is that both systems always evolve to the high conversion branch at the reference value of the feed temperature $T_0 = 680$ K.

Figure 4.11 shows the combination of the steady-state diagram shown in Figures 4.10a-4.10b. This figure shows that the larger range of the required feed temperature to operate at the high conversion branch is found for the two reactor cascade. In the region of
bistability we find that with a good choice of the initial conditions the system evolves to the high conversion branch rather than the low conversion branch. Figure 4.11 shows that when the feed temperature is smaller than some critical value, i.e. $T_0$ around 555.46 K, the conversion in the two reactor cascade is higher than that in the four reactor cascade.

4.4 Summary

In conclusion, when we take the total residence time $\tau_r$ as the primary bifurcation parameter the two reactor cascade is better than the four reactor cascade for the lowest value of the activation energy $E_2 = 120 \text{ kJ mol}^{-1}$. For the highest values of the activation energy $E_2$ the product conversion in the four reactor system is superior to the conversion in the two reactor system with a good choice of initial conditions. Finally we fixed the total residence time and took the feed temperature to be the primary bifurcation parameter. At a typical experimental feed temperature of 680 K we found that the conversion in the four reactor cascade was feeble whereas the conversion was around 80% in the two reactor cascade for the lowest value of the activation energy $E_2 = 50 \text{ kJmol}^{-1}$. However, at higher values for the feed temperature the four reactor cascade is superior. For higher values of the activation energy this pattern reoccurs, i.e. at lower values of the feed temperature
4. Four Reactors System

4.5 Conclusion

We conclude that although there are some conditions in which the two reactor cascade is superior, these conditions can be “tweaked” to conditions where the four reactor cascade is superior. This superiority occurs because the four reactor cascade allows for the possibility of achieving additional conversion of the reactant $A$ into the intermediate $B$ in the third reactor. However, the costs of increasing the number of reactors in series might be a financial obstacle to taking advantage of the increase in the yield.

Fig. 4.11: The combination of Figure 4.5a and Figure 4.5b. The product concentration in the two reactor cascade $C_2$ (red branch) and the product concentration in the four reactor cascade $C_4$ (blue branch).

the two reactor cascade is superior but at sufficiently high values of the feed temperature the four reactor cascade is superior.
5. THE JACKETED REACTOR: INDEPENDENT COOLANT TEMPERATURE AROUND THE REACTORS

The aim of this chapter is to investigate an extension of the model in Chapter 3 to include the dynamics of a jacket. In the diabatic model the ambient (jacket) temperature $T_{a,i}$, $i = 1, 2$ was assumed to be fixed. In this chapter the jacket temperature changes in response to temperature changes in the reactor. Background information on jacketed reactors is provided in Chapter 1. The conditions under which the jacketed reactor model “collapses” into the diabatic reactor model are discussed later.

5.1 Jacketed reactor configuration

Figure 5.1 shows the processes that occur in the reactor cascade. The concentrations of the reactant $A$ and the intermediate $B$ leaving reactor one are $A_1$ and $B_1$ respectively. The concentrations of the reactant $A$ and the intermediate $B$ and the product $C$ leaving reactor two are $A_2$, $B_2$ and $C_2$ respectively. The jacket temperatures in the feed stream for the jackets surrounding reactors one and two are $T_{0(c,1)}$ and $T_{0(c,2)}$ respectively. The temperatures of the jackets around reactors one and two are $T_{(c,1)}$ and $T_{(c,2)}$ respectively. The temperatures of the reacting mixture in reactors one and two are $T_1$ and $T_2$ respectively.

We are particularly interested in identifying the choice of catalysts and reactor operation conditions that ensure a minimum of 90% conversion of reactant $A$ to product $C$.

5.2 Model equations

In section 5.2.1 we give the model equations. In section 5.2.2 we non-dimensionalise the model. In section 5.3 we reduce the model equations from ten equations to seven equations.
The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

5.2.1 Dimensional equations

The difference between this system and the earlier model is that jacket temperature is now included as a state variable in equations (5.5) and (5.14). The inclusion of this variable changes the initial conditions for each reactor.

The system of equations in the first reactor is given by equations (5.1)–(5.9).

The rate of change of the concentration of the reactant $A$.

$$V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1.$$  \hspace{1cm} (5.1)

The rate of change of the concentration of the intermediate $B$.

$$V_1 \frac{dB_1}{dt} = -qB_1 + V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1.$$  \hspace{1cm} (5.2)

The rate of change of the concentration of the product $C$.

$$V_1 \frac{dC_1}{dt} = q(C_0 - C_1).$$  \hspace{1cm} (5.3)
The rate of change of the reactor temperature.

\[ c_{pg} \rho_g V_1 \frac{dT_1}{dt} = q c_{pg} \rho_g (T_0 - T_1) - Q_1 V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{(c,1)}) . \]  \hspace{1cm} (5.4)

The rate of change of the jacket temperature.

\[ c_{pg(c,1)} \rho_g T_{(c,1)} \frac{dT_{(c,1)}}{dt} = q_{(c,1)} c_{pg(c,1)} \rho_g T_{(c,1)} (T_{0(c,1)} - T_{(c,1)}) + J_1 \chi_1 S_1 (T_1 - T_{(c,1)}) . \]  \hspace{1cm} (5.5)

The definition of the pre-exponential factor \( a_1 \) in terms of the characteristic temperature \( T_{c1} \) (see chapter 1.5.1).

\[ a_1 = \frac{E_1 \alpha}{RT_{c1}^2} \exp \left[ \frac{E_1}{RT_{c1}} \right] . \]  \hspace{1cm} (5.6)

The initial conditions are given by equation (5.7). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

\[ A_1(0) = B_1(0) = C_1(0) = 0 , \]

\[ T_1(0) = \frac{q c_{pg} \rho_g T_0 + q_{(c,1)} c_{pg(c,1)} \rho_g T_{(c,1)}}{q c_{pg} \rho_g} \left[ T_{0(c,1)} - T_{(c,1)}(0) \right] , \]

\[ T_{(c,1)}(0) = \frac{q_{(c,1)} c_{pg(c,1)} \rho_g T_{(c,1)}}{q_{(c,1)} c_{pg(c,1)} \rho_g} \left( q c_{pg} \rho_g + J_1 \chi_1 S_1 \right) + J_1 \chi_1 S_1 q c_{pg} \rho_g T_0 + J_1 \chi_1 S_1 q c_{pg} \rho_g . \]  \hspace{1cm} (5.7)

The residence time in the reactor

\[ \tau_1 = \frac{V_1}{q} . \]  \hspace{1cm} (5.8)
The residence time in the jacket

\[ \tau_{(c,1)} = \frac{V_{(c,1)}}{q_{(c,1)}}, \] (5.9)

The system of equations in the second reactor is given by equations (5.10)–(5.18).

The rate of change of the concentration of the reactant A.

\[ V_2 \frac{dA_2}{dt} = q(A_1 - A_2). \] (5.10)

The rate of change of the concentration of reactant B.

\[ V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \] (5.11)

The rate of change of the concentration of reactant C.

\[ V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \] (5.12)

The rate of change of the reactor temperature.

\[ c_{pg} \rho_g V_2 \frac{dT_2}{dt} = q c_{pg} \rho_g (T_1 - T_2) + Q_2 V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2 - J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \] (5.13)

The rate of change of the jacket temperature.

\[ c_{pg(c,2)} \rho_{g(c,2)} V_{(c,2)} \frac{dT_{(c,2)}}{dt} = q_{(c,2)} c_{pg(c,2)} \rho_{g(c,2)} (T_{0_{(c,2)}} - T_{(c,2)}) + J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \] (5.14)
The definition of the pre-exponential factor $a_2$ in terms of the characteristic temperature $T_{c2}$ (see chapter 1.5.1).

$$a_2 = \frac{E_2\alpha}{RT_{c2}^2} \exp\left[\frac{E_2}{RT_{c2}}\right].$$  

(5.15)

The initial conditions are given by equation (5.16). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state:

$$A_2(0) = B_2(0) = C_2(0) = 0,$$

$$T_2(0) = \frac{qc_{pg}T_1(0) + q(c_{2})c_{pg(c_{2})}\rho_{g(c_{2})}[T_{0(c_{2})} - T_{(c_{2})}(0)]}{qc_{pg}},$$

$$T_{(c_{2})}(0) = \frac{q(c_{2})c_{pg(c_{2})}\rho_{g(c_{2})}(qc_{pg} + J_2\chi_2 S_2ә_{pg} + J_2\chi_2 S_2qc_{pg}\rho_g T_1(0))}{q(c_{2})c_{pg(c_{2})}\rho_{g(c_{2})}(qc_{pg} + J_2\chi_2 S_2 + J_2\chi_2 S_2qc_{pg}\rho_g)}.$$

(5.16)

The residence time in the reactor

$$\tau_2 = \frac{V_2}{q}.$$

(5.17)

The residence time in the jacket

$$\tau_{(c_{2})} = \frac{V_{(c_{2})}}{q(c_{2})}.$$

(5.18)

Note that the concentrations flowing into reactor two are the concentrations exiting from reactor one. Similarly the temperature of the fluid entering reactor two is equal to that leaving reactor one.

We are interested in the long-time behaviour of the reactor cascade. Thus we study the steady-state solutions. The terms appearing in equations (5.1)–(5.18) are defined in Appendix.1.
5.2.2 Dimensionless equations

In nondimensionalising equations (5.1)-(5.13) we introduce dimensionless concentrations \( A_i^* = A_i/A_0, B_i^* = B_i/A_0, C_i^* = C_i/A_0 \), dimensionless temperatures \( [\theta_i = (RT_i)/E_2] \), dimensionless jacket temperatures \( [\theta_{(c,i)} = (RT_{(c,i)})/E_2] \), where \((i = 1, 2)\), and dimensionless time \([t^* = (\chi_2 S_2 t)/(c_p \rho g V_2)]\).

From now on we assume that there is no intermediate or product in the feed stream, i.e. \( B_0 = B_0^* = 0 \) and \( C_0 = C_0^* = 0 \).

The non-dimensional equations in the first reactor are:

\[
\begin{align*}
\frac{dA_1^*}{dt^*} &= \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^*, \\
\frac{dB_1^*}{dt^*} &= \frac{B_0^* - B_1^*}{\tau_1^*} + a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^*, \\
\frac{dC_1^*}{dt^*} &= \frac{C_0^* - C_1^*}{\tau_1^*}, \\
\frac{d\theta_1}{dt^*} &= \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^* - J_1 \chi_{T,1}^* (\theta_1 - \theta_{(c,1)}), \\
\frac{d\theta_{(c,1)}}{dt^*} &= \frac{H_1 (\theta_{(c,1)} - \theta_{(c,1)})}{\tau_{(c,1)}^*} + J_1 H_1 g (\theta_1 - \theta_{(c,1)}), \\
a_1^* &= \frac{\alpha^* V^* E_1^*}{T_{c1}^2} \exp \left[ \frac{E_1^*}{T_{c1}^*} \right].
\end{align*}
\]  (5.19, 5.20, 5.21, 5.22, 5.23, 5.24)

The nondimensional initial conditions are:

\[
A_1^*(0) = B_1^*(0) = C_1^*(0) = 0, \quad \theta_1(0) = \frac{\tau_{(c,1)}^* g \theta_0 + \chi_{T,1}^* \tau_{(c,1)}^* (\theta_{(c,1)} - \theta_{(c,1)})}{\tau_{(c,1)}^* g}, \quad \theta_{(c,1)}(0) = \frac{(1 + J_1 \chi_{T,1}^* \tau_{(c,1)}^*) \theta_{(c,1)} + J_1 \tau_{(c,1)}^* g \theta_0}{(1 + J_1 \chi_{T,1}^* \tau_{(c,1)}^*) + J_1 \tau_{(c,1)}^* g}. \]  (5.25)

The non-dimensional equations in the second reactor are:
\[
\begin{align*}
\frac{dA^*_2}{dt^*} &= \frac{A^*_1 - A^*_2}{\tau^*_2}, \\
\frac{dB^*_2}{dt^*} &= \frac{1 - A^*_1 - B^*_2}{\tau^*_2} - a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2, \\
\frac{dC^*_2}{dt^*} &= \frac{C^*_1 - C^*_2}{\tau^*_2} + a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2, \\
\frac{d\theta^*_2}{dt^*} &= \frac{\theta^*_1 - \theta^*_2}{\tau^*_2} + Q^*_2 a^*_2 \exp \left[ -\frac{1}{\theta^*_2} \right] B^*_2 - J^*_2 (\theta^*_2 - \theta^*_2(\text{c,2})), \\
\frac{d\theta^*_2(\text{c,2})}{dt^*} &= \frac{H^*_2 (\theta^*_0(\text{c,2}) - \theta^*_2(\text{c,2}))}{\tau^*_2(\text{c,2})} + J^*_2 H^*_2 (\theta^*_2 - \theta^*_2(\text{c,2})).
\end{align*}
\]

The nondimensional initial conditions are:

\[
\begin{align*}
A^*_2(0) &= B^*_2(0) = C^*_2(0) = 0, \\
\theta^*_2(0) &= \frac{\tau^*_1(\text{c,1}) \theta^*_1(0) + \tau^*_1(\theta^*_0(\text{c,2}) - \theta^*_2(\text{c,2}))}{\tau^*_2(\text{c,2})}, \\
\theta^*_2(\text{c,2})(0) &= \frac{(1 + J^*_2 \tau^*_2) \theta^*_0(\text{c,2}) + J^*_2 \tau^*_2(\text{c,2}) \theta^*_1(0)}{(1 + J^*_2 \tau^*_2)^2 + J^*_2 \tau^*_2(\text{c,2})}.
\end{align*}
\]

All dimensionless variables are defined in Appendix.1.

### 5.3 Reduced system

The techniques used in the previous chapters are applied to reduce the number of model equations. As this procedure is similar to that employed previously, we do not provide the details. In this section the model equations are reduced from ten to seven.
The reduced system of non-dimensional equations in the first reactor is:

\[
\begin{align*}
\frac{dA^*_1}{dt^*} &= \frac{1 - A^*_1}{\tau^*_1} - a^*_1 \exp \left[ \frac{-E^*_1}{\theta^*_1} \right] A^*_1, \\
\frac{d\theta_1}{dt^*} &= \frac{\theta_0 - \theta_1}{\tau^*_1} - Q^*_1 a^*_1 \exp \left[ \frac{-E^*_1}{\theta^*_1} \right] A^*_1 - J_1 \chi^*_1 (\theta_1 - \theta_{(c,1)}), \\
\frac{d\theta_{(c,1)}}{dt^*} &= \frac{H_1 (\theta_{0(c,1)} - \theta_{(c,1)})}{\tau^*_1} + J_1 h_1(\theta_1 - \theta_{(c,1)}), \\
B^*_1(t^*) &= 1 - A^*_1(t^*), \\
C^*_1(t^*) &= 0.
\end{align*}
\]

The reduced system of non-dimensional equations in the second reactor is:

\[
\begin{align*}
\frac{dA^*_2}{dt^*} &= \frac{A^*_1 - A^*_2}{\tau^*_2}, \\
\frac{dB^*_2}{dt^*} &= \frac{1 - A^*_1 - B^*_2}{\tau^*_2} - a^*_2 \exp \left[ \frac{-1}{\theta^*_2} \right] B^*_2, \\
\frac{d\theta_2}{dt^*} &= \frac{\theta_1 - \theta_2}{\tau^*_2} + Q^*_2 a^*_2 \exp \left[ \frac{-1}{\theta^*_2} \right] B^*_2 - J_2 (\theta_2 - \theta_{(c,2)}), \\
\frac{d\theta_{(c,2)}}{dt^*} &= \frac{H_2 (\theta_{0(c,2)} - \theta_{(c,2)})}{\tau^*_2} + J_2 H_2 (\theta_2 - \theta_{(c,2)}), \\
C^*_2 &= 1 - A^*_2 - B^*_2.
\end{align*}
\]

5.3.1 Steady-state model reduction

From equations (5.35) and (5.41), the jacket steady-state is easily found in terms of the reactor temperature $\theta_{(c,1)}$ and $\theta_{(c,2)}$. By taking a linear combination of the steady-state for the reactor temperature and the species concentration we can reduce the system to either an equation for the concentration or an equation for the temperature. Thus at steady-state the model equations can be reduced to a two equation model.

**Reactor one:**

Under the assumption of the steady-state it is possible to reduce the model equations
for reactor one to either a scalar equation for the concentration \( A_1^* \)

\[
1 - A_1^* \frac{a_1^*}{\tau_1^*} \exp \left[ \frac{-[1 + J_1(\tau_{c,1}^* + \tau_{c,1}^*)]}{Q_1^*(1 + J_1\tau_{c,1}^*g)(A_1^* - 1) + J_1\tau_{c,1}^*\theta_{0,c,1} + (1 + J_1\tau_{c,1}^*g)\theta_0} \right] A_1^* = 0
\]

(5.43)

or to a scalar equation for the temperature \( \theta_1 \)

\[
\frac{\theta_0 - \theta_1}{\tau_1^*} - \frac{a_1^*}{1 + J_1\tau_{c,1}^*g} \exp \left[ \frac{-E_1^*}{\theta_1} \right] (Q_1^*(1 + J_1\tau_{c,1}^*g) - (1 + J_1\tau_{c,1}^*g)\theta_0) - J_1\tau_{c,1}^*\theta_{0,c,1} + [1 + J_1(\tau_{c,1}^* + \tau_{c,1}^*)]\theta_1 = 0.
\]

(5.44)

**Reactor two:**

As described previously, it is possible to reduce the model for reactor two to either a scalar equation for the concentration \( B_2^* \)

\[
1 - A_1^* - B_2^* \frac{a_2^*}{\tau_2^*} \exp \left[ \frac{-[1 + J_2(\tau_{c,2}^* + \tau_{c,2}^*)]}{Q_2^*(1 + J_2\tau_{c,2}^*g)(1 - A_1^* - B_2^*) + J_2\tau_{c,2}^*\theta_{0,c,2} + (1 + J_2\tau_{c,2}^*g)\theta_1} \right] B_2^* = 0,
\]

(5.45)

or a scalar equation for the temperature \( \theta_2 \)

\[
\frac{\theta_1 - \theta_2}{\tau_2^*} + \frac{a_2^*}{1 + J_2\tau_{c,2}^*g} \exp \left[ \frac{-1}{\theta_2} \right] (Q_2^*(1 + J_2\tau_{c,2}^*g)(1 - A_1^*) + (1 + J_2\tau_{c,2}^*g)\theta_1 + J_2\tau_{c,2}^*\theta_{0,c,2}) - [1 + J_2(\tau_{c,2}^* + \tau_2^*)]\theta_2 = 0.
\]

(5.46)

### 5.4 Steady-state analysis for reactor one

In this section we show that in the first reactor there is always a unique steady-state solution. Furthermore, we discuss how the adiabatic and diabatic models occur as limiting cases of the jacketed reactor model.

Thus, solving the steady-state equation for the reactant concentration \( A_1^* \) (5.33) and the jacket temperature (5.35), we obtain
\[ A_1^* = \frac{1}{1 + a_1^* \exp \left( \frac{-E_1^*}{\theta_1} \right) \tau_1^*}, \]  
\[ \theta_{(c,1)} = \frac{\theta_{0(c,1)} + J_1 \tau_{(c,1)}^* g \theta_1}{1 + J_1 \tau_{(c,1)}^* g}. \]  

Equation (5.48) shows that at the limit when the residence time in the jacket \( \tau_{(c,1)}^* \) goes to zero, the jacket temperature \( \theta_{(c,1)} \) is equal to the jacket temperature for the jacket in the feed \( \theta_{0(c,1)} \). In this limit we obtain the \textbf{Diabatic} model. At the limit when the residence time in the jacket \( \tau_{(c,1)}^* \) approaches infinity, the jacket temperature \( \theta_{(c,1)} \) is identical to the temperature inside the reactor \( \theta_1 \). This limit represents the \textbf{Adiabatic} model, as there will be no heat exchange between the reactor and the jacket.

Using equations (5.47) and (5.48) the steady-state equations for reactor one reduce to a scalar equation for the reactor temperature \( \theta_1 \):

\[ H(\theta_1) = \frac{\theta_0 - \theta_1}{\tau_1^*} - \frac{Q_1^* a_1^* \exp \left( \frac{-E_1^*}{\theta_1} \right)}{1 + a_1^* \tau_1^* \exp \left( \frac{-E_1^*}{\theta_1} \right)} - \frac{J_1 \lambda_{T,1}^*}{1 + J_1 \tau_{(c,1)}^* g} (\theta_1 - \theta_{0(c,1)}) = 0. \]  

\[ \text{(5.49)} \]

### 5.4.1 Unique steady-state solution

In this section we show that the equation (5.49) has a unique positive solution. We have

\[ H(\theta_1) = \frac{\theta_0 - \theta_1}{\tau_1^*} - \frac{Q_1^* a_1^* \exp \left( \frac{-E_1^*}{\theta_1} \right)}{1 + a_1^* \tau_1^* \exp \left( \frac{-E_1^*}{\theta_1} \right)} - \frac{J_1 \lambda_{T,1}^*}{1 + J_1 \tau_{(c,1)}^* g} (\theta_1 - \theta_{0(c,1)}). \]  

\[ \text{(5.50)} \]

Firstly we show that there is a solution for \( \theta_1 \) bounded by

\[ 0 \leq \theta_1 \leq \theta_{(1,v)}, \]

where

\[ \theta_{(1,v)} = \frac{(1 + J_1 \tau_{(c,1)}^* g) \theta_0 + J_1 \tau_{(c,1)}^* \lambda_{T,1}^* \theta_{0(c,1)}}{1 + J_1 \tau_{(c,1)}^* g + J_1 \tau_{(c,1)}^* \lambda_{T,1}^*}. \]

We have
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\[ H(0) = \frac{\theta_0}{\tau_1^*} + \frac{\theta_{0(c,1)}}{1 + J_1 \tau_{1(c,1)}^*} g > 0, \]

and

\[ H(\theta_{(1,v)}) = -\left( \frac{a_1^* Q_1^* \exp\left[ \frac{E_1^*}{\theta_{(1,v)}^*} \right]}{1 + a_1^* \tau_1^* \exp\left[ \frac{E_1^*}{\theta_{(1,v)}^*} \right]} \right) < 0. \]

Since \( H(0) > 0 \) and \( H(\theta_{(1,v)}) < 0 \), we know there exists at least one value of \( \theta_1 \) such that \( H(\theta_1) = 0 \). Hence, we have shown that there is at least one steady-state solution in the region:

\[ 0 < \theta_1 < \theta_{1,v}. \]

We now show that equation (5.50) has only one physically meaningful solution. Differentiating equation (5.50) we have

\[ \frac{dH}{d\theta_1} = -\frac{1}{\tau_1^*} - \frac{a_1^* Q_1^* E_1^* \exp\left[ \frac{-E_1^*}{\theta_1^*} \right]}{\theta_1^2 (1 + a_1^* \tau_1^* \exp\left[ \frac{-E_1^*}{\theta_1^*} \right])} - \frac{J_1 \chi_{T,1}^*}{1 + J_1 \tau_{c,1}^*} g < 0. \]

As \( dH/d\theta_1 \) is negative for all \( \theta_1 \) it follows that the function \( H(\theta_1) \) has a single steady-state solution.

### 5.4.2 Stability of the steady-state solutions

The Jacobian matrix of the equations (5.33)–(5.35) for reactor one is given by

\[
J(A_1, \theta_1, \theta_{(c,1)}) = \begin{bmatrix}
-(Z_1 + Z_6) & Z_1Z_2 & 0 \\
-Z_1^*Z_1 & -(Z_6 + Q_1 Z_1 Z_2 + Z_3) & Z_3 \\
0 & Z_4 & Z_5 - Z_4
\end{bmatrix}
\] (5.51)

where the coefficients \( Z_i, i = 1..6 \) are given by
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

\[ Z_1 = a_1^* \exp \left( - \frac{E_1^*}{\theta_1} \right), \]
\[ Z_2 = \frac{E_1^* A_1^*}{\theta_1^*}, \]
\[ Z_3 = J_1 \chi_{T,1}^*, \]
\[ Z_4 = J_1 H_1 g, \]
\[ Z_5 = \frac{H_1}{\tau_{(c,1)}^*}, \]
\[ Z_6 = \frac{1}{\tau_1^*}. \]

Note that we have \( Z_i > 0, i = 1..6. \)

The characteristic polynomial of the Jacobian matrix (5.51), is given by

\[ F(\lambda) = \lambda^3 + a_1 \lambda^2 + a_2 \lambda + a_3, \]
\[ a_1 = Z_1 \left( Q_1^* Z_2 + 1 \right) + Z_3 + Z_4 + Z_5 + 2Z_6, \]
\[ a_2 = Z_1 \left( Q_1^* Z_2 + 1 \right) \left( Z_4 + Z_5 + Z_6 \right) + Z_6 \left[ 2 \left( Z_4 + Z_5 \right) + Z_6 \right] + Z_3 \left( Z_1 + Z_5 + Z_6 \right), \]
\[ a_3 = Z_6 \left( Z_4 + Z_5 \right) \left[ Z_1 \left( Q_1^* Z_2 + 1 \right) + Z_6 \right] + Z_3 Z_5 \left( Z_1 + Z_6 \right) \]

According to the Routh Hurwitz theorem [36] it is sufficient to show that \( a_1 > 0, \)
\( a_3 > 0 \) and \( a_1 a_2 - a_3 > 0 \) to conclude that the steady-state solution is locally stable.

Observe that there are no negative terms in the formulae for \( a_1 \) and \( a_3. \) Thus they are immediately positive.

Directly substituting the expressions for \( a_i, i = 1..3 \) into the expression \( a_1 a_2 - a_3, \) we
find that

\[ a_1a_2 - a_3 = Z_1(Z_4 + Z_5 + Z_6)[Q_1^*Z_2(Z_1Z_2Q_1^* + Z_1 + Z_3 + Z_5) + Z_3 + 2Z_6] + (2Z_4 + 2Z_5 + Z_6)[Z_4Z_2Q_1^*(Z_3 + Z_6) + 2Z_6^2] + Z_3(Z_1 + Z_5 + Z_6)[Z_1Z_2Q_1^* + Z_3 + Z_4 + 2Z_6] + (Z_4 + Z_5)[Z_1(Z_2Z_4Q_1^* + Z_4 + Z_5) + 2Z_6(Z_4 + Z_5)] + Z_3Z_6^2 + Z_1Z_2Z_6Q_1^*(Z_4 + 2Z_5 + 2Z_6) > 0. \]

We conclude that the first reactor has a single steady-state solution that is locally stable.

### 5.5 Results and discussion

All calculations performed in this chapter used the industrial parameter values stated in Appendix.1 unless otherwise stated.

#### 5.5.1 Achieving 90% conversion in reactor one

##### 5.5.1.1 Varying the feed temperature \( T_0 \)

In order to achieve 90% conversion of the reactant \( A \) into the product \( C \) we must achieve at least 90% conversion of the reactant into the intermediate species \( B \) in the first reactor. By taking a suitable combination of equations (5.33), (5.34) & (5.35) we find an equation giving the feed temperature \( \theta_0 \) required to achieve a specified steady-state value of the reactant concentration.

\[
\theta_0 = \frac{\left[ 1 + J_1\tau_1^*\chi_{1,1}^*(1 + J_1\tau_{(c,1)}^*g) \right] E_1^*}{(1 + J_1\tau_{(c,1)}^*g) \ln \left[ \frac{1 - A_1^*}{\tau_1^*} \right]} - \frac{J_1\tau_1^*\chi_{1,1}^*}{1 + J_1\tau_{(c,1)}^*g} \theta_{0(c,1)} + Q_1^*(1 - A_1^*), \quad (5.52)
\]

This equation is same equation (3.35) as for the diabatic model when the residence time for the jacket \( \tau_{(c,1)} \) goes to zero.

Returning to dimensional values, the value for the feed temperature \( T_0 \) to obtain a conversion of 90% of the reactant \( A_1 \) as a function of the catalyst parameters \( E_1 \) and
$T_0(c,1)$ is shown in Table 5.1. Values are shown for an adiabatic reactor, a diabatic reactor and a jacketed reactor. The most obvious feature of this table is that there is little dependence of the required feed temperature upon the jacket temperature. This table shows that the required feed temperature $T_0$ is always realistic for any value of the jacket feed temperature and all the studied types of reactors.

Recall that the pre-exponential factor $a_1^*$ depends on the activation energy $E_1^*$. Differentiating (5.52) with respect to the activation energy $E_1^*$ and using equation (5.24) where appropriate, we obtain

$$\frac{d\theta_0}{dE_1^*} = -[1 + J_1^* \tau_{(c,1)}^* g] \frac{E_1^* + T_{c1}^* + T_{c1}^* \ln \left( \frac{1 - A_1^*}{a_1^* \tau_{(c,1)}^* A_1^*} \right)}{T_{c1}^* (1 + J_1^* \tau_{(c,1)}^* g) \left( \ln \left( \frac{1 - A_1^*}{a_1^* \tau_{(c,1)}^* A_1^*} \right) \right)} < 0, \quad (5.53)$$

for

$$\tau_{1}^* < \frac{1 - A_1^*}{a_1^* A_1^*} \exp \left[ 1 + \frac{E_1^*}{T_{c1}^*} \right]. \quad (5.54)$$

This holds for the parameter values in Appendix.1.

Equation (5.53) shows that the feed temperature is a decreasing function of the activation energy in the first reactor, i.e. a lower activation energy requires a higher feed temperature to achieve a specified conversion.

Table 5.1 shows the required feed temperature to obtain 90% conversion in the first reactor for the diabatic reactor (D R), the adiabatic reactor (AD R) and the jacketed reactor (J R). The feed temperature values in the diabatic reactor are usually smaller than those for both the jacketed reactor and the adiabatic reactor. The exception to this is that, for the smallest value of the feed jacket temperature $T_0(c,1) = 400$ K and the smallest value of the activation energy $E_1 = 50$ kJmol$^{-1}$, the feed temperature values in the jacketed reactor and the adiabatic reactor (written in bold) are smaller than those in the diabatic reactor. However, for this case the difference in the required jacket temperature is insignificant.

Figure 5.2 shows the parameter values required to achieve 90% conversion of the reactant $A$ as a function of the jacket feed temperature $T_0(c,1)$ for three values of the heat of endothermicity $Q_1$. This figure confirms that the required feed temperature $T_0$ does not depend significantly upon the jacket feed temperature $T_0(c,1)$. Substituting the parameter
values in equation (5.52) we obtain the following equation when the activation energy is \( E_1 = 80 \text{ kJ mol}^{-1} \):

\[
T_0 = 15.55882946 - 0.3304192695 \times 10^{-6}T_{0(c,1)} + 0.4761916049 \times 10^{-6}Q_1.
\]

This equation clarifies that there is little dependence of the feed temperature upon the jacket temperature. It is now obvious why the feed temperatures are flat lines in Figure 5.2.

Tab. 5.1: The feed temperature \( T_0 \) required to achieve 90\% conversion in the first reactor \( A_1^* = 0.1 \) as a function of the activation energy \( E_1 \) and the jacket feed temperature \( T_{0(c,1)} \).
The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}, \tau_{(c,1)} = 0.513 \text{ s}, \tau_1 = 8 \text{ s} \) and \( T_{c1} = 342 \text{ K} \). Note that (J R) means Jacketed Reactor, (AD R) means Adiabatic Reactor and (D R) means Diabatic Reactor.

<table>
<thead>
<tr>
<th>( T_{0,c,1} )</th>
<th>( T_0(E_1 = 50) )</th>
<th>( T_0(E_1 = 80) )</th>
<th>( T_0(E_1 = 120) )</th>
<th>( T_0(E_1 = 180) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>J R</td>
<td>D R</td>
<td>J R</td>
<td>D R</td>
<td>J R</td>
</tr>
<tr>
<td>400</td>
<td><strong>735.3</strong></td>
<td>680.4</td>
<td>680.1</td>
<td>657.4</td>
</tr>
<tr>
<td>600</td>
<td>734.9</td>
<td>728.2</td>
<td>680.0</td>
<td>670.9</td>
</tr>
<tr>
<td>800</td>
<td>734.5</td>
<td>718.9</td>
<td>679.6</td>
<td>661.6</td>
</tr>
<tr>
<td>1000</td>
<td>734.1</td>
<td>709.7</td>
<td>679.2</td>
<td>652.4</td>
</tr>
<tr>
<td>AD R</td>
<td><strong>735.3</strong></td>
<td>680.4</td>
<td></td>
<td>657.5</td>
</tr>
</tbody>
</table>

Figure 5.3 shows the feed temperature required to achieve 90\% conversion of the reactant \( A \) as a function of the characteristic temperature \( T_{c1} \) and the heat of endothermicity \( Q_1 \). Also, it shows that the heat of endothermicity \( Q_1 \) has a strong influence on the value of the required feed temperature; at higher values of the heat of endothermicity, a lower characteristic temperature is required to achieve 90\% conversion at realistic values for the feed temperature.

Differentiating (5.52) with respect to the characteristic temperature \( T_{c1}^* \) and using equation (5.6) where appropriate, we obtain

\[
\frac{d\theta_0}{dT_{c1}^*} = \frac{E_1^*[1 + J_1\tau_1^*(1 + J_1\tau_{(c,1)}^*)g][2T_{c1}^* + E_1^*]}{T_{c1}^*[1 + J_1\tau_{(c,1)}^* g][\ln \left( \frac{1 - A_1^*}{A_1^*\tau_{(c,1)}^*} \right)]^2} > 0. \tag{5.55}
\]

Equation (5.55) shows that the feed temperature \( T_0 \) is an increasing function of the characteristic temperature \( T_{c1} \).
Fig. 5.2: The parameters values in a jacketed reactor required to achieve 90% conversion in the first reactor as a function of the jacket feed temperature $T_{0c,1}$). The heat of endothermicity ($Q_1 = 50, 100$ and $205.8$ kJ mol$^{-1}$). The parameter values are $E_1 = 80$ kJ mol$^{-1}$, $E_2 = 50$ kJ mol$^{-1}$, $\tau(c,1) = 0.513$ s, $\tau_1 = 8$ s and $T_{c1} = 342$ K.

Differentiating (5.52) with respect to the endothermicity parameter $Q_1^*$ we obtain

$$\frac{d\theta_0}{dQ_1^*} = -A_1^* + 1 > 0,$$

(5.56)
as $0 < A_1^* < 1$. Equation (5.56) is the same equation as obtained in the diabatic model; see equation (3.39). It shows that the required feed temperature is an increasing function of $Q_1$; that is, a more endothermic reaction requires a higher feed temperature to achieve a specified conversion. This is shown in Figure 5.4. These figures show the inflow temperature required to achieve 90% conversion of the reactant $A_1$ in the first reactor as a function of the activation energy $E_1$, the characteristic temperature $T_{c1}$ and the heat of endothermicity $Q_1$. In these figures, feed temperatures higher than 1000 K are
considered to be unphysical. In Figure 5.4c a catalyst with the higher value of the characteristic temperature, $T_{c1} = 542$ K, is never viable. A catalyst with a lower value of the characteristic temperature is viable when the activation energy is sufficiently large, $E_1 \geq 57$ kJmol$^{-1}$. Figures 5.4a and 5.4b show that for intermediate or lower values of the heat of endothermicity a catalyst with a lower characteristic temperature value is always viable. A catalyst with the higher characteristic temperature value is viable when the activation energy is sufficiently large, $E_1 \geq 85$ kJmol$^{-1}$.

### 5.5.1.2 Varying the jacket feed temperature $T_{0(c,1)}$

From equation (5.52) we find an expression giving the jacket feed temperature $\theta_{0(c,1)}$ required to achieve a specified steady-state value of the reactant concentration.
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

(a) \( Q_1 = 50 \text{ kJ mol}^{-1} \).

(b) \( Q_1 = 100 \text{ kJ mol}^{-1} \).

(c) \( Q_1 = 200 \text{ kJ mol}^{-1} \).

Fig. 5.4: The feed temperature \( T_0 \) required to achieve 90% conversion in the first reactor as a function of the activation energy \( E_1 \). The parameter values are \( E_2 = 50 \text{ kJ mol}^{-1}, \tau_{(c,1)} = 0.513 \text{ s}, \tau_1 = 8 \text{ s} \) and \( T_{0(c,1)} = 800 \text{ K} \). The dashed lines show the maximum value of the feed temperature.

\[
\theta_{0(c,1)} = \frac{1 + J_1 \tau_{(c,1)}^* g}{J_1 \tau_1^* T_1} \left[ \frac{1}{(1 + J_1 \tau_{(c,1)}^* g) \ln \left( \frac{1 - A_1^*}{a_1^* \tau_1^* A_1^*} \right)} \left[ 1 + J_1 \tau_{(c,1)}^* g \right] \right] - \theta_0 + Q_1^* (1 - A_1^*). \quad (5.57)
\]

Figure 5.5 shows the value of the jacket feed temperature to achieve 90% conversion of the reactant \( A \) as a function of the residence time in the jacket \( \tau_{(c,1)} \). This figure confirms that the required jacket feed temperature is an increasing function of the residence time in the jacket \( \tau_{(c,1)} \), i.e. a lower jacket feed temperature requires a lower jacket residence
time to achieve the specified conversion.

![Graph showing the relationship between First Jacket Residence Time and Jacket Feed Temperature.](image)

*Fig. 5.5:* The values of the residence time in the jacket \( \tau_{c,1} \) and the feed jacket temperature \( T_{0,c,1} \) when conversion of the reactant concentration \( A^*_1 = 0.1 \). The parameter values are \( T_0 = 680 \text{ K} \). The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1} \) and \( T_{c1} = 342 \text{ K} \).

Figures 5.6 shows the required jacket temperature to achieve 90% conversion in the first reactor as a function of feed temperature for different values of the characteristic temperature \( T_{c1} \) and the residence time in the first jacket \( \tau_{(c,1)} \). All of the figures show that if the feed temperature is sufficiently large \( (T_0 \geq 681.2 \text{ K}) \) the required value of the feed jacket temperature is zero. Under such circumstances the actual value of the jacket feed temperature is irrelevant. Thus the system can achieve the desired conversion without having a jacket around the reactor.

The most notable feature of these figures is the existence of an “intersection point”. The behaviour of the system is different on either side of this point. The required feed temperature to obtain 90% conversion rises when the residence time in the jacket decreases...
for lower values of the jacket feed temperature, $T_{0(c,1)} \leq 394$ K. When the jacket feed temperature is higher than this critical value, a higher feed temperature is required for higher values of the residence time in the jacket. This difference is explained in the subsequent example.

Substituting the values of characteristic temperature $T_{c1}$ and the residence time in the jacket $\tau_{(c,1)}$ to be 342 K and 0.513 s respectively as in Figure 5.6a, we find

$$T_{0(c,1)} = 161808.6402 - 503.2642321 T_0.$$ 

This equation shows that, for the given values of the characteristic temperature and the residence time in the jacket, the jacket feed temperature $T_{0(c,1)}$ is a decreasing function of the feed temperature $T_0$.

This critical value of the feed temperature and the jacket feed temperature at the intersection point increase as the characteristic temperature increases as shown in Figures 5.6b and 5.6c.

In conclusion, in order to achieve 90% conversion in the first reactor at a realistic feed temperature $T_0 < 1000$K, the characteristic temperature $T_{c1}$ and the heat of endothermicity ($Q_1$) are required to be small whereas the activation energy $E_1$ is required to be large. Finally, the jacket feed temperature has negligible influence on the feed temperature if the feed temperature is higher than some critical value.

### 5.5.2 Achieving 90% conversion in reactor two

In section 5.5.2.1 we investigate the influence of having jackets around reactors one and two. In section 5.5.2.4 we examine the effects of having a jacket around the second reactor only. In section 5.5.2.6 we consider the influence of the feed temperature upon the conversion.

#### 5.5.2.1 Two jacketed reactors

In this section we fix the catalyst in the first reactor to ensure slightly more than 90% conversion of the reactant $A_1^*$. We investigate how the choice of the catalyst in the second reactor affects the steady-state concentration $C_2^*$. We consider the case $E_2 = 50$ kJ mol$^{-1}$
The values of the feed jacket temperature $T_{0(c,1)}$ to obtain 90% conversion as a function of the feed temperature $T_0$ for different values of the jacket residence time $\tau_{(c,1)}$ and the characteristic temperature $T_{c1}$. The values of the residence time in the first jacket are $\tau_{(c,1)} = 0.513 \, \text{s (red)}, 1 \, \text{s (blue)}, 2 \, \text{s (green)}, 3 \, \text{s (brown)}$ and $4 \, \text{s (yellow)}$. The parameter values are $\tau_1 = 8 \, \text{s}, Q_1 = 100 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}$ and $E_1 = 80 \text{ kJ mol}^{-1}$.

and $Q_2 = 100 \text{ kJ mol}^{-1}$ and examine how the steady-state diagram varies as a function of the residence time in the second jacket $\tau_{(c,2)}$. The red and black branches in the steady-state diagrams shown in Figure 5.7 are stable and unstable, respectively. The high branch is called the high conversion branch and the low branch is called the low conversion branch (both branches are red).

We consider three scenarios: $\tau_{(c,2)} = 0.513 \times 10^{-7} \, \text{s}$, in section 5.5.2.1.1, $\tau_{(c,2)} = 0.513 \times 10^{-2} \, \text{s}$, in section 5.5.2.1.2 and $\tau_{(c,2)} = 0.513 \, \text{s}$, in section 5.5.2.1.3. Although these scenarios are unrealistic as the residence time in the jacket is too small, we study them to show the effect of the jacket residence time on the conversion.
5.5.2.1.1 Scenario one $\tau_{(c,2)} = 0.513 \times 10^{-7}$ s

Figure 5.7a shows the steady-state product diagram when the residence time in the second jacket is $\tau_{(c,2)} = 0.513 \times 10^{-7}$ s. In this figure the extinction and ignition limit point bifurcations occur at a jacket feed temperature $T_{0(c,2)}$: 82.019 K and 940.072 K respectively. A high conversion can be achieved by temporarily increasing the value of the jacket temperature past that of the ignition limit point. There is a minimum value of the jacket temperature that is required in order to operate on the high conversion branch. If the jacket temperature is decreased through this value then the system will “fall off” onto the low conversion branch. As this minimum temperature is $\sim 82.019$ K we conclude that this scenario will not occur.

Numerical solutions show that when $\tau_{(c,2)} = 0.513 \times 10^{-7}$ s this system always converges to the high conversion branch for any value of the jacket feed temperature higher than the extinction limit point $T_{0(c,2)} \geq 82.019$ K for our standard initial conditions. The reason for this is that our standard initial conditions are in the basin of attraction for the steady-state solutions on the high conversion branch.

Figure 5.7b shows the product conversion as a function of time when the jacket feed temperature $T_{0(c,2)} = 400$ K is 77%. Figure 5.7b shows that the system achieves high conversion quickly for low feed jacket temperature $T_{0(c,2)}$.

5.5.2.1.2 Scenario two $\tau_{(c,2)} = 0.513 \times 10^{-2}$ s

As the jacket residence time is increased to $\tau_{(c,2)} = 0.513 \times 10^{-2}$ s, the value of the feed jacket temperature at the extinction limit point moves into the left plane to $-28.386$ K and the ignition limit point moves to the right to 1047.148 K, passing the assumed operating value of the feed jacket temperature. The steady-state diagram following this transition is shown in Figure 5.7c. As the value of the jacket temperature at the ignition limit point is higher than the maximum possible value, it is no longer possible to reach the high conversion branch by increasing the jacket temperature. Instead, a temporary perturbation of some kind must be imposed onto the system to “kick” it from the low conversion branch onto the high conversion branch. Figure 5.7d shows the product concentration using our standard initial conditions. As in the previous scenario Figure 5.7d
shows that when $\tau_{(c,2)} = 0.513 \times 10^{-2}$ s the system operates a conversion of 78% when the jacket feed temperature $T_{0_{(c,2)}} = 400$ K for our standard initial conditions in very short time. This figure shows that if we start from our initial condition the system operates on the high conversion branch even though the feed jacket temperature is below the value at the ignition limit point.

5.5.2.1.3 Scenario three: higher values of the residence time in the jacket $\tau_{(c,2)}$

For higher values of the jacket residence time the extinction and ignition limit points move to the left and right respectively. For example, in Figure 5.7e, when the jacket residence time is increased to $\tau_{(c,2)} = 0.513$ s, the value of the jacket feed temperature at the extinction limit point moves into the left plane to $-10992.3$ K and the ignition limit point moves to the right to 11672.3 K. They are unrealistic! However, Figure 5.7f shows that for a lower value of the jacket feed temperature $T_{0_{(c,2)}} = 400$ K the system produces a conversion of 80% at the given residence time in the jacket ($\tau_{(c,2)}$) for our standard initial conditions. This conversion is higher than in the previous two cases.
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

(a) \( \tau_{(c,2)} = 0.513 \times 10^{-7} \text{ s.} \)

(b) The product conversion diagram when \( T_{0,c,2} = 400 \text{ K.} \)

(c) \( \tau_{(c,2)} = 0.513 \times 10^{-2} \text{ s.} \)

(d) The product conversion diagram when \( T_{0,c,2} = 400 \text{ K.} \)

(e) \( \tau_{(c,2)} = 0.513 \text{ s.} \)

(f) The product conversion diagram when \( T_{0,c,2} = 400 \text{ K.} \)

Fig. 5.7: The steady-state structure in the diabatic reactor. The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}, \tau_1 = 8 \text{ s}, \tau_2 = 8 \text{ s}, \tau_{(c,1)} = 0.513 \text{ s}, T_{c1} = 342 \text{ K}, T_{c2} = 435 \text{ K}, T_0 = 680 \text{ K} \) and \( T_{0,c,1} = 800 \text{ K.} \)
5.5.2.2 Using the residence time in the jacket

Figure 5.8 shows the steady-state product concentration $C_2$ as a function of the jacket residence time $\tau_{(c,2)}$. At the limit where the jacket residence time approaches zero we obtain the three steady-state solutions for the diabatic reactor (0.81, 0.25, 0.06). At the limit where the jacket residence time approaches infinity we obtain the three steady-state solutions for the adiabatic reactor (0.80, 0.38, 0.02). This figure confirms that the jacket residence time $\tau_{(c,2)}$ has a very weak effect on the conversion.

![Graph showing the relationship between dimensionless product concentration $C_2^*$ and dimensionless residence time in jacket 2 $\tau_{c,2}^*$.](image)

**Fig. 5.8:** The dimensionless product concentration in the second reactor $C_2^*$ as a function of the dimensionless residence time in jacket 2 $\tau_{c,2}^*$. The parameter values are $T_0 = 680$ K, $Q_1 = 100$ kJ mol$^{-1}$, $Q_2 = 100$ kJ mol$^{-1}$, $E_2 = 50$ kJ mol$^{-1}$, $E_1 = 80$ kJ mol$^{-1}$, $T_0_{(c,1)} = 800$ K, $T_0_{(c,2)} = 800$ K, $\tau_{(c,1)} = 0.513$ s, $\tau_1 = \tau_2 = 8$ s, $T_{c,2} = 435$ K and $T_{c,1} = 342$ K.
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

5.5.2.3 Jacketed reactor (R1) and Diabatic/Adiabatic reactor (R2)

We have seen that the second jacketed reactor acts as a diabatic reactor at the limit when the jacket residence time $\tau_{(c,2)}$ reaches zero, or as an adiabatic reactor when the jacket residence time $\tau_{(c,2)}$ approaches infinity. From this point we assume that the second reactor is diabatic and adiabatic in Tables 5.2 and 5.3 respectively and investigate how the characteristic temperature $T_{c2}$ influences the product conversion. These tables show that to achieve high product conversion we need low values of the characteristic temperature in the second reactor. The conversion for the diabatic reactor is slightly higher than that for the adiabatic reactor. This is consistent with Figure 5.8. The conversion has a dramatic decrease for higher values of the characteristic temperature in the second reactor.

Figures 5.9a and 5.9b show the product conversion ($C^*_2$) as a function of the characteristic temperature in the second reactor when the second reactor is diabatic and adiabatic, respectively. They explain the sharp drop in the product conversion as the characteristic temperature increases shown in Tables 5.2 and 5.3.

Tab. 5.2: The product concentration $C^*_2$ for different values of the characteristic temperature in the second reactor $T_{c2}$. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, \tau_{c,1} = 0.513 \text{ s}, \tau_1 = \tau_2 = 8 \text{ s}, T_{0(c,1)} = 800 \text{ K}, T_{a,2} = 1000 \text{ K}$ and $T_{c1} = 342 \text{ K}. (\text{Jacketed reactor } (R1) \text{ and Diabatic reactor } (R2).)$

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>Reactor 1 (Jacketed)</th>
<th>Reactor 2 (Diabatic)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A^*_1$</td>
<td>$\theta_1(T_1 \text{ K})$</td>
</tr>
<tr>
<td>340</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>405</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>435</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>442</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>448</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>464</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>511</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
</tbody>
</table>

5.5.2.4 Diabatic reactor (R1) and Jacketed reactor (R2)

In this section we fix the catalyst in the first reactor to ensure more than 90% conversion of the reactant $A^*_1 = 0.066$. We consider a reactor configuration where the first reactor is assumed to be diabatic whilst the second reactor is jacketed. We investigate how the choice of the catalyst in the second reactor and the operation of its jacket affects the steady-state concentration $C^*_2$. We consider the case $E_2 = 50 \text{ kJ mol}^{-1}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$ and
Tab. 5.3: The product concentration \( C_2^* \) for different values of the characteristic temperature in the second reactor \( T_{c2} \). The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, \tau_{c,1} = 0.513 \text{ s}, \tau_1 = \tau_2 = 8 \text{ s}, T_{0(c,1)} = 800 \text{ K} \) and \( T_{c1} = 342 \text{ K} \). (Jacketed reactor (R1) and Adiabatic reactor (R2).)

<table>
<thead>
<tr>
<th>( T_{c2} )</th>
<th>Reactor 1 (Jacketed)</th>
<th>Reactor 2 (Adiabatic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1^* )</td>
<td>( \theta_1(T_1 \text{ K}) )</td>
<td>( \theta_{(c,1)}(T_{(c,1)} \text{ K}) )</td>
</tr>
<tr>
<td>340</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>405</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>435</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>442</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>448</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>464</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
<tr>
<td>511</td>
<td>0.099183</td>
<td>0.065548 (394.2)</td>
</tr>
</tbody>
</table>

Fig. 5.9: The steady-state product \( C_2 \) as a function of the characteristic temperature \( T_{c2} \) when the second reactor is diabatic (Figure 5.9a) and adiabatic (Figure 5.9b). The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}, \tau_1 = \tau_2 = 8 \text{ s}, \tau_{(c,1)} = 0.513 \text{ s}, T_{c1} = 342 \text{ K}, T_0 = 680 \text{ K} \) and \( T_{0(c,1)} = 800 \text{ K} \).

Examine different values for the residence time in the jacket \( \tau_{(c,2)} \). The red and black branches in the steady-state diagrams shown in Figure 5.10 represent stable and unstable solutions, respectively. The higher branch is called the high conversion branch and the lower branch is called the low conversion branch (both branches are red).

As mentioned in Section 5.5.2.1 the scenarios considered are for unrealistic small values of the jacket residence time. However, the obtained results are useful to investigate the influence of the jacket residence time on the conversion.
5.5.2.4.1 Scenario one  $\tau_{c,2} = 0.513 \times 10^{-7}$ s

Figure 5.10a shows the steady-state product diagram when the residence time in the second jacket is $\tau_{c,2} = 0.513 \times 10^{-7}$ s. In this figure the extinction and the ignition limit point bifurcations occur when the jacket temperatures in the feed $T_{0(c,2)}$ are $-236.93$ K and $751.39$ K, respectively. High conversion can be achieved by temporarily increasing the value of the jacket temperature past that of the ignition limit point. It is then possible to decrease the jacket temperature to a lower value, in theory any other positive value. This case is good in practice as the value for the feed jacket temperature at the extinction limit point is not physically meaningful.

Figure 5.10b shows the product conversion as a function of time when the jacket feed temperature $T_{0(c,2)} = 400$ K is 84%. This figure shows that if we start from our initial conditions the system evolves to the high conversion branch even though the feed jacket temperature is below the value of that at the ignition limit point. Figure 5.10b shows that the system achieves high conversion quickly for low feed jacket temperature $T_{0(c,2)}$. This conversion is higher than the conversion achieved when both reactors are jacketed; see Figure 5.7b.

5.5.2.4.2 Scenario two  $\tau_{c,2} = 0.513 \times 10^{-2}$ s

Figure 5.10c shows the steady-state diagram when the jacket residence time is increased to $\tau_{c,2} = 0.513 \times 10^{-2}$ s. The value of the feed jacket temperature at the extinction limit point moves further into the left half plane to $-419.08$ K whilst the ignition limit point further moves to the right to occur at $816.94$ K. As in the previous scenario the system can be moved to the high conversion branch by temporarily increasing the jacket temperature value. However, the range between the ignition limit point and the critical value of the jacket feed temperature, $T_{0(c,x)} = 1000$ K, is now smaller.

Figure 5.10d shows that when the jacket feed temperature $T_{0(c,2)} = 400$ K the system achieves a conversion of 84.5% for our standard initial conditions. Therefore, to achieve high conversion we do not need a high feed jacket temperature. It is also higher than the conversion achieved when both reactors are jacketed; see Figure 5.7d.

In both Figures 5.10a and 5.10c in practice we can obtain a high conversion by oper-
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

Operating at a low jacket temperature, even at room temperature 298 K.

\[ \tau_{(c,2)} = 0.513 \times 10^{-7} \text{ s.} \]

\[ \tau_{c,2} = 0.513 \times 10^{-2} \text{ s.} \]

Fig. 5.10: The steady-state structure in the diabatic reactor (R1) and jacketed reactor (R2). The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1} \), \( Q_2 = 100 \text{ kJ mol}^{-1} \), \( E_1 = 80 \text{ kJ mol}^{-1} \), \( E_2 = 50 \text{ kJ mol}^{-1} \), \( T_{c1} = 342 \text{ K} \), \( T_{c2} = 435 \text{ K} \) and \( T_0 = 680 \text{ K} \).

5.5.2.5 The influence of the characteristic temperature \( T_{c2} \)

Table 5.4 examines the steady-state conversion as a function of the characteristic temperature in the second reactor \( T_{c2} \) when we have a diabatic reactor (R1) and a jacketed
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

reactor (R2). This table shows that to achieve high product conversion we need low values of the characteristic temperature in the second reactor. The conversion decreases dramatically when the value of the characteristic temperature in the second reactor is higher than 448 K. Figure 5.11 shows this dramatic drop in the product conversion as the characteristic temperature increases. This figure is obtained using numerical solutions.

We were unable to do this because Xpp could not continue the low conversion branch through the limit point and onto the intermediate solution branch. The reason for this is that the steady-state diagram becomes very steep.

Tab. 5.4: The product concentration $C^*_2$ for different values of the characteristic temperature in the second reactor $T_{c2}$. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, \tau_1 = 8 \text{ s}, \tau_2 = 8 \text{ s}, \tau_{(c,2)} = 0.513 \text{ s}, T_{a,1} = 800 \text{ K}, T_{0(c,2)} = 1000 \text{ K}$ and $T_{c1} = 342 \text{ K}.$

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>Reactor 1 (Diabatic)</th>
<th>Reactor 2 (Jacketed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A^*_1$ $\theta_1$</td>
<td>$C^<em>_2$ $B^</em><em>2$ $\theta_2$ $\theta</em>{(c,2)}$</td>
</tr>
<tr>
<td>405</td>
<td>0.066373 0.066744</td>
<td>0.914027 0.019600 0.115207 0.117401</td>
</tr>
<tr>
<td>435</td>
<td>0.066373 0.066744</td>
<td>0.859719 0.073908 0.112339 0.114656</td>
</tr>
<tr>
<td>442</td>
<td>0.066373 0.066744</td>
<td>0.829413 0.104214 0.110739 0.113125</td>
</tr>
<tr>
<td>448</td>
<td>0.066373 0.066744</td>
<td>0.786541 0.147086 0.108475 0.110958</td>
</tr>
<tr>
<td>464</td>
<td>0.066373 0.066744</td>
<td>0.010775 0.922852 0.067510 0.071753</td>
</tr>
<tr>
<td>511</td>
<td>0.066373 0.066744</td>
<td>0.002470 0.931157 0.067072 0.071334</td>
</tr>
</tbody>
</table>

5.5.2.6 The influence of feed temperature $T_0$ on the steady-state conversion

We now investigate how the choice of the feed temperature $\theta_0$ affects the steady-state concentration $C^*_2$. We consider the case $E_2 = 50 \text{ kJ mol}^{-1}$ and $Q_2 = 100 \text{ kJ mol}^{-1}$ and examine different values for the jacket feed temperatures in the first jacket $T_{0(c,1)}$ and second jacket $T_{0(c,2)}$. For simplicity we assume the jacket feed temperatures in the first jacket $T_{0(c,1)}$ and the second jacket $T_{0(c,2)}$ are equal. The dashed line in the following figure indicates the critical value of the feed temperature $T_0$ when 90% conversion is achieved $C^*_2 = 0.9$.

Figures 5.12a-5.12d show that as the jacket feed temperature is increased the critical value of the feed temperature to obtain 90% conversion is slightly decreased. Numerical simulations reveal that for our standard choice of the initial conditions the system always evolves to the high conversion branch when the feed temperature is sufficiently high. However, to obtain 90% conversion we need the feed temperature to be higher than
Fig. 5.11: The steady-state product \( C_2 \) as a function of the characteristic temperature \( T_{c2} \) when the first reactor is diabatic and the second reactor is jacketed. The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}, \tau_1 = 8 \text{ s}, \tau_2 = 8 \text{ s}, \tau_{(c,2)} = 0.513 \text{ s}, T_{c1} = 342 \text{ K}, T_0 = 680 \text{ K} \) and \( T_{0c,2} = 800 \text{ K} \).

5.6 Conclusion

In this chapter we consider a cascade reaction scheme consisting of two sequential reactions. This reaction takes place in a two reactor cascade. It is assumed that the outside of each reaction vessel is surrounded by a jacket. As there is no recycling, the steady-state behaviour in the first reactor is independent of that in the second reactor.

We first examined the operating conditions required in the first reactor to obtain a minimum of 90% conversion. Realistic feed temperatures to achieve 90% conversion, i.e. a feed temperature lower than 1000 K, require high activation energy, high jacket temperature, low characteristic temperature and low endothermicity in the first reactor. We showed that the feed temperature is more important than the feed jacket temperature to giving 90% conversion. In fact, for sufficiently high values of the feed temperature the
5. The Jacketed Reactor: Independent Coolant Temperature Around the Reactors

Fig. 5.12: The steady-state structure in the two jacketed reactors as a function of the feed temperature. The parameter values are \( Q_1 = 100 \text{ kJ mol}^{-1} \), \( Q_2 = 100 \text{ kJ mol}^{-1} \), \( E_1 = 80 \text{ kJ mol}^{-1} \), \( E_2 = 50 \text{ kJ mol}^{-1} \), \( \tau_1 = \tau_2 = 8 \text{ s} \), \( \tau_{(c,1)} = 0.513 \text{ s} \), \( \tau_{(c,2)} = 0.513 \text{ s} \) and \( T_{c1} = 342 \text{ K} \).

Feed jacket temperature required to achieve 90% conversion becomes zero. Also, we found that the values of the jacket feed temperature and the jacket residence time are almost inconsequential when compared to the role played by the feed temperature. Thereafter, we fixed the catalyst in the first reactor and examined how the choice of the catalyst and jacket temperature in the second reactor affected the product concentration leaving the reactor. We found that if the residence time in the jacket is sufficiently high, then the value of the jacket feed temperature is irrelevant, i.e./ high conversions can be achieved...
for any value of the feed jacket temperature.
6. **TASTE OF FUTURE WORK: THE JACKET RECYCLE REACTOR**

In the previous chapter the feed temperature for the jackets is an independent variable. In this chapter we consider the case when the effluent stream leaving the second reactor is the influent stream for the jacket surrounding this reactor. We call this system configuration the *jacket recycle* system. We examine the process efficiency of such reactor configuration.

### 6.1 Case one: $\theta_{0_{(c,2)}} = \theta_2$

In this section we use the effluent stream leaving the second reactor, at a temperature ($\theta_2$), as the feed stream for the jacket of the second reactor. We retain the jacket temperature for the jacket surrounding the first reactor as an independent variable.

#### 6.1.1 Reactor configuration

Figure 6.1 shows the processes that occur in the reactor cascade. The concentrations of the reactant $A$ and the intermediate $B$ leaving reactor one are $A_1$ and $B_1$ respectively. The concentrations of the reactant $A$ and the intermediate $B$ and the product $C$ leaving reactor two are $A_2$, $B_2$ and $C_2$ respectively. The jacket temperatures in the feed stream for reactors one and two are $T_{0_{(c,1)}}$ and $T_2$ respectively. The temperatures of the jackets around reactors one and two are $T_{(c,1)}$ and $T_{(c,2)}$ respectively. The temperatures of the reacting mixture in reactors one and two are $T_1$ and $T_2$ respectively.

#### 6.1.2 Dimensional equations

The system of equations in the first reactor is given by equations (6.1)–(6.8).
Fig. 6.1: Prototype reactor configuration. \( A_0 \) is the feed concentration, \( T_0 \) is the feed temperature, \( T_{0(c,1)} \) is the jacket temperatures in the feed stream for reactors one, \( T_{(c,1)} \) and \( T_{(c,2)} \) are the temperatures of the jacket around reactors one and two respectively, \( T_2 \) is the recycled effluent stream for the second reactor and \( q \) is the flow rate.

The rate of change of the concentration of the reactant \( A \).

\[
V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp\left[-\frac{E_1}{RT_1}\right] A_1. \tag{6.1}
\]

The rate of change of the concentration of the intermediate \( B \).

\[
V_1 \frac{dB_1}{dt} = -qB_1 + V_1 a_1 \exp\left[-\frac{E_1}{RT_1}\right] A_1. \tag{6.2}
\]

The rate of change of the concentration of the product \( C \).

\[
V_1 \frac{dC_1}{dt} = q(C_0 - C_1). \tag{6.3}
\]

The rate of change of the reactor temperature.

\[
c_{pg} \rho_g V_1 \frac{dT_1}{dt} = q c_{pg} \rho_g (T_0 - T_1) - Q_1 V_1 a_1 \exp\left[-\frac{E_1}{RT_1}\right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{(c,1)}). \tag{6.4}
\]

The rate of change of the jacket temperature.

\[
c_{pg(c,1)} \rho_{g(c,1)} V_{(c,1)} \frac{dT_{(c,1)}}{dt} = q_{(c,1)} c_{pg(c,1)} \rho_{g(c,1)} (T_{0(c,1)} - T_{(c,1)}) + J_1 \chi_1 S_1 (T_1 - T_{(c,1)}). \tag{6.5}
\]
The initial conditions are given by equation (6.6). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state

$$\begin{align*}
A_1(0) &= B_1(0) = C_1(0) = 0, \\
T_1(0) &= \frac{q c_{pg} \rho_g T_0 + q_{(c,1)} c_{pg(r,1)} \rho_{g(r,1)} (T_{0(r,1)} - T_{(c,1)}(0))}{q c_{pg} \rho_g}, \\
T_{(c,1)}(0) &= \frac{q_{(c,1)} c_{pg(r,1)} \rho_{g(r,1)} (q c_{pg} \rho_g + J_{1} \chi_{1} S_{1}) T_{0(r,1)} + J_{1} \chi_{1} S_{1} q c_{pg} \rho_g T_0}{q_{(c,1)} c_{pg(r,1)} \rho_{g(r,1)} (q c_{pg} \rho_g + J_{1} \chi_{1} S_{1}) + J_{1} \chi_{1} S_{1} q c_{pg} \rho_g}.
\end{align*}$$

(6.6)

The residence time in the reactor

$$\tau_1 = \frac{V_1}{q}. \quad (6.7)$$

The residence time in the jacket

$$\tau_{(c,1)} = \frac{V_{(c,1)}}{q_{(c,1)}}. \quad (6.8)$$

The system of equations in the second reactor are equations (6.9)–(6.16).

The rate of change of the concentration of the reactant $A$.

$$V_2 \frac{dA_2}{dt} = q(A_1 - A_2). \quad (6.9)$$

The rate of change of the concentration of reactant $B$.

$$V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \quad (6.10)$$
The rate of change of the concentration of reactant $C$.

$$V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \quad (6.11)$$

The rate of change of the reactor temperature.

$$c_{pg} \rho_g V_2 \frac{dT_2}{dt} =qc_{pg} \rho_g (T_1 - T_2) + Q_2 V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2 - J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \quad (6.12)$$

The rate of change of the jacket temperature.

$$c_{pg} \rho_g V_{(c,2)} \frac{dT_{(c,2)}}{dt} = q_{(c,2)} c_{pg} \rho_g (T_2 - T_{(c,2)}) + J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \quad (6.13)$$

We assume that there is no heat loss in the fluid between leaving the second reactor and entering the jacket. The feed stream for the jacket around the second reactor is the stream leaving reactor two. To reiterate what is new in this model the feed temperature entering the second jacket is the effluent stream leaving the second reactor, i.e. $T_{0_{(c,2)}} = T_2$.

The initial conditions are given by equation (6.14). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state.

$$A_2(0) = B_2(0) = C_2(0) = 0, \quad T_2(0) = T_1(0), \quad T_{(c,2)}(0) = T_2(0) = T_1(0). \quad (6.14)$$

The residence time in the reactor

$$\tau_2 = \frac{V_2}{q}, \quad (6.15)$$
The residence time in the jacket

\[ \tau_{(c,2)} = \frac{V_{(c,2)}}{q_{(c,2)}}. \] (6.16)

6.1.3 Dimensionless equations

In non-dimensionalising equations we introduce dimensionless concentrations \( A_i^* = A_i/A_0, B_i^* = B_i/A_0 \) and \( C_i^* = C_i/A_0 \), dimensionless temperatures \( \theta_i = (RT_i)/E_2 \), dimensionless jacket temperatures \( \theta_{c,i} = (RT_{c,i})/E_2 \), where \( i = 1, 2 \), and dimensionless time \( t^* = (\chi_2 S_2 t)/(c_p \rho_g V_2) \).

From now on we assume that there is no intermediate or product in the feed stream, i.e. \( B_0 = B_0^* = [B_0/A_0] = 0 \) and \( C_0 = C_0^* = [C_0/A_0] = 0 \). The non-dimensional equations in the first reactor are given by equations (6.17)–(6.21):

\[
\frac{dA_1^*}{dt^*} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[-\frac{E_1^*}{\theta_1}\right] A_1^*, \tag{6.17}
\]

\[
\frac{dB_1^*}{dt^*} = \frac{B_0^* - B_1^*}{\tau_1^*} + a_1^* \exp \left[-\frac{E_1^*}{\theta_1}\right] A_1^*, \tag{6.18}
\]

\[
\frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[-\frac{E_1^*}{\theta_1}\right] A_1^* - J_1 \chi_{T,1}^* (\theta_1 - \theta_{c,1}), \tag{6.19}
\]

\[
\frac{d\theta_{c,1}}{dt^*} = \frac{H_1 (\theta_{0,c,1} - \theta_{c,1})}{\tau_{c,1}^*} + J_1 H_1 G (\theta_1 - \theta_{c,1}). \tag{6.20}
\]

The nondimensional initial conditions are

\[ A_1^*(0) = B_1^*(0) = C_1^*(0) = 0, \]

\[ \theta_1(0) = \frac{\tau_{c,1}^* G \theta_0 + \chi_{T,1}^* \tau_1^* (\theta_{0,c,1} - \theta_{c,1})}{\tau_{c,1}^* G}, \]

\[ \theta_{c,1}(0) = \frac{(1 + J_1 \chi_{T,1}^* \tau_1^*) \theta_{0,c,1} + J_1 \tau_{c,1}^* G \theta_0}{(1 + J_1 \chi_{T,1}^* \tau_1^*) + J_1 \tau_{c,1}^* G}. \tag{6.21} \]
The non-dimensional equations in the second reactor are given by equations (6.22)–(6.27):

\[
\begin{align*}
\frac{dA^*_2}{dt^*} &= \frac{A^*_1 - A^*_2}{\tau^*_2}, \\
\frac{dB^*_2}{dt^*} &= \frac{1 - A^*_1 - B^*_2}{\tau^*_2} - a^*_2 \exp \left( -\frac{1}{\theta_2} \right) B^*_2, \\
\frac{dC^*_2}{dt^*} &= \frac{-C^*_2}{\tau^*_2} + a^*_2 \exp \left( -\frac{1}{\theta_2} \right) B^*_2, \\
\frac{db^*_2}{dt^*} &= \frac{\theta_1 - \theta_2}{\tau^*_2} + Q^*_2 a^*_2 \exp \left( -\frac{1}{\theta_2} \right) B^*_2 - J_2(\theta_2 - \theta_{c,2}), \\
\frac{d\theta_{c,2}}{dt^*} &= \frac{H_2(\theta_2 - \theta_{c,2})}{\tau^*_{c,2}} + J_2 H_2(\theta_2 - \theta_{c,2}).
\end{align*}
\]

The nondimensional initial conditions are

\[
A^*_2(0) = B^*_2(0) = C^*_2(0) = 0, \quad \theta_2(0) = \theta_1(0), \quad \theta_{(c,2)}(0) = \theta_2(0).
\]

6.1.4 Steady-state jacket equation

In this section we find the steady-state jacket temperature. At the steady-state we have

\[
\frac{H_2(\theta_2 - \theta_{c,2})}{\tau^*_{c,2}} + J_2 H_2(\theta_2 - \theta_{c,2}) = 0
\]

\[
\Rightarrow \theta_{(c,2)} = \theta_2.
\]

This means that the steady-state jacket temperature equals the steady-state reactor temperature. Consequently, at the steady-state there is no heat transfer between the fluid in the second reactor and the jacket. Under these conditions the second reactor effectively operates as an adiabatic reactor. We do not investigate this model configuration as we discussed this case in chapter 5.5.2.2.

6.2 Case two: \( \theta_{0(c,2)} = \theta_2 \) and \( \theta_{0(c,1)} = \theta_{c,2} \)

In this section we change the model from the previous section. We use the exit stream from the jacket surrounding the second reactor as the feed stream for the jacket surrounding the first reactor. We generally discuss the influence of the recycled stream upon the product conversion.
6.2.1 Reactor configuration

Figure 6.2 shows the processes that occur in the reactor cascade. The concentrations of the reactant \( A \) and the intermediate \( B \) leaving reactor one are \( A_1 \) and \( B_1 \) respectively. The concentrations of the reactant \( A \) and the intermediate \( B \) and the product \( C \) leaving reactor two are \( A_2, B_2 \) and \( C_2 \) respectively. The jacket temperature in the feed stream is \( T_2 \). At the steady-state we know from the previous section that the jacket temperature for the first jacket is \( T_2 \). The temperatures of the jackets around reactors one and two are \( T_{(c,1)} \) and \( T_{(c,2)} \), respectively. The temperatures of the reacting mixture in reactors one and two are \( T_1 \) and \( T_2 \), respectively. To clarify the difference between the recycle system in case one 6.1 and case two 6.2 look at Figures 6.1 and 6.2, respectively.

![Prototype reactor configuration](image)

Fig. 6.2: Prototype reactor configuration. \( A_0 \) is the feed concentration, \( T_0 \) is the feed temperature, \( T_{0(c,1)} \) and \( T_{0(c,2)} \) are the jacket temperatures in the feed stream for reactors one and two respectively, \( T_{(c,1)} \) and \( T_{(c,2)} \) are the temperatures of the jackets around reactors one and two respectively and \( q \) is the flow rate.

6.2.2 Dimensional equations

The system of equations in the first reactor is:

The rate of change of the concentration of the reactant \( A \).

\[
V_1 \frac{dA_1}{dt} = q(A_0 - A_1) - V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1. \tag{6.28}
\]

The rate of change of the concentration of the intermediate \( B \).

\[
V_1 \frac{dB_1}{dt} = -qB_1 + V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1. \tag{6.29}
\]
The rate of change of the concentration of the product $C$.

$$V_1 \frac{dC_1}{dt} = q(C_0 - C_1). \quad (6.30)$$

The rate of change of the reactor temperature.

$$c_{pg}\rho_g V_1 \frac{dT_1}{dt} = q c_{pg}\rho_g (T_0 - T_1) - Q_1 V_1 a_1 \exp \left[ \frac{-E_1}{RT_1} \right] A_1 - J_1 \chi_1 S_1 (T_1 - T_{(c,1)}). \quad (6.31)$$

The rate of change of the jacket temperature.

$$c_{pg}\rho_g V_{(c,1)} \frac{dT_{(c,1)}}{dt} = q_{(c,1)} c_{pg}\rho_g (T_{(c,2)} - T_{(c,1)}) + J_1 \chi_1 S_1 (T_1 - T_{(c,1)}). \quad (6.32)$$

The feed steam in this jacket is the exit stream coming from the jacket around the second reactor. The difference in this model is that the feed temperature entering the first jacket is the effluent stream leaving the second jacket, i.e. $T_0_{(c,1)} = T_{(c,2)}$.

The initial conditions are given by equation (6.33). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when $t = 0$. During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state.

$$A_1(0) = B_1(0) = C_1(0) = 0, \quad T_1(0) = T_0, \quad T_{(c,1)}(0) = T_1(0) = T_0. \quad (6.33)$$

The residence time in the reactor

$$\tau_1 = \frac{V_1}{q}. \quad (6.34)$$
The residence time in the jacket

\[ \tau_{(c,1)} = \frac{V_{(c,1)}}{q_{(c,1)}}. \]  

(6.35)

The system of equations in the second reactor is:

The rate of change of the concentration of the reactant A.

\[ V_2 \frac{dA_2}{dt} = q(A_1 - A_2). \]  

(6.36)

The rate of change of the concentration of reactant B.

\[ V_2 \frac{dB_2}{dt} = q(B_1 - B_2) - V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \]  

(6.37)

The rate of change of the concentration of reactant C.

\[ V_2 \frac{dC_2}{dt} = q(C_1 - C_2) + V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2. \]  

(6.38)

The rate of change of the reactor temperature.

\[ c_{pg} \rho_g V_2 \frac{dT_2}{dt} = q c_{pg} \rho_g (T_1 - T_2) + Q_2 V_2 a_2 \exp \left[ \frac{-E_2}{RT_2} \right] B_2 - J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \]  

(6.39)

The rate of change of the jacket temperature.

\[ c_{pg} \rho_g V_{(c,2)} \frac{dT_{(c,2)}}{dt} = q_{(c,2)} c_{pg} \rho_g (T_2 - T_{(c,2)}) + J_2 \chi_2 S_2 (T_2 - T_{(c,2)}). \]  

(6.40)

The feed stream in the jacket around the second reactor is the stream leaving reactor two, i.e. \( T_{0_{(c,2)}} = T_2 \).
The initial conditions are given by equation (6.41). Before the reaction is started it is assumed that an inert gas flows inside both reactors so that all concentrations are equal to zero when \( t = 0 \). During this pre-reaction period, the temperature is assumed to have reached the corresponding steady-state.

\[
A_2(0) = B_2(0) = C_2(0) = 0, \quad T_2(0) = T_1(0), \quad T_{(c,2)}(0) = T_2(0) = T_1(0).
\] (6.41)

The residence time in the reactor

\[
\tau_2 = \frac{V_2}{q}.
\] (6.42)

The residence time in the jacket

\[
\tau_{(c,2)} = \frac{V_{(c,2)}}{q_{(c,2)}}.
\] (6.43)

### 6.2.3 Dimensionless equations

In nondimensionalising equations we introduce dimensionless concentrations (\( A_i^* = A_i/A_0, B_i^* = B_i/A_0, C_i^* = C_i/A_0 \)), dimensionless temperatures (\( \theta_i = (RT_i)/E_2 \)), dimensionless jacket temperatures (\( \theta_{c,i} = (RT_{c,i})/E_2 \)), where \( i = 1, 2 \), and dimensionless time (\( t^* = (\chi_2 S_2 t)/(c_p \rho_g V_2) \)).

From now on we assume that there is no intermediate or product in the feed stream, i.e. \( B_0 = B_0^* = [B_0/A_0] = 0 \) and \( C_0 = C_0^* = [C_0/A_0] = 0 \). The non-dimensional equations in the first reactor are:

\[
\frac{dA_1^*}{dt^*} = \frac{1 - A_1^*}{\tau_1^*} - a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^*,
\] (6.44)

\[
\frac{dB_1^*}{dt^*} = \frac{B_0^* - B_1^*}{\tau_1^*} + a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^*,
\] (6.45)

\[
\frac{d\theta_1}{dt^*} = \frac{\theta_0 - \theta_1}{\tau_1^*} - Q_1^* a_1^* \exp \left[ \frac{-E_1^*}{\theta_1} \right] A_1^* - J_1 \chi_{T,1}^*(\theta_1 - \theta_{c,1}),
\] (6.46)

\[
\frac{d\theta_{c,1}}{dt^*} = \frac{H_1(\theta_{0c,1} - \theta_{c,1})}{\tau_{c,1}^*} + J_1 H_1 G(\theta_1 - \theta_{c,1}).
\] (6.47)
The nondimensional initial conditions are

\[ A_1^*(0) = B_1^*(0) = C_1^*(0) = 0, \quad \theta_1(0) = \theta_0, \quad \theta_{c,1}(0) = \theta_1(0) = \theta_0. \] (6.48)

The non-dimensional equations in the second reactor are:

\[
\frac{dA_2^*}{dt^*} = \frac{A_1^* - A_2^*}{\tau_2^*}, \quad (6.49)
\]
\[
\frac{dB_2^*}{dt^*} = 1 - \frac{A_1^* - B_2^*}{\tau_2^*} - a_2^* \exp \left[ \frac{-1}{\theta_2} \right] B_2^*, \quad (6.50)
\]
\[
\frac{dC_2^*}{dt^*} = \frac{-C_2^*}{\tau_2^*} + a_2^* \exp \left[ \frac{-1}{\theta_2} \right] B_2^*, \quad (6.51)
\]
\[
\frac{d\theta_2}{dt^*} = \frac{\theta_1 - \theta_2}{\tau_2^*} + Q_2^* a_2^* \exp \left[ \frac{-1}{\theta_2} \right] B_2^* - J_2(\theta_2 - \theta_{c,2}), \quad (6.52)
\]
\[
\frac{d\theta_{c,2}}{dt^*} = \frac{H_2(\theta_2 - \theta_{c,2})}{\tau_{c,2}^*} + J_2 H_2(\theta_2 - \theta_{c,2}). \quad (6.53)
\]

The nondimensional initial conditions are

\[ A_2^*(0) = B_2^*(0) = C_2^*(0) = 0, \quad \theta_2(0) = \theta_1(0), \quad \theta_{(c,2)}(0) = \theta_2(0) = \theta_1(0) \] (6.54)

\[ \theta_{(c,2)}(0) = \theta_1(0) \] (6.55)

### 6.2.4 General results and discussion

All calculations performed in this thesis use the industrial parameter values stated in Appendix .1, unless otherwise stated. The analysis of this section is not claimed to be complete. Rather it is included as a “taster” for future work.

#### 6.2.4.1 Varying the feed temperature \( T_0 \)

To achieve 90% conversion of the reactant \( A \) into the product \( C \) we must achieve at least 90% conversion of the reactant into the intermediate species \( B \) in the first reactor. We now investigate how the choice of the feed temperature \( \theta_0 \) affects the steady-state concentration \( C_2^* \).

In the previous chapter the behaviour of the first reactor was independent of the behaviour of the second reactor. Consequently we could cordially investigate the influence of the feed temperature \( \theta_0 \) and the jacket feed temperature \( \theta_{0(c,1)} \) on the conversion in the
first reactor independently. We could use this to identify a good catalyst in the first reactor that gives at least 90% conversion of the reactant $A$. We could then investigate the behaviour of the second reactor.

In this chapter the behaviour of the first reactor is no longer independent of the behaviour of the second reactor. The jacket system around the first reactor depends upon the effluent stream leaving the second reactor. The feed temperature entering the second jacket is the temperature leaving the second reactor. The feed temperature entering the first jacket is the exit temperature from the second jacket. Thus we cannot examine the first reactor separately before analysing the second reactor. We will only examine the influence of the feed temperature on the product conversion.

Figures 6.3 and 6.4 show the steady state diagrams for the product concentration as function of the feed temperature when the heat of exothermicity $Q_2$ is 50 and 100 kJ mol$^{-1}$, respectively. The red and black branches in the steady-state diagrams shown in Figures 6.3 and 6.4 are stable and unstable, respectively. The high branch is called the high conversion branch and the low branch is called the low conversion branch (both branches are red). The intermediate branch is unstable. The vertical line at $T_0 = 680$ K represents our experimental feed temperature.

Figure 6.3a shows that for the smallest value of the activation energy $E_2 = 50$ kJ mol$^{-1}$ the steady-state diagram has no limit points. For this value of the activation energy a very high feed temperature is required to achieve the desired conversion. This value is approximately 832 K.

Figure 6.3b shows that when the activation energy is increased to 100 kJ mol$^{-1}$ the high conversion branch exists. Numerical simulations reveal that the system always evolves to the high conversion branch for our standard initial conditions. In this figure the extinction and the ignition limit points occur at 650.2 K and 720.4 K, respectively. The critical value of the feed temperature to obtain 90% conversion is approximately 692 K.

In Figure 6.3c, the extinction and the ignition limit point bifurcations occur at 599.6 K and 718.2 K, respectively. The required feed temperature to obtain 90% conversion is slightly decreased to approximately 681 K when the activation energy $E_2$ is 150 kJ mol$^{-1}$.

Figures 6.3b and 6.3c show that for any value of the feed temperature higher than the feed temperature at the extinction limit point the system always evolves to the high
Figure 6.4 shows that when the heat of exothermicity $Q_2$ is increased from 50 kJ mol$^{-1}$ to 100 kJ mol$^{-1}$ there is now two limit points for each chosen value of the activation energy. The critical value of the feed temperature to obtain high yield of the product is approximately 752 K for the lowest value of the activation energy $E_2 = 50$ kJ mol$^{-1}$ and 679 K for both of the higher values of the activation energy. These values are lower than the values when the heat of exothermicity is $Q_2 = 50$ kJ mol$^{-1}$.

Figures 6.3 and 6.4 show that the product conversion when the heat of exothermicity $Q_2 = 50$ kJ mol$^{-1}$ is lower than that when the heat of exothermicity $Q_2 = 100$ kJ mol$^{-1}$ for our standard initial conditions.

Figures 6.5 and 6.6 show the product conversion as a function of the heat of exothermicity $Q_2$ for a fixed value of the feed temperature $T_0 = 680$ K and the characteristic temperature $T_{c2} = 435$ K when the activation energy is either 50 kJmol$^{-1}$ or 100 kJmol$^{-1}$, respectively. These figures explain the reason for the decrease in the critical value of the feed temperature required to achieve high conversion. Figure 6.6 shows that the system operates at a low conversion branch when the heat of exothermicity is lower than 70 kJmol$^{-1}$. These results make sense. It is easier to obtain high product concentration at lower values of the feed temperature for reactions with a high heat of exothermicity.
(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 100 \text{ kJ mol}^{-1}$.

(c) $E_2 = 150 \text{ kJ mol}^{-1}$.

Fig. 6.3: The steady-state structure in the two recycle reactor as a function of the feed temperature. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}, Q_2 = 50 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, \tau_1 = \tau_2 = 8 \text{ s}, \tau_{(c,1)} = 0.513 \text{ s}, \tau_{(c,2)} = 0.513 \text{ s}, T_{c1} = 435 \text{ K}$ and $T_{c2} = 342 \text{ K}$. 
6. Taste of Future Work: The Jacket Recycle Reactor

Fig. 6.4: The steady-state structure in the two recycle reactor as a function of the feed temperature. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}$, $Q_2 = 100 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $\tau_1 = \tau_2 = 8 \text{ s}$, $\tau_{(c,1)} = 0.513 \text{ s}$, $\tau_{(c,2)} = 0.513 \text{ s}$, $T_{c2} = 435 \text{ K}$ and $T_{c1} = 342 \text{ K}$.

(a) $E_2 = 50 \text{ kJ mol}^{-1}$.

(b) $E_2 = 100 \text{ kJ mol}^{-1}$.

(c) $E_2 = 150 \text{ kJ mol}^{-1}$.
Fig. 6.5: The steady-state product $C_2$ as a function of the heat of exothermicity $Q_2$. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$, $E_2 = 100 \text{ kJ mol}^{-1}$, $\tau_1 = 8 \text{ s}$, $\tau_2 = 8 \text{ s}$, $\tau_{(c,1)} = \tau_{(c,2)} = 0.513 \text{ s}$, $T_{c1} = 342 \text{ K}$, $T_{c2} = 435 \text{ K}$ and $T_0 = 680 \text{ K}$. 
Fig. 6.6: The steady-state product $C_2$ as a function of the heat of exothermicity $Q_2$. The parameter values are $Q_1 = 100 \text{ kJ mol}^{-1}, E_1 = 80 \text{ kJ mol}^{-1}, E_2 = 50 \text{ kJ mol}^{-1}, \tau_1 = 8 \text{ s}, \tau_2 = 8 \text{ s}, \tau_{(c,1)} = \tau_{(c,2)} = 0.513(\text{s}), T_{c1} = 342 \text{ K}, T_{c2} = 435 \text{ K}$ and $T_0 = 680 \text{ K}.$
6.2.4.2 Varying the characteristic temperature $T_{c2}$

Tables 6.1 shows the product concentration as a function of the characteristic temperature $T_{c2}$ and the activation energy $E_2$ for the jacket recycle reactor. It also shows that to achieve high product conversion we need low values of the characteristic temperature in the second reactor. The conversion decreases dramatically when the values of the characteristic temperature in the second reactor is higher than 500 K. Figure 6.7 shows this dramatic drop in the product conversion as the characteristic temperature increases in the recycle stream.

Figures 6.5, 6.6 and 6.7 were obtained by integrating the governing equations. In theory, it should have been possible to obtain the steady-state diagram using Xpp. However, we were unable to do this because Xpp could not continue the low conversion branch through the limit point and onto the intermediate solution branch. The reason for this is that the steady-state becomes very steep near the limit point.

Tab. 6.1: The product concentration $C_2^*$ for different values of the characteristic temperature in the second reactor $T_{c2}$ and the activation energy for the exothermic reaction $E_2$. The parameter values are $Q_1 = 100$ kJ mol$^{-1}$, $Q_2 = 100$ kJ mol$^{-1}$, $\tau_{c,1} = \tau_{c,2} = 0.513$ s, $\tau_1 = \tau_2 = 8$ s, $T_{0(c,1)} = T_{0(c,2)} = 800$ K, $T_0 = 680$ K and $T_{c1} = 342$ K. (Recycled reactor)

<table>
<thead>
<tr>
<th>$T_{c2}$</th>
<th>$C_2^*(E_2 = 50)$</th>
<th>$C_2^*(E_2 = 80)$</th>
<th>$C_2^*(E_2 = 120)$</th>
<th>$C_2^*(E_2 = 180)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.881</td>
<td>0.901</td>
<td>0.900</td>
<td>0.900</td>
</tr>
<tr>
<td>500</td>
<td>0.002</td>
<td>0.813</td>
<td>0.898</td>
<td>0.900</td>
</tr>
<tr>
<td>600</td>
<td>0.0002</td>
<td>0.00002</td>
<td>$4 \times 10^{-6}$</td>
<td>$1 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

6.3 Conclusion

In this chapter, the effluent stream leaving the second reactor is recycled in the feed stream for the jacket surrounding the second reactor. At the steady-state, the second reactor operates as an adiabatic reactor. This case is discussed in chapter 5.5.2.2.

We briefly investigated what happens when the feed temperature for the second jacket is the effluent stream leaving the second reactor $\theta_{0(c,2)} = \theta_2$ and the feed temperature for the first jacket is the effluent stream leaving the second jacket $\theta_{0(c,1)} = \theta_{(c,2)}$. We examined the process efficiency of such reactor configuration. For the parameter values considered we need a high feed temperature to start up the reaction and to have a hot stream leaving
the second reactor to heat up the reactors. We found that we need a high value of the heat of exothermicity \( Q_2 \) and a low value of the characteristic temperature \( T_{c2} \) to achieve the desired conversion for realistic feed temperature.

The ideal scenario is to achieve 90% product conversion. What catalyst properties will ensure this? Is there a minimum value for the heat of exothermicity for this to happen? This model is interesting and will be investigated wisely in the future.
7. CONCLUSIONS

In our final chapter we summarize the contributions of this thesis and discuss important directions for further work.

7.1 Summary of thesis contributions

The central problem addressed in this thesis is to develop mathematical models which describe the operation of autothermal process. Before we summarize the specific technical contributions, below are the main conclusions emerging from our work:

- It is beneficial to obtain at least 90% conversion in the first reactor to ensure that the system achieves the desired product conversion of 90%. Obtaining a high conversion in the first reactor does not guarantee that the second reactor will provide the desired conversion. This can only be achieved by finding a good choice of catalyst in the second reactor.

- To find a good choice of catalyst in the second reactor we should work backwards by fixing the product conversion to 90%. From this we can find the catalyst properties that will give the desired conversion.

7.1.1 The research outcomes

The basic outcome for our thesis is to construct a model configuration for the cascade reaction

\[ A \rightarrow B \rightarrow C \]

occurring in two separate reactors where there is a catalyst for the endothermic process in the first reactor and a catalyst for the exothermic process in the second reactor. The main advantage of this system is that it achieves an important goal:
7. Conclusions

- It provides us with a general method to discover which catalysts are superior to obtain the desired conversion.

7.1.1.1 Discussion

What all chapters in this thesis have in common is that they used two continuously stirred tank reactors (CSTR). In Chapter 2 we described a model configuration for adiabatic operation in which the heat-transfer across the walls of the reactor is assumed to be negligible.

It is shown that the number of equations for the system can be reduced. In the adiabatic case the model can be reduced to two equations, one in each reactor. The main result in this chapter that it is very difficult to obtain high conversion in the first reactor. The conversion in the second reactor critically depends upon what leaves the first reactor. To obtain a high product conversion we need to increase the feed temperature and combine it with a good choice of parameter values for the catalyst in the first reactor.

In Chapter 3 we developed a mathematical model describing the operation of a diabatic reactor. This model relaxes the assumption that the heat-transfer through the walls of the reactor is negligible. However, it is assumed that the reactor walls are held at a constant temperature.

We showed that in order to achieve 90% conversion in the first reactor at a realistic feed temperature, i.e. a feed temperature lower than 1000 (K), a catalyst with a high activation energy, a low characteristic temperature and a high coolant temperature are all required. Reactions with a high heat of endothermicity are harder to operate autothermally. For reactions with a lower heat of endothermicity it is easier to operate autothermally. We also showed how the choice of the catalyst and the coolant temperature in the second reactor affect the product concentration leaving the reactor. We found seven steady-state diagrams for the chosen parameters.

The important contribution of this chapter is the use of the limit point unfolding diagram to identify all different transitions between the steady-state diagrams. The best possible region, which we called the ‘autothermal region’, requires a catalyst with a low characteristic temperature in the second reactor. In this region both limit points occur at a negative value for the primary bifurcation parameter. In practice the second region,
where the ignition limit point is positive and below the value of the operating temperature, is still highly desirable.

Chapter 4 is based on a question asked at the NSW ANZIAM conference (6-9/12/2015). To answer this question we extended the diabatic model from Chapter 3 by increasing the number of reactors to four. We found that the four reactor cascade is mostly superior to the two reactor cascade. This is not unexpected because if we obtain 90% product concentration $C$ it is good but there is 10% of the reactant $A$ left. Consequently, reactor number three ‘can’ convert this 10% into intermediate $B$ and then reactor number four is going to clear it up.

A cascade with six reactors will show insignificant improvement because a very small amount of the reactant $A$ left will leave reactor four. The cost of increasing the number of reactors in series might be a financial obstacle. For the system considered in this thesis the four reactor system is mostly superior to the two reactor system and it is always superior to the six reactor system.

In Chapter 5 we consider the placement of a jacket around the outside of the reaction vessels to control the reaction temperature. This relaxes the assumption that the temperature of the reactor walls is constant. We found that for sufficiently high values of the feed temperature, the feed jacket temperature required to achieve the desired conversion in the first reactor is negligible. We found that high product conversion can be achieved for smaller values of the residence time in the second jacket.

In Chapter 5 the feed temperature for the jackets is an independent variable. In Chapter 6 we consider the case when the effluent stream leaving the second reactor is the influent stream for the jacket surrounding this reactor. The feed temperature for the jackets is not an independent variable anymore. We briefly investigated the process efficiency of such a reactor configuration. We found that we need a high value of the heat of exothermicity ($Q_2$) and a low value of the characteristic temperature ($T_{c2}$) to achieve the desired conversion for a realistic feed temperature. This model is interesting and will be investigated wisely in the future.
7. Conclusions

7.1.2 Future work

From a physical point of view, the energy coming out from the second reactor can be reused to supply energy to heat up the jacket surrounding the first reactor. This idea is introduced in Chapter 6. The main result in this model is that high feed temperature is required. It would interesting to explore the operating conditions to improve the product yield. Also, we will look at the two reactors in concentric arrangement i.e. exothermic reactor enveloping the endothermal reactor or vice-versa, e.g. a double-pipe heat exchanger configuration or concentric spherical reactors.

For irreversible reaction steps having 1st order kinetics, a plug flow reactor PFR will always perform better than a continuously stirred tank reactor CSTR. It is interesting to compare the performance of a n-CSTR train approach and a PFR. We will investigate which reactor permits easier maximization of intermediate species, $B$ (in the architecture, $A \rightarrow B \rightarrow C$). In this case we will work with a differential equation rather than an integro-differential equation.

7.2 Autobiographical reflection

Undertaking this research study has been an invaluable experience. I have gained an understanding of the research nature and process.

This research study has also provided some key ideas which have helped me examine my own professional values and guidelines for possible changes to my own future practice. I am able to articulate the skills developed through my PhD. Experience obtained from this research inspire me to achieve my goals, think both analytically and creatively and overcome problems for an academic/research career. I intend to explore further the impact of some applications on the model configurations involved.

The research process has also encouraged me to learn new programming packages including Maple, Xpp and LaTex in order to improve the quality of my research.
8. PUBLICATIONS

I have published one paper from this thesis to date

APPENDIX
.1 Nomenclature

A superscript * refers to a dimensionless quantity, i.e. $A_1^*$ is a dimensionless parameter whose dimensional counterpart is $A_1$.

In the following an index $i$ can take values 1, 2, 3 and 4, referring to a property in either reactor one or reactor two.

$a_i$ Pre-exponential factor.
\[
a_i = \frac{a_i^*}{R T_0^*} \exp \left( \frac{E_i}{R T_0^*} \right) \quad (s^{-1})
\]

$a_i^*$ Dimensionless pre-exponential factor. (-)
\[
a_i^* = \frac{V_i c_{pg} \rho_g}{\chi^2 S_2} \cdot a_i
\]

$A_i$ Concentration of reactant $A$. (mol m$^{-3}$)

$A_i^*$ Dimensionless concentration of reactant $A$. (-)
\[
A_i^* = A_i / A_0
\]

$A_i(0)$ Concentration of reactant $A$ at time $t = 0$. (mol m$^{-3}$)

$A_i^*(0)$ Dimensionless concentration of reactant $A$ at time $t^* = 0$. (-)
\[
A_i^*(0) = A_i(0) / A_0
\]

$A_0$ Concentration of reactant $A$ in the feed. (mol m$^{-3}$)

$B_i$ Concentration of intermediate $B$. (mol m$^{-3}$)

$B_i^*$ Dimensionless concentration of intermediate $B$. (-)
\[
B_i^* = B_i / A_0
\]

$B_i(0)$ Concentration of intermediate $B$ at time $t = 0$. (mol m$^{-3}$)

$B_i^*(0)$ Dimensionless concentration of intermediate $B$ at time $t^* = 0$. (-)
\[
B_i^*(0) = B_i(0) / A_0
\]

$B_0$ Concentration of intermediate $B$ in the feed. (mol m$^{-3}$)

$B_0^*$ Dimensionless concentration of intermediate $B$ in the feed. (-)
\[
B_0^* = B_0 / A_0
\]

$C_i$ Concentration of product $C$. (mol m$^{-3}$)

$C_i^*$ Dimensionless concentration of product $C$. (-)
\[
C_i^* = C_i / A_0
\]

$C_i(0)$ Concentration of product $C$ at time $t = 0$. (mol m$^{-3}$)

$C_i^*(0)$ Dimensionless concentration of product $C$ at time $t^* = 0$. (-)
\[ C_i^*(0) = \frac{C_i(0)}{A_0} \]

- **\( C_0 \)**: Concentration of product \( C \) in the feed. (mol m\(^{-3}\))

- **\( C_0^* \)**: Dimensionless concentration of product \( C \) in the feed. (–)

\[ C_0^* = \frac{C_0}{A_0} \]

- **\( E_i \)**: Activation energy. (Jmol\(^{-1}\))

- **\( E_1^* \)**: Dimensionless activation energy. (–)

\[ E_1^* = \frac{E_1}{E_2} \]

- **\( J_i \)**: A constant. \( J = 0 \) corresponds to adiabatic operation. (–)

- **\( Q_1 \)**: Heat of endothermicity. (Jmol\(^{-1}\))

- **\( Q_1^* \)**: Dimensionless heat of endothermicity. (–)

\[ Q_1^* = \frac{A_0 R}{E_2 c_{pg} \rho_g} \cdot Q_1 \]

- **\( Q_2 \)**: Heat of exothermicity. (Jmol\(^{-1}\))

- **\( Q_2^* \)**: Dimensionless heat of exothermicity. (–)

\[ Q_2^* = \frac{A_0 R}{E_2 c_{pg} \rho_g} \cdot Q_2 \]

- **\( R \)**: Ideal gas constant. (JK\(^{-1}\)mol\(^{-1}\))

- **\( S_i \)**: Internal surface area. (m\(^2\))

- **\( T_i \)**: Temperature. (K)

- **\( T_i(0) \)**: Temperature at time \( t = 0 \). (K)

- **\( T_{a,i} \)**: Coolant temperature around the reactor. (K)

- **\( T_{(c,i)} \)**: Coolant temperature of the reactor jackets. (K)

- **\( T_{0(c,i)} \)**: Coolant feed temperature of the reactor jackets. (K)

- **\( T_0 \)**: Feed temperature. (K)

- **\( T_{ci} \)**: Characteristic temperature. (K)

\[ T_{ci}^* = \frac{RT_{ci}}{E_2} \]

- **\( V_i \)**: Reactor volume. (m\(^3\))

- **\( V_{(c,i)} \)**: Jacket volume. (m\(^3\))

- **\( V_i^* \)**: Dimensionless reactor volume. (–)

\[ V_i^* = \frac{V_1}{V_2} \]

- **\( c_{pg} \)**: Heat capacity of the reaction mixture. (JK\(^{-1}\)kg\(^{-1}\))

- **\( c_{pg(c,i)} \)**: Heat capacity of the reaction mixture in the jacket. (JK\(^{-1}\)kg\(^{-1}\))

- **\( q \)**: Flowrate. (m\(^3\)s\(^{-1}\))
Jacket flowrate. \((\text{m}^3\text{s}^{-1})\)

\(q_{(c,i)}^* = q_1 \cdot \frac{c_p \rho_g}{X S}\)  

A constant heating rate. \((\text{Ks}^{-1})\)

Dimensionless timescale. \((-\))

\(\alpha^* = \frac{2R}{E_2} \cdot \frac{Y_2 \rho_g \rho_g}{X_2 S_2}\)

Time. \((\text{s})\)

Dimensionless timescale. \((-\))

\(t^* = t \cdot \frac{X_2 S_2}{c_p \rho_g V_2}\)

Dimensionless temperature. \((-\))

\(\theta_i = \frac{RT_i}{E_2}\)

Coolant temperature around the reactor. \((-\))

\(\theta_{a,i} = \frac{R}{E_2} T_{a,i}\)

Coolant temperature of the reactor jackets. \((-\))

\(\theta_{(c,i)} = \frac{R}{E_2} T_{(c,i)}\)

Coolant feed temperature of the reactor jackets. \((-\))

\(\theta_{0(c,i)} = \frac{R}{E_2} T_{0(c,i)}\)

Dimensionless temperature at time \(t^* = 0\). \((-\))

\(\theta_i (0) = \frac{R}{E_2} T_i (0)\)

Dimensionless feed temperature. \((-\))

\(\theta_0 = \frac{R}{E_2} T_0\)

Density of the reaction mixture. \((\text{kg m}^{-3})\)

\(\rho_g\)

Density of the reaction mixture in the jacket. \((\text{kg m}^{-3})\)

\(\rho_g^{(c,1)}\)

Residence time. \((\text{s})\)

\(\tau_i = \frac{V_i}{q}\)

Residence time for the jacket. \((\text{s})\)

\(\tau_{(c,i)} = \frac{V_{(c,i)}}{q_{(c,i)}}\)

Dimensionless residence time. \((-\))

\(\tau_i^* = \frac{X_2 S_2}{c_p \rho_g V_2} \tau_i\)

Dimensionless residence time for the jacket. \((-\))

\(\tau_{(c,i)}^* = \frac{X_2 S_2}{c_p^{(c,1)} \rho_g^{(c,1)} V_{(c,2)}} \tau_{(c,i)}\)
\( \chi_i \) Heat transfer coefficient between the reaction mixture and the reactor walls. \((\text{Js}^{-1}\text{m}^{-2}\text{K}^{-1})\)

\( \chi_{T,1}^* \) Dimensionless heat-transfer rate in reactor one. \((-\text{)}\)

\[
\chi_{T,1}^* = \frac{\chi_1 S_1 V_2}{\chi_2 S_2 V_1}
\]

\( H(\theta_1) \) Steady-state equation for the temperature in reactor one. \((-\text{)}\)

\( G(\theta_2) \) Singularity equation. \((-\text{)}\)

\( H_1 \) Dimensionless variable.

\[
H_1 = \frac{c_{pg} \rho_g V_2}{c_{pg(c,1)} \rho_{\eta(c,1)} V(c,1)}
\]

\( H_2 \) Dimensionless variable.

\[
H_2 = \frac{c_{pg} \rho_g V_2}{c_{pg(c,1)} \rho_{\eta(c,1)} V(c,2)}
\]

\( g \) Dimensionless variable.

\[
g = \frac{S_1 \chi_1}{S_2 \chi_2}
\]

**Tab. 1:** The default parameter values in the industrial process are taken from [18, 53, 56] and [33, page 110].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>8008.298025 mol m(^{-3})</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>23.22576 m(^2)</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>23.22576 m(^2)</td>
</tr>
<tr>
<td>( V_1 )</td>
<td>1.35936 m(^3)</td>
</tr>
<tr>
<td>( V_2 )</td>
<td>1.35936 m(^3)</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>294.4 K</td>
</tr>
<tr>
<td>( c_{pg} )</td>
<td>3.140 J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>( \rho_g )</td>
<td>801.554 \times 10^2 mol m(^{-3})</td>
</tr>
<tr>
<td>( \chi_1 )</td>
<td>851.735 Js(^{-1}) m(^{-2}) K(^{-1})</td>
</tr>
<tr>
<td>( \chi_2 )</td>
<td>851.735 Js(^{-1}) m(^{-2}) K(^{-1})</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>20/60 K s(^{-1})</td>
</tr>
<tr>
<td>( R )</td>
<td>8.31441 J mol(^{-1}) K(^{-1})</td>
</tr>
</tbody>
</table>
Tab. 2: The default parameter values in the lab scale model are taken from [3].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>$4.68 \text{ mol m}^{-3}$</td>
</tr>
<tr>
<td>$S_1$</td>
<td>$2 \times 10^{-3} \text{ m}^2$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$2 \times 10^{-3} \text{ m}^2$</td>
</tr>
<tr>
<td>$V_1$</td>
<td>$5.1 \times 10^{-6} \text{ m}^3$</td>
</tr>
<tr>
<td>$V_2$</td>
<td>$5.1 \times 10^{-6} \text{ m}^3$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>403 K</td>
</tr>
<tr>
<td>$c_{pg}$</td>
<td>$1.35 \text{ kJ mol}^{-1}, \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>$0.405 \text{ mol m}^{-3}$</td>
</tr>
<tr>
<td>$\chi_1$</td>
<td>$25 \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$\chi_2$</td>
<td>$25 \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$20/60 \text{ K s}^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$8.31441 \text{ J mol}^{-1}$</td>
</tr>
</tbody>
</table>

Tab. 3: The default parameter values in the jacket are taken from [54].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{(c,1)}$</td>
<td>$5.1 \times 10^{-6} \text{ m}^3$</td>
</tr>
<tr>
<td>$V_{(c,2)}$</td>
<td>$5.1 \times 10^{-6} \text{ m}^3$</td>
</tr>
<tr>
<td>$c_{pg(c,1)}$</td>
<td>$1.35 \text{ kJ mol}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$c_{pg(c,2)}$</td>
<td>$1.35 \text{ kJ mol}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$\rho_{g(c,1)}$</td>
<td>$0.405 \text{ mol m}^{-3}$</td>
</tr>
<tr>
<td>$\rho_{g(c,2)}$</td>
<td>$0.405 \text{ mol m}^{-3}$</td>
</tr>
</tbody>
</table>

Tab. 4: The other physical parameters are chosen for illustration.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>$50 \text{ kJ mol}^{-1} \leq E_1 \leq 180 \text{ kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>$50 \text{ kJ mol}^{-1} \leq Q_1 \leq 200 \text{ kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>$41.2 \text{ kJ mol}^{-1} \leq Q_2 \leq 200 \text{ kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$T_{c1}$</td>
<td>$342 \text{ K} \leq T_{c1} \leq 942 \text{ K}$</td>
</tr>
<tr>
<td>$T_{c2}$</td>
<td>$342 \text{ K} \leq T_{c2} \leq 942 \text{ K}$</td>
</tr>
<tr>
<td>$T_{a,1}$</td>
<td>$300 \text{ K} \leq T_{a,1} \leq 1000 \text{ K}$</td>
</tr>
<tr>
<td>$T_{a,2}$</td>
<td>$300 \text{ K} \leq T_{a,2} \leq 1000 \text{ K}$</td>
</tr>
<tr>
<td>$T_{(c,1)}$</td>
<td>$300 \text{ K} \leq T_{(c,1)} \leq 1000 \text{ K}$</td>
</tr>
<tr>
<td>$T_{(c,2)}$</td>
<td>$300 \text{ K} \leq T_{(c,2)} \leq 1000 \text{ K}$</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>$4 \text{ s}$</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>$4 \text{ s}$</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>$4 \text{ s}$</td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>$4 \text{ s}$</td>
</tr>
<tr>
<td>$\tau_{(c,1)}$</td>
<td>$0.513 \text{ s}$</td>
</tr>
<tr>
<td>$\tau_{(c,2)}$</td>
<td>$0.513 \text{ s}$</td>
</tr>
</tbody>
</table>


