Model Predictive Control for Ethanol Steam Reformers

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This thesis firstly proposes a new approach of modelling an ethanol steam reformer (ESR) for producing pure hydrogen. Hydrogen has obvious benefits as an alternative for feeding the proton exchange membrane fuel cells (PEMFCs) to produce electricity. However, an important drawback is that the hydrogen distribution and storage have high cost. So the ESR is regarded as a way to overcome these difficulties. Ethanol is currently considered as a promising energy source under the research for its renewable and easy-access. The modelled reformer has been divided into two stages in order to maximize the output of pure hydrogen. Specifically, the hydrogen is generated in the first stage by steam reforming (SR) over the Cobalt-based catalysts. The second stage is used to purify the hydrogen from the mixture gas through a Pd-Ag membrane separation. Unlike the conventional way, the two stages are carried out in a same module, since only one heating device is required. The main idea of the modelling approach is to develop a one-dimensional, pseudo-homogeneous and non-steady-state model based on the mass balance. Finite difference method is applied to transform the partial differential equations (PDEs) into ordinary differential equations (ODEs).

Furthermore, the control of the ESR system is also discussed in this thesis. Some Model predictive control (MPC) strategies have been designed for the linear and non-linear models of the ESR. The mathematical model of the ESR by using the proposed approach is used for the design of a MPC controller. The first part of this thesis has been devoted to obtain the non-linear mathematical model with the assumptions of isothermal and isobaric conditions and perform simulations. The numerical linearisation of the mathematical model towards a control-oriented model has been performed as well as the method of model-order reduction with Hankel norm approximation and temporal discretization with zero-order hold, which will be used as the prediction model of the MPC. The control objectives of the ESR system are to maximize the hydrogen yield and minimize the ethanol flow rate, which result in a multi-objective problem. Open-loop and close-loop simulations are developed to highlight the proposed controller results. The analysis has taken into account relevant indices such as the ethanol conversion,
input smoothness and output error.

Keywords: Mathematical Modelling; Ethanol Steam Reformer; Model Predictive Control; Membrane Separation; Staged-separation Membrane Reactor
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Mingming Li
Barcelona, Jun 2014
NOTATION

Throughout the thesis, the main notations are explained as follows:

\begin{itemize}
\item \( C \) \hspace{1cm} \text{concentration, \ [ \text{mol/m}^3 \ ]}
\item \( F \) \hspace{1cm} \text{molar flow rate, \ [ \text{mol/min} \ ]}
\item \( Q \) \hspace{1cm} \text{volumetric flow rate, \ [ \text{m}^3/\text{min} \ ]}
\item \( A \) \hspace{1cm} \text{section of tubular reactor, \ [ \text{m}^2 \ ]}
\item \( X \) \hspace{1cm} \text{conversion of ethanol, \ [ \% \ ]}
\item \( v \) \hspace{1cm} \text{linear velocity of the gases, \ [ \text{m/s} \ ]}
\item \( T \) \hspace{1cm} \text{temperature, \ [ \text{K} \ ]}
\item \( P \) \hspace{1cm} \text{pressure, \ [ \text{Pa} \ ]}
\item \( R \) \hspace{1cm} \text{universal gas constant, \ [ \text{J/(K-mol)} \ ]}
\item \( \tau \) \hspace{1cm} \text{space time, \ [ \text{min} \ ]}
\item \( r \) \hspace{1cm} \text{reaction rate, \ [ \text{mol/(m}^3 \cdot \text{min}) \ ]}
\item \( k_i \) \hspace{1cm} \text{reaction rate constant, \ [ \text{mol/(m}^3 \cdot \text{min-bar}) \ ]}
\item \( \varepsilon \) \hspace{1cm} \text{molar relation, \ [ \]}
\item \( S/C \) \hspace{1cm} \text{steam carbon ratio in feed, \ [ \]}
\item \( \delta \) \hspace{1cm} \text{the thickness of Pd-Ag membrane, \ [ \mu \text{m} \ ]}
\item \( D \) \hspace{1cm} \text{membrane diameter, \ [ \text{m} \ ]}
\item \( S \) \hspace{1cm} \text{surface area of the membrane, \ [ \text{m}^2 \ ]}
\item \( E_a \) \hspace{1cm} \text{apparent activation energy, \ [ \text{J/mol} \ ]}
\item \( P_e \) \hspace{1cm} \text{gas permeability, \ [ \text{mol/(m-min-Pa}^{0.5}) \ ]}
\item \( P_{e0} \) \hspace{1cm} \text{pre-exponential factor, \ [ \text{mol/(m-min-Pa}^{0.5}) \ ]}
\item \( P_{H_2,\text{retentate}} \) \hspace{1cm} \text{partial pressure of hydrogen in the retentate side, \ [ \text{Pa} \ ]}
\item \( P_{H_2,\text{permeate}} \) \hspace{1cm} \text{partial pressure of hydrogen in the permeate side, \ [ \text{Pa} \ ]}
\item \( J_{H_2} \) \hspace{1cm} \text{hydrogen permeating flux, \ [ \text{mol/min} \ ]}
\item \( \text{C}_2\text{H}_5\text{OH} \) \hspace{1cm} \text{ethanol}
\end{itemize}
<table>
<thead>
<tr>
<th>Chemical Symbol</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CHO</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>H₂O</td>
<td>water</td>
</tr>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>H₂</td>
<td>hydrogen</td>
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CHAPTER 1

INTRODUCTION

This chapter briefly introduces the motivation and objectives of this thesis. The motivation contains reasons of choosing the hydrogen as the research object, using ethanol to produce the hydrogen, purifying the hydrogen with separation membrane and applying the Model Predictive Control (MPC) strategy for the ESR. The general objectives of this thesis are also described. Finally, the outline of this thesis has been drawn.

1.1 Motivation

It is widely known that the global warming and the increasing demand for oil reserves have a great influence on public awareness. Nowadays, more and more automotive industries are looking for a new propulsion to drive the automotive systems instead of conventional combustion engine with poor efficiency, high emission and dependence on oil by an internal engine. Hydrogen is currently considered as a promising future fuel for both stationary and mobile applications. Making use of the hydrogen is able to decrease the quantity of the waste gases emission and the dependence on the oil [SO14]. Furthermore, hydrogen-powered fuel cells have more than two times efficiency of traditional combustion technologies. Especially, the durability and reliability of the fuel cells are significantly improved when the pure hydrogen rather than the hydrogen with mixture gas is supplied to the fuel cells.

However, the main challenge for the application of fuel cells is the development of a sustainable source of hydrogen. Although hydrogen can be generated from many kinds of ways, most of them come from using large chemical plants, which have huge expenses including money and time. In terms of the physical property of the hydrogen, it is difficult to transport and store
with strict conditions. The reforming technologies can overcome aforementioned problems, see [HHKW09], [DCLL11], [DTML12]. In a reforming process, a liquid or gaseous hydrocarbon is mixed up with steam or a mixture of air and steam (oxidative reforming) loaded on an appropriate catalyst to yield mostly hydrogen and some other gases (carbon monoxide, carbon dioxide, methane). However, carbon monoxide potentially poison the hydrogen reaction at the anode of the fuel cell resulting in such a lower fuel cell potential and lower energy conversion efficiency. Hence, it is necessary to purify the hydrogen before feeding fuel cells. Compared with traditional method of water gas shift (WGS) for purifying hydrogen, membrane separation technique is a wise choice [LAP09], [Kik00].

Ethanol is an available source to produce hydrogen because of its renewable nature and easily being obtained from biomass. Ethanol has attracted increasing interests for hydrogen production by the steam reformer in the past decade. Compared with other families of oxygenated fuels, ethanol is a better alternative fuel for its less toxic, high content of hydrogen and environmental friendly. Currently, hydrogen can be produced from ethanol by using different kinds of the reforming techniques, such as the ethanol steam reformer, oxidation steam reformer, partial oxidation and decomposition [HHKW09]. Among these techniques, steam reforming isolating oxygen is widely adopted.

The MPC strategy is an advanced method of process control that has been widely used in industries and chemical plants since the 1980s. The most advantage of MPC is that it not only allows the current timeslot to be optimized, but also takes future timeslots into account. Moreover, the MPC is able to anticipate future events and apply control actions accordingly. Under some circumstance, the MPC is rather than a control technique, but a set of control methodologies using a mathematical model of a considered system to seek a control action through minimizing a cost function related to controlled objectives under constraints. The MPC strategy is also adapted to deal with complex systems, such as ESR system which is an MIMO\(^1\) system with physical constraints. The MPC strategy can track the dynamic performance of the ESR and apply the control actions for the sake of achieving a suitable and desired behaviours.

---

\(^1\)MIMO: Multi-input and multi-output.
1.2 Thesis Objectives

The main objectives of this thesis are modelling the ESR and designing a LMPC controller for the ESR. The ESR is a complex chemical process which is modelled as a non-linear, non-minimum phase and MIMO model with disturbances. After obtained an accurate model of the ESR, it will be used for designing a LMPC with multiple objectives and constraints. To realise these objectives, two specific objectives are shown. Specifically, the general objective is divided into model and control objectives.

1.2.1 Model Objectives

The objectives related to model are included as follows:

- Review the main techniques about the SR, such as catalytic selection, reforming techniques, membrane separation among other related topics.
- Review the main idea of mathematical modelling of a non-linear system, especially mass balance and spatial discretization.
- Develop and implement the ESR non-linear model according to experimental data and analysis of the static and dynamic behaviours of non-linear system.
- Obtain the linear control-oriented model of the ESR based on the non-linear model. The linear model should be suitable for LMPC design.
- Validate and compare of simulation results of the designed control-oriented models.

1.2.2 Control Objectives

The control objectives is split to the following steps:

- Review the existing LMPC techniques applied to plug-flow reactors (PFRs).
- Design a multi-objective LMPC controller that will be implemented in the closed loop so that the non-linear system can be automatically regulated following a step reference of the hydrogen output.
Chapter 1: Introduction

- Simulate the closed-loop system with different parameters, such as weights of cost function and prediction horizon.

1.3 Outline of the Thesis

This dissertation is organized as follows:

Chapter 2: State of the Art

This chapter presents the background of the ESR in the chemical process, which includes selections of catalysts, techniques of producing hydrogen and membrane separation technology of obtaining the pure hydrogen. Besides, a basic MPC strategy is briefly introduced.

Chapter 3: System Description

This chapter describes the whole system of the ESR. The experimental setup and system description are described.

Chapter 4: Mathematical Modelling of the ESR

This chapter proposes the approach of modelling the ESR system as a non-linear model and the linearised model that is going to be used as the prediction model of the LMPC.

Chapter 5: LMPC Controller Design for the ESR

This chapter discusses the formulation of the LMPC for the ESR and its configuration.

Chapter 6: Simulation Results

This chapter shows the simulation results gathered from the open-loop analysis of mathematical model of the ESR and closed-loop control system with the LMPC and non-linear model of the ESR.
Chapter 7: Concluding Remarks

This chapter gives the summary of this thesis and the most relevant contribution. Some future works are also outlined in this chapter.
CHAPTER 2

STATE OF THE ART

This chapter reviews on the techniques of hydrogen generation by the ESR that includes catalysts selection, reforming and membrane separation of purifying hydrogen. Moreover, the MPC for the ESR is briefly introduced. The advantages and disadvantages of the MPC are also highlighted.

2.1 Reforming Techniques of Hydrogen Production

Currently, there are three conventional techniques namely steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR), which have been used to produce hydrogen for feeding PEMFCs [HHKW10], [NLL07], [PSV+06]. Each technique has its own features:

- For the SR technique, the steam reformer must be supplied with a high temperature mixture of fuel and steam. Since the reforming reactions are endothermic, so it requires an external heat source. The products of SR are mixture of hydrogen, carbon monoxide, carbon dioxide and methane. Compared with the other techniques, SR has a lower operating temperature with special catalysts and does not need oxygen. The SR generates the highest ratio of $\text{H}_2/\text{CO}$ among the three techniques. However, the SR has the highest emission of CO content. So it is essential to purify the hydrogen before feeding to the PEMFCs.

- For the POX technique, it transforms the fuel into hydrogen by partially oxidizing it with oxygen. It is a highly exothermic process and leads the reactants to a high temperature.
Chapter 2 : State of the Art

The temperature with the POX has a wide range, which can be in excess of 1000°C without the participation of catalysts. Moreover, the POX has some other advantages including compactness, light-weight and rapid-startup. However, the POX has lower efficiency than the SR on account of the reaction process being exothermic.

- For the ATR technique, the combination of SR and POX is termed as ATR. The ATR is operated in the presence of catalysts to determine the relative extents of the POX and the SR. Furthermore, the SR reaction can absorb the partial heat produced by the POX reaction. The maximal temperature in the reactor can be limited to some certain degree. However, in reality, it is still under the research and not carried out into the practice importantly.

Among the above three techniques for producing the hydrogen, SR technique is widely used due to its high efficiency and lower operating temperature.

2.2 Catalyst Selection

Nowadays, the increasing catalysts are acted as the research target for ESR for the purpose of producing hydrogen in a costless and high efficient way [DCLL11], [DTML12], [HHKW09]. Among these catalysts, those based on Co and Ni are considered as a suitable choice due to their inexpensive, high activity and selectivity [DCLL11], [LVR10]. However, these catalysts are suffered from severe deactivation during the SR process because of the extensive carbon deposition. A new kind of catalyst based on noble metal of Pd, Pt, Rh and Ru has aroused many interests, which is believed to be more stable and more active among other catalysts [GAd04], [Har05]. Although Cobalt-based catalysts have their own drawbacks, they have been proved out the most effective way for ESR to produce hydrogen, see [DTML12], [HHKW09], [HHKW09], [NLL07]. In this thesis, the Cobalt-based catalyst is chosen and all the experimental data has been collected from INTE (UPC).

2.3 Hydrogen Separation Techniques

The major drawback of conventional reactors is that the products of reactions are mixture of hydrogen, carbon monoxide, carbon dioxide, methane and the unreacted fuels, which are not benefit for the PEMFCs. The carbon monoxide can poison the anode catalyst if the quantity is
more than 100 ppm (parts per million). It is widely known that the hydrogen must be purified before feeding PEMFCs.

In terms of the conventional method, the process of generating the pure hydrogen there as been divided into SR, WGS and a purification system (pressure-swing adsorption), respectively. The process of conventional method is also complicated because each stage has different temperatures, pressures and catalysts. Membrane reactor is proposed to overcome these issues by the combination of the SR and separation in the same module. During past years, a number of publications about membrane reactor have exponentially grown. The membrane reactor is firstly proposed by Mcleary etc. [MJK06]. With a comparison among the conventional, hydrogen separation membrane techniques could offer a number of advantages:

- It has lower capital costs by making use of the membrane reactor saving the number of devices and the required physical space.
- The process units and the required total reactor volume are decreased when the dense palladium-based membrane reactor is applied to generate the pure hydrogen. The pure hydrogen moves towards the permeate side, which enables the reactions to proceed towards completion.
- Higher hydrogen recovery rates and ethanol conversion rates can be obtained with the same operating conditions.
- It is able to produce hydrogen at steady state and generate high-purity hydrogen without polishing filters.

### 2.4 Staged-separation Membrane Reactor

The term of staged-separation membrane reactor is originally introduced by Anwu etc. [LLG08]. This kind of Staged-separation membrane reactors can not only inherit the advantage of regular membrane reactors, but also operate the steam reformer and hydrogen separation with different conditions in order to achieve the overall performance. Figure 2.1 schematically shows the concept of the staged-separation membrane reactor for ESR. The steam reformer and membrane separation are carried out in a single device. Five pieces of the functional cordierite of catalytic honeycomb were disposed in series into the reactor followed by the membrane tube which results a staged membrane reactor. The reactor was measured with 230mm tall where
the dimension of the upper part was 154mm and the lower part was 76mm, and 22mm outside diameter (OD) (Red Research & Consulting), which was made up of a reaction-separation chamber and a lower head to allow the exit of the separated streams (retentate and permeate). A feed evaporation conduit was applied to evaporate the ethanol and water before they enter the reactor. Some advantages are accomplished using the staged-separation membrane reactor in one module:

- Only one heating device is required for both the steam reformer and membrane separation stages, so the device occupied space is obviously reduced.

- A liquid pump is applied to supply the feed and regulate the desired operation pressure.

- Lower cost is required because the membrane module has the ability to operate at a milder temperature.

- System is very compacted so the typical catalysts for ESR can be quite efficient.
2.5 Model Predictive Control

_Model Predictive Control_ (MPC) can be tracked until 1970s. It was firstly applied in the industrial processes in the 1980s. Nowadays, MPC is one of advanced control strategies, which has played a significant role in the industrial production processes. Compared with other control strategies, MPC does not designate a specific control strategy but a range of control methods that make explicit use of the a model of the process to obtain the control action by minimizing an objective function. The main ideas contained in the prediction control family are generally as following shown:

- Explicit use of a model to predict the system output within the prediction horizon.
- Computation of a control sequence through minimizing an objective function.
- Receding strategy applied in order that at each instant the horizon is moved towards the future. Only the first control applied to the system at each step.

MPC has presented some obvious advantages over other methods [Mac02], such as

- It is easy to deal with the multi-variables system.
- It intrinsically has the compensation for dead times.
- A great variety of processes can be controlled, for example, a system with delay or non-minimum phase.
- Feed-forward control can be used in a natural way to compensate measurable disturbances.
- It is beneficial for the system output to follow the given future reference.
- It is easy to implement the resulting control law.

However, the MPC strategy also has its own shortcomings. Even though the resulting control law can be easy to be implemented and requires no significant computation for the MPC strategy, the derivation of is much more complex than the PID controller when the constraints are considered. Moreover, the amount of required computation is even higher when the constraints are taken into the account. The main limitation is the requirement for an appropriate model of the process to be available.
2.5.1 MPC Strategy

In order to implement the MPC strategy, its basic structure shown in Figure 2.2 is shown. It is clearly found that four main elements are contained:

- Prediction model: it captures all the system dynamics, which is potentially used to predict the future behaviours of the system over the MPC prediction horizon.

- Objective function: it is the mathematical expression that penalizes deviations of the predicted controlled outputs from a given reference trajectory. Besides, the objective function can take into account more than one term at the same time.

- Constraints: they can represent the physical limitations of the system states, the control actions and measured outputs.

- Optimization problem: it is the merging of previous three points. Through solving an optimization problem, receding horizon strategy is executed to apply the first optimization result as the control action to the system.
2.5.2 Standard MPC Formulation

Generally, the MPC formulation is described in the state-space and shows a simple representation of the strategy. The standard MPC model based on the linear discrete prediction model is presented as

\[
x(k + 1) = Ax(k) + Bu(k),
\]

\[
y(k) = Cx(k) + Du(k - 1),
\]

where \(x(k), u(k), y(k)\) denote the state, input and measured output vectors, respectively. The cost function is assumed to be quadratic and the constraints are in the form of linear inequalities [Mac02]. The standard MPC optimization problem is defined as Problem 2.1.

**Problem 2.1 (Basic MPC formulation).**

\[
J \equiv \min_{u(k)} \sum_{i=0}^{H_p-1} \left[ y(k+i+1|k)^T Py(k+i+1|k) + u(k+i)^T Qu(k+i) \right],
\]

subject to:

\[
x(k+i+1|k) = Ax(k+i|k) + Bu(k+i),
\]

\[
y(k+i+1|k) = Cx(k+i+1|k) + Du(k+i),
\]

\[
u_{\min} \leq u(k+i|k) \leq u_{\max},
\]

\[
y_{\min} \leq y(k+i+1|k) \leq y_{\max},
\]

\[
x(k|k) = x(k),
\]

where \(x(0)\) is the initial state, \(H_p\) is the prediction horizon, \(u_{\min}\) and \(u_{\max}\) are saturation constraints on inputs, \(y_{\min}\) and \(y_{\max}\) are saturation constraints on outputs. Problem 2.1 can be transformed as Quadratic programming problem [Mac02], and its solution is

\[
U^*(k) \triangleq [u(k|k)...u(k+H_p-1|k)]
\]

which is a sequence of optimal control actions solved with for a given \(x(k)\). Only the first control action \(u(k|k)\) of \(U^*(k)\) is applied to the real system,

\[
u_{\text{opt}}(k) = u(k|k).
\]
The remaining optimal control actions are neglected and the optimization is launched again for time $k+1$ and repeated until the end of the simulation scenario.

### 2.5.3 LMPC Controllers for ESR

Most of industrial processes are complex, non-linear and constrained MIMO systems, whose dynamic behaviours are vulnerably changed by the effects of operating conditions and components aging. The ESR process just one of them. However, few literatures can be found where LMPC controller has already been applied on the ESR. The reason is that non-linear partial differential equations (PDEs) are usually used to describe the dynamics of the tubular reactors. The PDEs are derived from mass and energy balance in principle. Therefore, a distributed parameter system can be obtained. In order to control such a system, a way of transforming the PDEs and the constraints into a set of ordinary differential equations (ODEs) can be taken. It is possible to use the control theory developed for lumped parameter systems. However, it is difficult to design a controller for such a system due to its high order obtained from discretizing the PDEs. Hence, one way is model order reduction. But the resulting controller can present poor performance if the linear reduced order model can not represent all the non-linear system dynamics. As a result, it is significant to develop the methodologies of the model order reduction in order to obtain the efficient application of LMPC for the ESR.

The proposed method of model order reduction is the combination of the proper orthogonal decomposition and Galerkin projection [PLC12]. The reduced model still represents some certain aspects of the original system at least appropriately. In spite of the spatial discretization of the non-linear PDEs that model the ESR, the controller can still performs well when the linearization and discretization in time of the equations and the dramatic model order reduction is calculated by means of transforming the PDEs to the ODEs. However, the behaviours of the MPC controller may be quite good only if the disturbance of the tubular reactor system is limited to a appropriate range.

An MPC scheme for output control of distributed parameter system using the method of characteristic presented in [SFG04]. Any hyperbolic PDEs system can be transformed into an ODEs system that involves differentiations in only one direction, namely, along the characteristics. Then, PDEs can be reduced to ODEs along characteristic curves, which leads to a powerful method for solving hyperbolic PDEs [Arn88], [McO96]. The drawback of this method is that the complexity increase dramatically when a set of first-order PDEs exist.
CHAPTER 3

SYSTEM DESCRIPTION

This chapter describes the entire system of the ESR. The experimental setup is introduced as well as the experimental conditions of the ESR. The system description includes the reaction equations at each step. The fitting of reaction kinetics are prepared for building the mathematical model of the ESR, which will be acted as the parameters of mathematical model of the ESR.

3.1 Experimental Setup

For the purpose of simplifying the experimental setup, the process of generating hydrogen via ethanol steam reforming and purifying hydrogen using selective membrane were adopted in a single reaction and separation module. As shown in Figure 3.1, the reactor was measured with 230mm tall and 22mm OD (outside diameter) (Red Research & Consulting), which was made up of a reaction-separation chamber and a lower head to allow the exit of the separated streams which are retentate and permeate streams. A feed evaporation conduit was applied to evaporate the ethanol and water before they entering the reactor. Five pieces of catalytic honeycomb and in total 1.32g were disposed in series into the reactor followed by the membrane tube which results in a staged membrane reactor. The 76mm tall, 1/8 inch diameter, pin-hole free, dead-end membrane tube with a total area of 7.1cm² was used. The Pd-Ag active layer amounts 30µm thick over a 43 layer of an appropriate support. The liquid mixture of the ethanol and water are feeding directly from the storage tank by a HPLC pump (Knauer). Moreover, the retentate pressure was adjusted and controlled by a manually operated back-pressure regulator (Swagelok). The permeate pressure is regarded as atmospheric pressure, so no pressure regulation was applied to the permeate side.
3.2 System Description

In this thesis, the ESR is conducted by using a new cobalt-based catalyst over cordierite monoliths that were implemented in series into a stainless-steel Pd-Ag membrane reactor. The experiment of this research is performed with different pressures (1bar~14bar), temperatures (500°C~600°C) and S/C ratio in order to obtain the dynamic behaviour. Compared with traditional method with three stages to generate the hydrogen, only two stages are proposed to generate the pure hydrogen, as shown in Figure 3.2. The 100% conversion rate of the ethanol and acetaldehyde are considered in the reaction part. Equations (3.1a)-(3.1d) describe the reaction process of the ESR with Co$_3$O$_4$–ZnO catalysts [NLL07], [RHJMC08], [LVR10].

\[
\begin{align*}
C_2H_5OH & \rightarrow CH_3CHO + H_2, \\
C_2H_5OH & \rightarrow CO + CH_4 + H_2, \\
CO + H_2O & \rightarrow CO_2 + H_2, \\
CH_3CHO + 3H_2O & \rightarrow 2CO_2 + 5H_2. 
\end{align*}
\]
where C₂H₅OH, H₂O, CH₃CHO, H₂, CO, CO₂ and CH₄ denote the ethanol, water, acetaldehyde, hydrogen, carbon monoxide, carbon dioxide and methane, respectively.

It has been demonstrated that the simultaneous presence of metallic cobalt and oxide is required for the process of the reaction. In fact, ethanol dehydrogenates into hydrogen and acetaldehyde over cobalt oxide (3.1a) that is further reformed with water to carbon dioxide over metallic cobalt (3.1d). In addition, cobalt catalysts are active for the WGS reaction (3.1c) under typical operating conditions. An undesired mixture product of carbon monoxide and methane is part of the decomposition of the ethanol (3.1b).

### 3.3 Reaction Kinetics

A reaction rate illustrates how fast each chemical reaction happened, which depends on the joint conditions of concentration, temperature, pressure and time. Each reaction has different reaction rates. A phenomenological kinetic model with power-law rate expressions has been
adopted [UAL+11]:

\[ r_1 = k_1 P_{C_2H_5OH}, \]  
\[ r_2 = k_2 P_{C_2H_5OH}, \]  
\[ r_3 = k_3 \left( P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{k_{WGS}} \right), \]  
\[ r_4 = k_4 P_{CH_3CHO} P_{H_2O}^3, \]  
\[ k_i = k_{i\infty} \exp \left( -E_{ai} \left( \frac{1}{RT} - \frac{1}{RT_{ref}} \right) \right), \]  
\[ k_{WGS} = \exp \left( \frac{4577.8}{T} - 4.33 \right), \]

where \( k_{i\infty} \) are the pre-exponential factors, \( k_i \) are kinetic constants of each reaction, \( E_{ai} \) are the activation energies, \( T \) is the temperature, \( T_{ref} \) is the reference temperature as a constant with 873.15K and \( P_{C_2H_5OH}, P_{CO}, P_{H_2O}, P_{CO_2}, P_{CH_3CHO} \) are corresponding to partial pressure of each component.

### 3.3.1 Process of Fitting the Reaction Rates

In order to ensure that all the ethanol and acetaldehyde are completely transformed and the quantity of each component fulfils the experimental data, a process of fitting the reaction rate is applied to achieve this goal. The pre-exponential factors and activation energies are adjusted to fit the reaction rate instead of adjusting the reaction rate directly. First step is to adjust pre-exponential factors when \( T = 600^\circ C \) because the expression of \( \exp \left( -E_{ai} \left( \frac{1}{RT} - \frac{1}{RT_{ref}} \right) \right) \) is always zero. Some parts are included in the first step:

- Adjust \( k_{i\infty 2} \) to fit the quantity of \( CH_4 \) which was only produced in reaction (3.1b).
- Adjust \( k_{i\infty 1} \) to ensure that all the conversion rate of ethanol is 100%.
- Adjust \( k_{i\infty 4} \) to ensure that all the conversion rate of acetaldehyde is 100%.
- Adjust \( k_{i\infty 3} \) according to the quantity of \( H_2 \) from the experimental data.

Then, the parameters of activation energy are adjusted by setting the temperature as 540°C, which has the same steps as the pre-exponential factors adjusted. The exact values of the pre-exponential factors and activation energies are shown in Appendix B.
CHAPTER 4

MATHEMATICAL MODELLING OF THE ESR

This chapter presents a new mathematical modelling approach of the ESR based on mass balance. The calculations of some variables related to modelling the ESR are proposed. Besides, a linearised model and features of the control-oriented model are also discussed.

4.1 Non-linear Model of the ESR

It is widely known that the dynamic response of the reactor is significant. It is essential to perform the design of the chemical control system for the whole unit. Therefore, the development of a dynamic model of the reactor is an indispensable tool for designing model-based controllers, especially for the MPC control strategy.

4.1.1 Mass Balance of the ESR

A one-dimensional, pseudo-homogeneous, non-steady-state model has been used to represent the process of the ESR with membrane separation. The mole balance equation for modelling
Chapter 4: Mathematical Modelling of the ESR

check redaction in [GLSL09], [RGMSP12]:

\[
\frac{\partial C_j}{\partial t} + C_j \frac{\partial \nu}{\partial z} + \nu \frac{\partial C_j}{\partial z} = \nu_j r_i \quad i = 1, \ldots, 4; j = 1, \ldots, 7, \tag{4.1a}
\]

\[
C_j (0, z) = C_{j,0} (z) \quad \forall z \in [in, out], \tag{4.1b}
\]

\[
C_j (t, 0) = C_{j,in} (t) \quad \forall t > 0, \tag{4.1c}
\]

where \( j \) is the component of \( \text{C}_2\text{H}_5\text{OH}, \text{H}_2\text{O}, \text{CH}_4, \text{CO}, \text{CO}_2, \text{CH}_3\text{CHO} \) and \( \text{H}_2 \), respectively and \( i \) is reaction number (3.1a)-(3.1d), \( C \) is the concentration of each component, \( r \) is the reaction rate, \( \nu \) is the linear velocity of the gases, \( 0 \) represents the initial time, \( in \) denotes the reactor inlet, \( t \) is the continuous time, \( out \) represents the reactor outlet and \( \nu \) denotes the stoichiometric coefficient of component in reaction.

4.1.2 Membrane Separation

The stage of membrane separation for obtaining the pure hydrogen is the process of the hydrogen selective separation. In this stage, a Pd-Ag metallic membrane permeates only the hydrogen leaving the rest of the gas on the retentate side. The mass transfer mechanism can be expressed by using the Sievert law as [KLD+13]

\[
J_{H_2} = \frac{P_e}{\delta} S \left( \sqrt{P_{H_2,\text{retentate}}} - \sqrt{P_{H_2,\text{permeate}}} \right), \tag{4.2}
\]

s.t. \( P_e = P_{e0} \cdot \exp \left( - \frac{E_a}{RT} \right), \tag{4.3} \)

where \( P_e \) presents the gas permeability [ mol/(m-min-Pa^{0.5}) ], \( P_{e0} \) the pre-exponential factor [ mol/(m-min-Pa^{0.5}) ], \( R \) ideal gas constant [ J/(mol·K) ], \( T \) temperature [ K ], \( P_{H_2,\text{retentate}} \) hydrogen partial pressure in the retentate side [ Pa ], \( P_{H_2,\text{permeate}} \) hydrogen partial pressure in the permeate side [ Pa ], \( E_a \) the apparent activation energy [ J/mol ], \( S \) the surface area of the membrane [ m² ] and \( J_{H_2} \) is the permeating hydrogen flux [ mol/min ].

Main Assumptions

The reactor is divided into several slices of smaller size and each slice is considered as a continuous stirred tank reactor. Hence, for a series of a specific number of reactors, space independence
is assumed with homogeneous conditions. Specifically, the assumptions are divided into the following points:

- Isothermal operation conditions within each stage are used.

- Isobaric operation conditions are applied due to the void fraction of the monolithic structures.

- Modelling a catalytic packed bed reactor as a PFR is valid for the flow inside the laminar channels.

- Terms related to diffusion are neglected because diffusion action is assumed to be slower than the convection action.

- The use of low-diameter with 22mm monoliths supports the assumption of 1D model avoiding the occurrence of pronounced radial mass profiles.

- Gas properties are respect to temperature and gas concentration. Ideal gases law is applicable for low operating pressure.

- The fluid velocity only depends on the axial position (z-axial) in the tube.

**Molar Flow Rate**

In Equation (4.1a), the linear velocity \( v \) of gases inside each stage should be related to the concentrations [GLSL09] in order to solve the set of PDEs. It varies with the time and position within the reactor. In PFR with isobaric and isothermal conditions, the concentration and linear velocity have the relationship as

\[
v = v_{in} \left( 1 + \varepsilon X \right),
\]

\[
C_j = C_{j,in} \frac{1 - X}{1 + \varepsilon X},
\]

where \( X[\%] \) is the conversion rate of the ethanol while \( \varepsilon \) is the molar relation of the considered reaction.
Molar Relation $\varepsilon$

The parameter $\varepsilon$ can be defined as

$$\varepsilon = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total number of moles fed to the reactor}}$$  \hspace{1cm} (4.5)

For a regular chemical reaction

$$aA + bB = cC + dD.$$  \hspace{1cm} (4.6)

The parameter $\varepsilon$ is computed as

$$\varepsilon = \left( \frac{d}{a} + \frac{c}{a} + \frac{b}{a} - 1 \right) \frac{N_A}{N_{\text{total}}},$$  \hspace{1cm} (4.7)

where $N_A$ is the quantity of the input of component $A$ and $N_{\text{total}}$ is the total quantity of the inputs.

Conversion, Volumetric Flow Rate and Molar Flow Rate

Deriving Equation (4.4a), the derivative of $\nu$ with respect to z-axial can be obtained as

$$\frac{\partial \nu}{\partial z} = \frac{\partial X}{\partial z} \varepsilon_{\nu_{\text{in}}},$$  \hspace{1cm} (4.8)

The conversion $X$ can be derived from Equation (4.4b), which is written as

$$X = \frac{C_{j,\text{in}} - C_j}{C_j \varepsilon + C_{j,\text{in}}}$$  \hspace{1cm} (4.9)

The velocity of the gases inside the reactor is called volumetric flow rate $Q$ in this thesis, which has the linear relationship with $\nu$ as

$$Q = Av$$  \hspace{1cm} (4.10)

where $A$ is the section area of the tubular reactor.

Combined Equation (4.4a) and Equation (4.10), the expression of $Q$ can be rewritten as

$$Q = Q_{\text{in}} (1 + \varepsilon X)$$  \hspace{1cm} (4.11)
where $Q_{\text{in}}$ denotes the initial volumetric flow rate.

In this thesis, the molar flow rate of each component is observed in the inlet and outlet of the reactor. It is related with concentration and volumetric flow rate expressed as

$$F_j = Q C_j$$

where $F_j$ represents the molar flow rate of each component $j$.

**Axial Discretization**

All the parameters in the mass balance have been expressed as the function of the concentration. So the mass balance equations corresponding to each component for both stages can be solved. However, a step of spatial discretization is carried out in order to solve the mass balance, which transforms the set of PDEs into ODEs with numerical algorithms. An algorithm of backwards finite differences is used to discretize PDEs to obtain a group of differential volumes at each stage. The backwards finite difference is expressed as

$$\frac{\partial C_j}{\partial z} = \frac{C_j(z) - C_j(z - 1)}{\Delta z}.$$ 

(4.13)

One advantage of this method is to form a lump parameters system. Hence, the lumped system theory can be applied to build the PFR model.

### 4.2 Linearised Model for LMPC

According to the aforementioned modelling steps, a non-linear model of the ESR model can be obtained. In order to design a LMPC controller, the non-linear model $NLsys$ is firstly linearised as a linear model decoded here as $Lsys$ and then an order reduction procedure is applied taking observability and controllability of the resultant linear prediction model into account to get the linear reduced model $LRsys$. Finally, the $LRsys$ is discretized as the linear reduced discrete model $LRDsys$ that will be used as the prediction model of the LMPC.
4.2.1 Lsys Model

In the simulation model of the ESR, each stage has 20 discretization points and the total number of states is $15 \times 20$, in which there are $7 \times 20$ in first stage and $8 \times 20$ in the second stage. So the non-linear system is complex because there are 300 ($15 \times 20$) states variables representing all the system states. Due to the high complexity as well as the high number of the non-linear equations, linearisation will be executed by means of numerical methods. The Lsys model is obtained from linearising the NLsys model around the working point by the Control Toolbox in Matlab, which can be expressed in the form of the state space as

$$\dot{x}_f(t) = A_f x_f(t) + B_f u(t),$$

$$y(t) = C_f x_f(t) + D_f u(t),$$

(4.14a)

(4.14b)

where $x_f(t) \in \mathbb{R}^{300}$ are the full states variables, $u(t) \in \mathbb{R}^4$ the manipulated inputs and $y(t) \in \mathbb{R}^1$ are the measured controlled output variables. $A_f, B_f, C_f, D_f$ are matrices and their dimensions are $300 \times 300, 300 \times 4, 1 \times 300$ and $1 \times 4$, respectively.

The location of the poles and zeros provides qualitative insight into the response characteristics of a system, which is considered to evaluate the resultant stability of the Lsys.

As the Figure 4.1 shows, where the cross (×) denotes the poles and the circle (○) represents the zeros, the real parts of the 300th poles of the Lsys model are on the left half plane. Hence, the Lsys model around the selected working point is stable.

4.2.2 LRsys Model

Hankel Singular value method plays an important role for model order reduction. It is the basis of balanced model reduction, which provides a way to compute the energy of each state in a system. In this process, states with high energy are retained while states with low energy are discarded. Meanwhile, the reduced model maintains the important features of the original model. Moreover, it provides an effective and easy way to reduce the complexity of the Lsys at least in term of size. Keeping larger energy states of a system preserves most of its characteristics in terms of stability, frequency, and time responses. Some model reduction techniques are based on the Hankel singular values of a system. Mathematically, a given stable state-space system, its Hankel singular values are defined as the square roots of the eigenvalues of the system.
controllability and observability Gramian matrices defined as.

\[
\sigma_H = \sqrt{\lambda_i(PQ)},
\]

(4.15)

where \( P \) and \( Q \) are controllability and observability Gramian matrices that satisfy

\[
AP + PA^T = -BB^T, \quad (4.16a)
\]

\[
A^TQ + QA = -C^TC. \quad (4.16b)
\]

In this way, the Hankel-singular values of 300th order model are obtained but only the first eight values are presented in Figure 4.2.
The reduced-order model can be also computed in the state-space representation as follows:

\[
\dot{x}_r(t) = A_r x_r(t) + B_r u(t), \\
y(t) = C_r x_r(t) + D_r u(t),
\]

where \( x_r(t) \in \mathbb{R}^8 \) are the states variables for the reduced model, \( u(t) \in \mathbb{R}^2 \) is the manipulated inputs and \( y(t) \in \mathbb{R}^1 \) are the measured controlled output variable.

However, after order reduction, the original meanings of system states have been shifted. They no longer represent the concentrations of each differential volume but a combination of them.

### 4.2.3 LRDsys Model

The discretization with respect to time is required to obtain a discrete model based the linear reduced model, since the discrete model will be used as the prediction model of the LMPC.
4.2 : Linearised Model for LMPC

controller. The \( LRD_{sys} \) model is converted by using Function \( c2d \) in Matlab with the zero-order hold method which assumes the control inputs are piecewise constant over the sampling period \( T_s \). The sampling time is chosen as \( 0.2s \), which ensures that the simulation with the non-linear model can be finished in a sampling period.

The reduced-order discrete linear model can be expressed in state-space representation as follows:

\[
\begin{align*}
x_r(k+1) &= A_{rd}x_r(k) + B_{rd}u(k), \\
y(k) &= C_{rd}x_r(k) + D_{rd}u(k-1),
\end{align*}
\] (4.18a)\( \) (4.18b)

where \( x_r(k) \in \mathbb{R}^8 \) are the states variables of the reduced model, \( u(k) \in \mathbb{R}^2 \) the manipulated inputs and \( y(k) \in \mathbb{R}^1 \) are the measured controlled output variable.

After obtaining the \( LRD_{sys} \) model, it is necessary to verify its stability before designing the LMPC controller. As the Figure 4.3 of \( LRD_{sys} \) pole-zero map shows, all the poles are located inside the unit circle so that the system is stable. The \( LRD_{sys} \) model can be further utilized as the prediction model of the LMPC.
Figure 4.3: Pole-zero map of the \( LRD_{sys} \) model
This chapter collects two parts, the design of the LMPC controller for the ESR and the related configurations. The LMPC utilizes the linearised model of ESR as the prediction model. The specific parameter setting are also discussed.

5.1 LMPC strategy for the ESR

As it mentioned in Chapter 2, there are four elements in the design of the LMPC controller, which are prediction model, constraints, cost function and optimization problem. Hence, these will be discussed in the following subsections, respectively.

5.1.1 Prediction Model

For the ESR system, the \( LRDSys \) model is adopted as the prediction model. Therefore, the prediction model is expressed as:

\[
\begin{align*}
x_r(k + i + 1|k) &= A_{rd}x_r(k + i|k) + B_{rd}u(k + i|k), \\
y(k + i + 1|k) &= C_{rd}x_r(k + i + 1|k) + D_{rd}u(k + i|k),
\end{align*}
\] (5.1a)
where $x_r$ denotes the state vector, $y$ is the measured output that is pure hydrogen, $u$ are the manipulated control actions which are ethanol, water, pressure, and temperature, $k$ is the discrete-time instant over the simulation time, $i$ is the discrete-time instant over the prediction horizon ($i = 0, \ldots, H_p - 1$) and $H_p$ is the prediction horizon.

### 5.1.2 Constraints

Unlike other controllers, the MPC strategy takes the constraints into account. Generally, the constraints of the ESR may be defined in the form of inequalities as

$$ u_{min} \leq u(k+i|k) \leq u_{max}, $$

$$ y_{min} \leq y(k+i+1|k) \leq y_{max}, $$

$$ \Delta u_{min} \leq \Delta u(k+i|k) \leq \Delta u_{max}, $$

where $u_{min}$ and $u_{max}$ are vectors of the lower and upper bounds on the manipulated inputs, respectively. $y_{min}$ and $y_{max}$ are the vectors of lower and upper bounds on the measured controlled outputs. $\Delta u_{min}$ and $\Delta u_{max}$ are the vectors of the lower and upper bounds on the slew rates, respectively. Considering the physical meaning of the inputs and outputs for the ESR, their values must be positive.

### 5.1.3 Cost Function

The cost function is the expression of the control objectives. Compared with the conventional technology of purifying the hydrogen by the WGS, it is not necessary to observe the quantity of the carbon monoxide. In this thesis, one control objective is to keep the pure hydrogen at its set point. Another is to minimize the intake of the ethanol. The whole cost function is expressed as

$$ J(k) = \sum_{i=0}^{H_p-1} [\| y(k+i+1|k) - r_y(k|k) \|^2_Q + \| u_1(k+i|k) \|^2_R], $$

where $y(k+i|k)$ is the controlled measured output with respect to time instant $k$, $u_1(k+i|k)$ is the predicted input of ethanol with respect to time instant $k$, $r_y(k|k)$ is the constant reference at time instant $k$, $Q$ and $R$ are the weighting matrices that are assumed to be constant over the simulation time. The choices of the weights reflect the priority and the importance of the objectives.
5.2 : Closed-loop Configuration

5.1.4 LMPC Problem for the ESR

Combining the prediction model, constraints on the inputs and outputs, objectives of ESR control problem and cost function, the LMPC problem for ESR is formulated in Problem 5.1.

Problem 5.1 (LMPC for ESR).

\[
\begin{align*}
\min_{u_1} & \sum_{i=0}^{H_p-1} \left[ ||y(k+i+1|k) - r_y(k|k)||_Q^2 + ||u_1(k+i|k)||_R^2 \right], \\
\text{subject to:} & \\
& x_r(k+i+1|k) = A_{rd}x_r(k+i|k) + B_{rd}u(k+i|k), \\
& y(k+i+1|k) = C_{rd}x_r(k+i+1|k) + D_{rd}u(k+i|k), \\
& u_{\min} \leq u(k+i|k) \leq u_{\max}, \\
& y_{\min} \leq y(k+i+1|k) \leq y_{\max}, \\
& x_r(k|k) = \hat{x}_r(0|k),
\end{align*}
\]

where \(\hat{x}_r(0|k)\) is the vector of estimated states, which will be regarded as the initial value of the LMPC. Only the first optimal control action of the optimal sequence is applied to the process. In this thesis, the Problem 5.1 is solved by the YALMIP Toolbox with cplex solver [Lof04].

5.2 Closed-loop Configuration

In this section, the configuration of LMPC with output feedback is explained. Figure 5.1 shows the scheme of this configuration. The LMPC controller computes the optimal control action at each sampling time based on Problem 5.1. Besides, a full-order state observer is described in this block diagram in order to estimate the full state vector from the measurement of the NLsys output. Since the estimate of the state vector is proposed to solve the optimization problem instead of using the true vector. According to [SSC93], a full state Luenberger observer without considering the disturbance can be expressed as

\[
\hat{x}_r(k+1) = (A_{rk} - LC_{rk})\hat{x}_r(k) + B_{rk}u(k) + L(y(k) - D_{rk}u(k)),
\]

where \(L\) is the estimator gain matrix that can be computed by Function dlqr in MATLAB.
Figure 5.1: The LMPC closed-loop configuration
This chapter shows all the simulation results of the ESR control system in the open and closed loops. The analysis of the static and dynamic behaviours of the NLsys simulation model are presented in the open-loop analysis. For the sake of comparing simulation results with different configurations, two key performance indicators (KPIs) are applied to evaluate the performance of the designed MPC controller. After finding the appropriate LMPC configuration, the simulation results of the closed loop has shown the performance of the proposed entire system.

6.1 Analysis of Open-loop Behaviours

The static and dynamic behaviours of the mathematical model have been analysed in a open loop, which plays a significant role in designing a MPC controller and acting as a guidance on the manual tuning of the MPC controller. Moreover, a comparison between the NLsys model and linear models is executed in order to validate whether the different linear models follow the behaviour of the NLsys system around the selected working point.

6.1.1 Static Analysis of the NLsys Model

The static profiles of molar flow rate of each component with respect to the position in z direction of the reactor are considered. In fact, the static analysis consists in solving the differential algebraic equations (4.1) until all the derivatives with respect to time are equal to zero. Figure 6.1 shows the molar flow rates of all the species vary with z-axial direction in the first stage of the reactor.
Chapter 6 : Simulation Results Analysis

In Figure 6.1, the horizontal axis denotes volume number, since the reactor is divided into 20 parts. All the reactions in (3.1) take place with same conditions simultaneously. Ethanol
is completely transformed into other products. Acetaldehyde firstly increases by the ethanol dehydrogenation and then decreases because it is reformed to hydrogen and carbon dioxide. Hydrogen, carbon monoxide, methane and carbon dioxide are always increasing until the reaction finishes. Water are decreasing because of its participation into the reforming process. The conversion rate of the ethanol can reach 100%, which is presented in Figure 6.2.

### 6.1.2 Dynamic Analysis of the NLsys Model

The behaviours of the non-liner model are tested by using step changes in nominal point of the inputs. Figures 6.3, 6.4 and 6.5 show the output molar flow rates with step changes of ±10% and ±20% of the ethanol, water and pressure inputs, respectively. In these figures, the ethanol, water and pure hydrogen are plotted. The yellow and cyan lines represent output with +10% and -10% total inputs, respectively while the magenta and red lines represent output with +20% and -20% total inputs. Through the observation of the output responses, some analyses are drawn as follows:

- For keeping a constant pressure in the reactor, responses of all the outputs are rapid, as consequence of changes in the inlet flow rates.
- For the step change of the ethanol input, the response of pure hydrogen has the same tendency as the one of the ethanol.
- For the step change of the water input, the pure hydrogen has the inverse response.
- For the step change of the pressure input, the output response of the pure hydrogen has the same tendency as the pressure. Because the law of the membrane separation use the pressure difference between the pressures in the retentate side and permeate side, so the output of pure hydrogen has the same tendency as the pressure change.
Figure 6.3: The molar flow rates with ±10%, ±20% step of the ethanol input
Figure 6.4: The molar flow rates with $\pm 10\%$, $\pm 20\%$ step of the water input
6.1.3 Comparison between the NLsys Model and Lsys, LRsys, LRDsys Models

The comparison of the behaviours between the NLsys and the linearised models is proposed to verify whether the control-oriented linearised model has the quite similar dynamic behaviours as the NLsys.

The response of pure hydrogen is regarded as the measured output. Figures 6.6, 6.7, 6.8
Table 6.1: Difference of the molar flow rates of pure hydrogen between \( NL_{sys} \) and \( L_{sys}, LR_{sys}, LRD_{sys} \) models

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
<th>+10%</th>
<th>+20%</th>
<th>-10%</th>
<th>-20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Hydrogen</td>
<td>0.0055</td>
<td>0.0196</td>
<td>0.0074</td>
<td>0.0359</td>
</tr>
<tr>
<td>Water</td>
<td>Hydrogen</td>
<td>-0.0017</td>
<td>-0.0076</td>
<td>-0.0013</td>
<td>-0.0046</td>
</tr>
<tr>
<td>Pressure</td>
<td>Hydrogen</td>
<td>-0.00013</td>
<td>-0.00035</td>
<td>-0.00025</td>
<td>-0.00046</td>
</tr>
</tbody>
</table>

show the response of pure hydrogen from the \( NL_{sys} \) compared to the responses of all the linearised models including \( L_{sys}, LR_{sys} \) and \( LRD_{sys} \). The blue line, cyan line, red line and magenta line represent the response of pure hydrogen from the \( NL_{sys}, LRD_{sys}, L_{sys} \) and \( LR_{sys} \), respectively. The delay of the \( LRD_{sys} \) model is a sampling time, that is \( T_s = 0.2s \). It is found that the divergences between the linearised models and non-linear model are quite small so that it can be negligible. Moreover, there is no difference between the response of linear discrete model and the linear model. So the error of responses among the non-linear and linearised models comes from the linearisation rather than the time discretization nor the model order reduction.

Table 6.1 presents the error percentage of the linear models respect to the non-linear model. According to this table, the divergences of the hydrogen can be negligible, which is no more than 4% when ± 10% and ±20% step change in the ethanol input. Regarding to the step change in the water input, the divergences of the hydrogen can be negligible, which is no more than 1%. For the step change in the pressure input, the divergences of the hydrogen can be also negligible.
Figure 6.6: Comparison of the molar flow rates of pure hydrogen between NLsys and Lsys, LRsys, LRDsys models with ± 10% and ± 20% step change in the ethanol input

Figure 6.7: Comparison of the molar flow rates of pure hydrogen between NLsys and Lsys, LRsys, LRDsys models with ± 10% and ± 20% step change in the water input
6.1 : Analysis of Open-loop Behaviours

6.1.4 Summary

The static and dynamic analysis lead to understand the process of the ESR and give a guidance on manual tuning of the LPMC controller to achieve a suitable performance. According to the comparison results in table 6.1, the difference between the linearised models and non-linear model with step changes in the inputs can be negligible. Moreover, since errors among the linearised models are zero, the response divergence between the non-linear and linearised models comes from the linearisation rather than time discretization nor the model order reduction.

Figure 6.8: Comparison of the molar flow rates of pure hydrogen between NLsys and Lsys, LRsyps, LRDsys models with ± 10% and ± 20% step change in the pressure input
6.2 Key Performance Indicators and Control Objectives

In this thesis, two key performance indicators (KPIs) are used to evaluate the system performances, which are smoothness and output error. Moreover, the specific control objectives are presented in this section. The control specification is that the controller should accomplish the tasks with a set of rules.

6.2.1 Smoothness KPI

This KPI describes the smoothness of the control action movements, which is expressed as

\[
KPI_{\Delta u_j} = \sqrt{\frac{1}{N} \sum_{k=1}^{N} (\Delta u_j(k))^2},
\]

(6.1)

where \( N \) is the total number of samples, \( \Delta u \) is the slew rate, \( j \) is the number of the inputs that are C\(_2\)H\(_5\)OH, H\(_2\)O, pressure and temperature.

6.2.2 Output Error KPI

This KPI presents the mean-square error between the outputs and their reference, which is described as

\[
KPI_{\Delta y_i} = \sqrt{\frac{1}{N} \sum_{k=1}^{N} (y_i(k) - r_i(k))^2},
\]

(6.2)

where \( r_i(k) \) are the reference of outputs, \( y_i(k) \) are the measured outputs, \( i \in H_2 \).

6.2.3 Control Objectives

As three manipulated inputs and one controlled measured output of the system presented in Chapter 4, main objective is to minimise the output error of pure hydrogen referred to the given reference while the secondary objective is to minimise the ethanol input. The two objectives should be satisfied within the operational constraints. Table 6.2 shows the control specification for the ESR, where MI denotes the manipulated inputs and CMO means the controlled measured outputs.
6.3 : LMPC with Output Feedback

Table 6.2: Control specifications for the ESR

<table>
<thead>
<tr>
<th>Molar flow rate</th>
<th>Role</th>
<th>Symbol</th>
<th>Set point</th>
<th>Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>MI</td>
<td>( u_{C_2H_5OH} )</td>
<td>–</td>
<td>±20%</td>
</tr>
<tr>
<td>Water</td>
<td>MI</td>
<td>( u_{H_2O} )</td>
<td>–</td>
<td>±20%</td>
</tr>
<tr>
<td>Pressure</td>
<td>MI</td>
<td>( P )</td>
<td>–</td>
<td>±20%</td>
</tr>
<tr>
<td>Pure hydrogen</td>
<td>CMO</td>
<td>( u_{H_2} )</td>
<td>±10%</td>
<td>±20%</td>
</tr>
</tbody>
</table>

6.3 LMPC with Output Feedback

The configuration of LMPC with output feedback has presented in Figure 5.1.

6.3.1 LMPC Tuning

The LMPC tuning is an indispensable step for obtaining the appropriate parameters to improve the performance and stability of the closed-loop response. There are two parameters required to be tuned, which are the weights of cost function and prediction horizon. These parameters are adjusted via a trial and error procedure with the previous knowledge of the chemical system from the behaviour analysis in the open loop.

Cost Function Weights

According to the primary and secondary objectives in MPC, the weights of cost function have been defined in the different options. The normalizations of all the terms in the cost function are defined in (6.3), for the purpose of maintaining weights in the range from 0 to 1 [RGMSP12].

\[
Q_{ii} = \frac{q_{ii}}{[y_{i,max} - y_{i,min}]^2}, \tag{6.3a}
\]

\[
R_{jj} = \frac{r_{jj}}{[\Delta u_{j,max} - \Delta u_{j,min}]^2}, \tag{6.3b}
\]

where \( Q_{ii} \) is the weight to penalize the errors of pure hydrogen and \( R_{jj} \) is the weight to penalize the ethanol input. \( q_{ii} \) and \( r_{jj} \) represent the given parameters to compute the weights in cost function.
Table 6.4: KPIs with different weights for the LMPC

<table>
<thead>
<tr>
<th>Controller</th>
<th>( \text{KPI}_{H_2} )</th>
<th>( \text{KPI}_{C_2H_5OH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMPC1</td>
<td>3.6181e-6</td>
<td>4.1147e-10</td>
</tr>
<tr>
<td>LMPC2</td>
<td>3.5818e-6</td>
<td>1.2465e-9</td>
</tr>
<tr>
<td>LMPC3</td>
<td>2.2477e-6</td>
<td>4.8648e-7</td>
</tr>
</tbody>
</table>

Table 6.3: The LMPC weights tuning

<table>
<thead>
<tr>
<th>Controller</th>
<th>( q_{H_2} )</th>
<th>( r_{C_2H_5OH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMPC1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>LMPC2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>LMPC3</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.3 shows the three selections of weights in the cost function, in which all the penalized weights to maintain the output of the hydrogen followed the reference are always one, because the primary control objective is to generate pure hydrogen. In LMPC1, two objectives have the same priority. In LMPC2, the objective for penalizing the output error has a higher priority than the one for penalizing ethanol input. In LMPC3, the objective for penalizing the output error has the higher priority while the objective for penalizing ethanol input is ignored.

After simulations, the KPIs for each weight selection have been shown in the Table 6.4. The KPIs of LMPC2 are in the middle among the three cases and two control objectives are required. Hence, it is concluded that the weights of LMPC2 are chosen as desired parameters.

**Prediction Horizon**

In the LMPC for ESR, it is assumed that the control horizon is equal to the prediction horizon. It is essential to select an appropriate prediction horizon. So some selected prediction horizons to be verified have been proposed in the Table 6.5. According to the KPIs, the best prediction horizon will be chosen.

Table 6.6 shows the results of KPIs with different prediction horizons. The one having the lowest values of KPIs is the best selection. So the prediction horizon is selected as 20.
Table 6.5: The LMPC prediction horizon tuning

<table>
<thead>
<tr>
<th>Controller</th>
<th>H_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMPC4</td>
<td>10</td>
</tr>
<tr>
<td>LMPC5</td>
<td>15</td>
</tr>
<tr>
<td>LMPC6</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 6.6: The KPIs with different prediction horizons for LMPC

<table>
<thead>
<tr>
<th>Controller</th>
<th>KPI_{\phi_H}</th>
<th>KPI_{u_{C_2H_5OH}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMPC4</td>
<td>2.6029e-9</td>
<td>4.8592e-7</td>
</tr>
<tr>
<td>LMPC5</td>
<td>2.2308e-9</td>
<td>4.8582e-7</td>
</tr>
<tr>
<td>LMPC6</td>
<td>1.0370e-9</td>
<td>4.8484e-7</td>
</tr>
</tbody>
</table>

6.3.2 Simulation Results

As the cost function weights and prediction horizon decided before, different alternatives are proposed by changing the set point of the hydrogen reference to evaluate the behaviours of the ESR. Figure 6.9 and 6.11 show the control actions of closed-loop system with two references. The constraint for temperature is set as a constant because it is not expected as the manipulated inputs instead of the disturbance, so the control action of temperature stays as a nominal point. With the given control objectives, all the control actions are varying smoothly. Figure 6.10 and 6.12 present the output of hydrogen in blue line and its reference in magenta line. The constraint for output is set as the range between ±20% of the nominal point. The hydrogen output properly follows its reference in two simulations. Hence, the control objectives have been successfully reached.
Figure 6.9: Control actions of the closed-loop system with a positive reference

Figure 6.10: Hydrogen output of the closed-loop system with a positive reference
6.3: LMPC with Output Feedback

Figure 6.11: Control actions of the closed-loop system with a negative reference

Figure 6.12: Hydrogen output of the closed-loop system with a negative reference
CHAPTER 7

CONCLUDING REMARKS

This chapter gives the summary from this thesis and proposes some future works based on conclusions.

7.1 Conclusion

This thesis has proposed a novel mathematical model for the ESR with membrane separation. Besides, the resultant linear model has been computed facing the design of MPC controllers for regulating the production of pure hydrogen. advanced MPC control strategy for the ESR system, which has been achieved with a desired performance. Furthermore, a one-dimensional, pseudo-homogeneous and non-steady-state model has been built up for the ethanol staged membrane reformer process. The simulation results have been shown and discussed in chapter 6, some specific comments are presented as follows:

- The simulation model has been implemented successfully in Simulink/Matlab and the comparison between the simulation results and experimental data has proved out the precision of the simulation model of the ESR.

- Numerical linearisation and model order reduction are the significant steps to obtain the control-oriented model for the LMPC design.

- The comparison of the output response between the non-linear model and linear models has proved that it is possible to use linear models around a selective working point as control-oriented models facing the LMPC design.
• Parameters tuning is a critical approach to achieve a satisfied control performance, for instance weights of cost function and prediction horizon.

7.2 Contributions

The general contributions have been achieved in this thesis including the following aspects:

• Propose a new modelling approach considering using the Pd-Ag membrane without the sweep gases to generate the pure hydrogen, which has been verified by comparing with the experimental data.

• Take the spatial variable volumetric flow rate into the account to improve the whole mathematical model.

• Apply the mass balance law into modelling the membrane separation of ESR.

• Design an advanced MPC controller for the ESR to let the output of hydrogen follow a given reference of pure hydrogen.

7.3 Future Research

There are still some undone work to be continued in the future so that the simulation model can reflect the real process accurately and the controller can be much more suitable for the ESR system. Some ideas can be followed to continue this research in the following:

• Design other controllers for the ESR system for comparisons, such as PID and LPV.

• Combine the mass balance and energy balance to build the simulation model in order that more realistic model can be used.

• The simulation model can be fitted for the non-isothermal and non-isobaric conditions.

• Build a model with disturbances for the MPC strategy.

• Design a non-liner predictive controller for the ESR system and make a comparison with LMPC.
Part

Appendices
Appendix A

Acronyms

ATR Auto-thermal Reforming
CMO Control and Measured Outputs
ESR Ethanol Steam Reformer
KPIs Key Performance Indicators
LMPC Linear Model Predictive Control
LPV Linear Parameter Varying
$L_{RD_{sys}}$ Linear Reduced Discrete Model
$L_{Rsys}$ Linear Model with Order Reduction
$L_{sys}$ Linear Full-order Continuous Model
MI Manipulated Inputs
MPC Model Predictive Control
$N_{Lsys}$ Non-linear Continuous Model
NMPC Non-linear Model Predictive Control
ODEs Ordinary Differential Equations
PDEs Partial Differential Equations
PEMFCs Polymer Electrolyte Membrane Fuel Cells
PFR Plug Flow Reactor
PID Proportion Integration Differentiation
POX Partial Oxidation
ppm Parts Per Million
QP Quadratic Programming
SR Steam Reforming
WGS Water Gas Shift
# Appendix B

## Parameters

<table>
<thead>
<tr>
<th>First Stage Parameters</th>
<th>Volume, [m³]</th>
<th>Molar Relation, [ ]</th>
</tr>
</thead>
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<tr>
<td>$V_1 = 3.1416e-6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 0.4286$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Ea_1 = 7.0e+3$</td>
<td>Activation Energy for reaction 1, [J/mol]</td>
<td></td>
</tr>
<tr>
<td>$Ea_2 = 1.3e+4$</td>
<td>Activation Energy for reaction 2, [J/mol]</td>
<td></td>
</tr>
<tr>
<td>$Ea_3 = 7.0e+3$</td>
<td>Activation Energy for reaction 3, [J/mol]</td>
<td></td>
</tr>
<tr>
<td>$Ea_4 = 8.9e+3$</td>
<td>Activation Energy for reaction 4, [J/mol]</td>
<td></td>
</tr>
<tr>
<td>$k_{\infty 1} = 5.025e+3$</td>
<td>Pre-exponential Factor for Reaction 1, [mol/(m³·min·bar)]</td>
<td></td>
</tr>
<tr>
<td>$k_{\infty 2} = 0.4788e+3$</td>
<td>Pre-exponential Factor for Reaction 2, [mol/(m³·min·bar)]</td>
<td></td>
</tr>
<tr>
<td>$k_{\infty 3} = 4.548e+3$</td>
<td>Pre-exponential Factor for Reaction 3, [mol/(m³·min·bar²)]</td>
<td></td>
</tr>
<tr>
<td>$k_{\infty 4} = 4.7880e+4$</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Second Stage Parameters</th>
<th>Volume, [m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2 = 2.3297e-5$</td>
<td></td>
</tr>
<tr>
<td>$\delta = 3.0e-5$</td>
<td>Thickness of the Pd-Ag Membrane, [m]</td>
</tr>
<tr>
<td>$A = 7.1e-4$</td>
<td>Surfance area of the Pd-Ag Membrane, [m²]</td>
</tr>
<tr>
<td>$D = 3.2e-3$</td>
<td>Diameter of the Pd-Ag Membrane, [m]</td>
</tr>
<tr>
<td>$Ea = 8.8e3$</td>
<td>Activation Energy for the Membrane Separation, [J/mol]</td>
</tr>
<tr>
<td>$P_{e0} = 6e-7$</td>
<td>Pre-exponential Factor, [mol/(m³·min·Pa⁰.⁵)]</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


