Design, Modelling and Optimization of a Heat Integrated Coal Gasification Process

by

ZHU Yi

A Thesis Submitted to
The Hong Kong University of Science and Technology
in Partial Fulfillment of the Requirements for
the Degree of Master of Philosophy
in Chemical and Biomolecular Engineering

August 2015, Hong Kong
Authorization

I hereby declare that I am the sole author of the thesis.

I authorize the Hong Kong University of Science and Technology to lend this thesis to other institutions or individuals for the purpose of scholarly research.

I further authorize the Hong Kong University of Science and Technology to reproduce the thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

ZHU Yi

August, 2015
Design, Modelling and Optimization of a Heat Integrated Coal Gasification Process

by

ZHU Yi

This is to certify that I have examined the above MPhil thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

Prof. HUI Chi Wai, Thesis Supervisor

Prof. CHEN Guohua, Department Head

Department of Chemical and Biomolecular Engineering
August, 2015
Acknowledgements

First and foremost I want to thank my supervisor Prof. David, HUI Chi Wai. It has been a great fortune and an honor in my life to be his student. He has taught me, both consciously and unconsciously, how beautiful and exciting research is. I appreciate all his contributions of time, ideas, and guidance to make my academic experience productive and stimulating. He patiently taught me, not only on various aspects of process system engineering theory, but also the right attitude in which to conduct research and toward life. The joy, humility and devotion he has for his research and teaching was deeply contagious and motivational for me to become an outstanding person in my future career.

I wish to thank Prof. GAO Furong and SUN Fei for serving on my defense committees, as well as Prof. HU Xijun for being my thesis committee member. It has been a great experience to study and work with them. I am also grateful to Prof. Richard LAKERVELD and Prof. Henry TONG. The experience of being teaching assistant for CENG 4670 instructed by them taught me what is responsibility and efficient communication.

I also would like to appreciate my research group members and office mates, Dr. Adetoyese Olajire OYEDUN, Dr. Tesfaldet GEBREEGZIABHER, Dr. Alireza BAZARGAN, Mr. LIANG Yingzong, Mr. ZHANG Yu, Mr. LIU Jin, Mr. Ergys PAHIJA and Mr. WANG Maojian. It has been a memorable time with them all and all their comments and contributions during the group meetings are well appreciated. Special thanks to all the administrative staffs of the department particularly Ms. Floret WONG and Ms. Cherry K.C. SIN who had providing major administrative support throughout my research studies at HKUST.

I have met many good friends here at HKUST. It is hard to acknowledge all of them here. Some of them are JIN Rui, NING Chao, ZHAN Ning, OUYANG Weiyi and SUI Xiao. Their support and sharing parts of their lives kept with me has me grounded and helped me grow. Special thanks would be given to OilProbe team members CAO Wenbin and ZHOU Bingpu. With our efforts, the team broke into the final round of The Fifth Annual HKUST One Million Dollar Entrepreneurship Competition. The journey with them is one of the most impressive experiences at HKUST.
Over the past year, I have been deeply grateful for the love that my wife ZHANG Di has brought to me. Her smile and encouragement enabled me to be the best of myself and go through all the tough times in the research. This thesis is dedicated to her.

Last but not least, it was because of the love of my families and friends that I treasure every minute in life. I would like to thank my mother for bringing me up. I would also like to thank my friends in the dormitory, in the department and in every trip, for their greetings, support and jokes that keep me smile every day.
# TABLE OF CONTENTS

| TITLE PAGE | i |
| AUTHORIZATION PAGE | ii |
| SIGNATURE PAGE | iii |
| ACKNOWLEDGEMENTS | iv |
| TABLE OF CONTENTS | vi |
| LIST OF FIGURES | ix |
| LIST OF TABLES | xi |

## CHAPTER 1 INTRODUCTION

1.1 Background 1

1.2 Motivation and challenge 3

1.3 Gasification modelling 4

1.4 Heat integration modelling 7

1.5 Thesis Outline 9

## CHAPTER 2 GASIFICATION MODELLING AND OPTIMIZATION

2.1 Equilibrium model based on the Gibbs free energy minimization 10

2.1.1 Introduction 10

2.1.2 System Gibbs free energy 10

2.1.3 Heat balance and elemental balances 12

2.1.4 Model implementation 13

2.1.5 Model validation 15

2.1.6 Optimization results and discussion 17

2.1.7 Conclusions 20

2.2 Equilibrium model with KKT conditions 21

2.2.1 Introduction 21
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.2</td>
<td>KKT algorithm</td>
<td>21</td>
</tr>
<tr>
<td>2.2.3</td>
<td>KKT conditions of minimizing Gibbs free energy</td>
<td>23</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Example</td>
<td>25</td>
</tr>
<tr>
<td>2.2.5</td>
<td>Conclusion</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>Single objective model</td>
<td>29</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Introduction</td>
<td>29</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Target function development</td>
<td>29</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Example</td>
<td>34</td>
</tr>
<tr>
<td>2.4</td>
<td>Conclusions</td>
<td>36</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>39</td>
</tr>
<tr>
<td>3.2</td>
<td>Heat integration modelling</td>
<td>40</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Pinch analysis</td>
<td>40</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Mathematical formulations of temperature difference and phase change</td>
<td>42</td>
</tr>
<tr>
<td>3.2.3</td>
<td>The detailed formulations</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Example</td>
<td>49</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Maximum heat recovery with fixed stream parameters</td>
<td>49</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Maximum heat recovery with variable stream parameters</td>
<td>52</td>
</tr>
<tr>
<td>4.1</td>
<td>Problem Statement</td>
<td>56</td>
</tr>
<tr>
<td>4.2</td>
<td>Model summary</td>
<td>57</td>
</tr>
<tr>
<td>4.3</td>
<td>Case study</td>
<td>59</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Base case – Iterative approach for profit maximization</td>
<td>60</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Case 1 – Simultaneous approach for profit maximization</td>
<td>60</td>
</tr>
</tbody>
</table>
4.3.3 Case 2 – Simultaneous approach for profit optimization with heat integration 62
4.3.4 Comparison of the cases 64
4.3.5 Profit with steam price variation 66
4.3.6 Profit with variations of combined cycle efficiency and electricity price 67
4.4 Conclusions 68

CHAPTER 5 CONCLUSIONS AND FUTURE WORK 70
5.1 Conclusions 70
5.2 Future work 72

BIBLIOGRAPHY AND REFERENCES 73
APPENDIX A Formulations of enthalpy, entropy and heat capacity of typical coal gasification components 79
APPENDIX B Publications 81
LIST OF FIGURES

Figure 2.1. The calculation procedure of equilibrium model 14
Figure 2.2. The optimization procedure using the equilibrium model 15
Figure 2.3. Variation of equilibrium composition with air for RTC-coal gasification [16] 16
Figure 2.4. Results of RTC-coal gasification with air for model validation 16
Figure 2.5. Results of RTC-coal gasification with 0.3 kmole GFW by varying air 17
Figure 2.6. Results of RTC-coal gasification with 0.6 kmole air by varying GFW 18
Figure 2.7. Validation procedure of the single objective model and the equilibrium model 33
Figure 2.8. Temperature profile of the single objective model and the equilibrium model 34
Figure 2.9. The results of conventional approach by iterative searching 35
Figure 3.1. Graphic determination of pinch point and definitions 41
Figure 3.2. Composite curves of heat transfer with phase change in the hot stream 44
Figure 3.3. The calculation of heat source above a pinch candidate for a hot stream with phase change 45
Figure 3.4. The calculation of heat source above a pinch candidate for a hot stream 46
Figure 3.5. The calculation of cooling source above a pinch candidate for a cold stream 46
Figure 3.6. Composite curves of heat recovery network with fixed stream parameters 51
Figure 3.7. Composite curves of heat recovery network without considering phase change 51
Figure 3.8. Composite curves of heat recovery network with variable stream parameters 53
Figure 4.1. Flow diagram of a heat integrated gasification process 57
Figure 4.2. Process flowsheet of Case 1 61
Figure 4.3. Composite curves of Case 1 61
Figure 4.4. Process flowsheet of Case 2 62
Figure 4.5. Composite curves of Case 2 63
Figure 4.6. Network design of heat recovery in Case 2 64
Figure 4.7. Profit maximization results with steam price change 66

Figure 4.8. The profit maximization results corresponding to combined cycle efficiency and electricity unit price change 68
LIST OF TABLES

Table 2.1. Solutions to Gibbs free energy minimization at one operating condition 19
Table 2.2. Optimization results of global minimum Gibbs free energy 26
Table 2.3. Optimization results of one local minimum Gibbs free energy 27
Table 2.4. LHV of gases 30
Table 2.5. Equilibrium constants for the six major reactions. 31
Table 3.1. Data of process streams 49
Table 3.2. Pinch candidates and heat duty 50
Table 3.3. Calculations of heat demand and cooling demand 50
Table 3.4. The stream data with optimization results 52
Table 4.1. Parameters of the heat integrated gasification process 60
Table 4.2. The data of unit prices and LHV [56] 60
Table 4.3. Stream data of heat recovery network in Case 2 62
Table 4.4. Heat transfer coefficient [58] 63
Table 4.5. Data of heat exchangers 64
Table 4.6. Summary of the three case study results 65
Abstract

Power generation used around 40% of primary energy with coal as the major contribution, which causes not only severe environmental pollutions but also increases the threat of global warming. As a result, utilizing coal gasification technology which has many environmental benefits in electricity generation has attracted increasing attention worldwide. However, most gasification studies focus on optimizing cold gas efficiency (CGE) by sensitivity analysis or control variant method and ignore how the integration of sensible heat would affect the power generation.

In this study, a novel mathematical model which simultaneously optimizes the key operating parameters of a heat integrated coal gasification process to achieve maximum economic profit is developed. Based on the equilibrium modelling work, it is found that, at above 1400 K, the operating conditions that maximize the profit automatically lead to minimized Gibbs free energy of products. Thus, the complicated multi-objective problem of profit optimization (profit maximization and Gibbs free energy minimization) is directly simplified to a single objective problem of profit maximization, and the model can be developed accordingly. Further, how the integration of sensible heat would influence the overall performance is taken into account. One way of handling such heat integration problem is to use pinch analysis method to ensure the feasibility of heat exchange and maximum heat recovery. To achieve simultaneous optimization, a set of constraints and piecewise functions are developed to handle the variable temperatures, flow rates as well as the phase change of process streams. Case studies have been conducted to illustrate the effectiveness and robustness of the profit optimization using the developed models. The results indicates that by assigning part of the sensible heat to preheat the reactants, the profit can be increased by 40% compared with that of using sensible heat for HP steam production indifferently.
CHAPTER 1

INTRODUCTION

1.1 Background

The global annual primary energy consumption was estimated to be 12,928 million tonnes of oil equivalent in 2014 [1]. Fossil fuels accounted for 86.4% of the primary energy consumption, with oil (32.9%), coal (29.9%) and natural gas (23.6%) as the major fuels [1]. Among them, power generation used around 40% of primary energy with coal as the major contribution, which causes not only severe environmental pollutions but also increases the threat of global warming [2]. Despite of the call for renewable energy like biomass, solar and nuclear etc., their high capital cost, difficulty in scaling up or the safety issues involved make the substitution of power generation by coal still impossible currently. For the foreseeable future, the role of coal as an important global energy source, especially in non-OECD countries, will remain unchanged. Therefore, cleaner and more efficient coal conversion technologies are urged.

Combustion, gasification and pyrolysis are three major coal conversion technologies for power generation. Combustion is to burn the coal completely to produce heat which can be utilized for steam generation to produce electricity. Gasification is a process that converts carbonaceous feedstock (coal) into synthesis gas (syngas), primarily composed of carbon monoxide (CO) and hydrogen (H₂), which can be directly used as fuels in a combined cycle power plant. In the gasification process, the coal is reacted in the presence of controlled amounts of oxygen and gasification feed water (GFW) at high temperatures (>700°C). In pyrolysis, however, coal is decomposed into the volatile components, in the temperature range of 200-760°C, and in the absence of air or oxygen, forming syngas and/or liquids. A mixture of un-reacted carbon char (the non-volatile components) and ash remains as a residual. In comparison with combustion and gasification, pyrolysis has less conversion efficiency and its processing time is slow [3-4]. Additionally, it needs complex processes to recover energy from multi-phase products. Thus, pyrolysis is not suitable for power generation in large capacity. The most promising application of pyrolysis is to produce fuels and chemical feedstocks using biomass, waste and plastics etc. [5].
Combustion and gasification, on the other hand, have faster conversions, and thus are two feasible options for power generation. The conventional coal-fired power plants using combustion process have dominated the electricity generation industry for many years. In a conventional power plant, coal undergoes complete combustion to generate steam in a boiler. This steam is expanded in a steam turbine to generate electricity. The solution using gasification for power generation is called the Integrated Gasification Combined Cycle (IGCC), which consists of an open loop (Brayton) and a closed loop (Rankine). First, coal undergoes gasification to produce flammable synthesis gas (syngas). This syngas, then, is cleaned up and mixed with compressed air/O₂. The mixture is combusted and expanded in a gas turbine to generate power. The exhaust gas is further used to generate steam which can produce electricity in a steam turbine. As a result, IGCC has a much higher thermal efficiency of 58% around compared to a conventional coal-fired power plant [6].

In addition to the higher thermal efficiency, gasification is also favorable in terms of pollution and greenhouse gas emissions. The carbon dioxide (CO₂) in the flue gas from combustion is at a lower partial pressure, and is expensive to capture with currently available technology. On the other hand, fuels undergoes partial oxidation (gasification) result in a smaller volume of gas produced, which offers more efficient and economical capture of CO₂. Moreover, combustion requires stringent control measures for NOx and SOx, while gasification produces negligible NOx and the sulfur (S) in the form of H₂S and COS which is much easier to capture. What’s more, IGCC with gasification process uses approximately 14–24% less water to produce electric power compared to conventional power plant using combustion process, and water losses during operation are about 32–36% less [7]. This is a major issue in many countries where water supplies have already reached critical levels in certain regions. Therefore, gasification has attracted increasing attention in terms of power generation.
1.2 Motivation and challenge

Although an IGCC plant has obvious advantages over a conventional coal fired power plant in terms of both efficiency and emissions, there is a debate over whether the IGCC performance is reliable and efficiency can be further improved to offset the relatively higher capital cost. As the combined cycle primarily composed of steam turbine and gas turbine that are already well established, the efficient electricity generation in IGCC highly depends on the gasification performance.

The gasification performance is reflected by its product, syngas which has two forms of energy. The first form is the calorific value that is reflected by the cold gas efficiency (CGE) defined in Eq. (1.1) and the second form is the sensible heat that is released when the syngas is cooled.

\[
CGE = \frac{\text{LHV of syngas}}{\text{LHV of feedstock}}
\]  

(1.1)

where LHV stands for lower heating value which is determined experimentally by subtracting the heat of vaporization of the water vapor from the higher heating value. Higher heating value is determined as the heat released by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced.

Most of the gasification studies focus on optimizing CGE by either varying certain key parameters one at a time [8-9] or fixing important operating parameters based on vendor-specific data [10]. How to conduct a simultaneous optimization has seldom considered. Moreover, the sensible heat recovered from syngas cooling could be used for feed preheating and/or steam generation. The former would facilitate the gasification and increase the electricity by gas turbine, and the latter would raise the power generated by steam turbine. How the integration of sensible heat would affect the power generation is often ignored. In this thesis, a novel mathematical model for optimizing a heat integrated coal gasification process has been attempted, which simultaneously optimizes the key operating parameters to maximize economic profit.
To optimize the entire process, we need to consider two parts. The first part is the gasification process itself. To optimize the gasification process, it needs to minimize Gibbs free energy on one hand and maximize the CGE on the other hand. It is difficult to solve such problem of multi-extremum. However, in this part, the sensible heat that the syngas carries has not been considered. Therefore, a second part is introduced that describes the different ways of using the sensible heat and allows its optimization, which is the heat integration model. Generally speaking, this model is based on the pinch analysis method. But it should be noticed that there are several special requirements in this case. The heat integration model must be able to handle phase change and variable flow rates and temperatures. And these challenges will be addressed in the following work.

1.3 Gasification modelling

As discussed above, the efficient electricity generation in IGCC highly depends on the gasification performance. The production of syngas via gasification is a complex process that is strongly affected by the composition of feedstock, the gasifying temperature and pressure, the amount of GFW and oxygen, etc. [11]. These parameters coupled with the sensitivity of the syngas to the rate of heating and residence time in the reactor, require the development of mathematical models. Through modelling, the thermochemical processes during gasification can be studied and how operating parameters, such as oxidant/fuel ratio, syngas composition and heating value would influence the gasification performance can be evaluated.

Recent modelling efforts include the application of equilibrium models [12-16] to predict the performance of commercial gasifiers, as well as several kinetic models for particular reactor types [17-24]. Kinetically modified equilibrium models that are integrated with carbon conversion correlations determined experimentally have also been reported [25-28].
Kinetic models based on computational fluid dynamics have the highest level of fidelity. Numerous researchers have focused on kinetic models to improve gasification technology. Wang and Kinoshita proposed the kinetic model based on a mechanism of surface reaction in the reduction zone assuming a given residence time and reaction temperature [20]. Simulations were performed to evaluate the effects of parameters like particle size and moisture etc. Giltrap et al. developed a model of downdraft gasification based on the reaction kinetics in the reduction zone to predict the syngas composition [22]. However, the model over-predicted the methane concentration as the limited availability of data on the initial conditions at the top of reduction zone. Babu and Sheth modified Giltrap’s model by incorporating the variation of the char reactivity factor along the reduction zone of the downdraft gasifier [23]. As a result, the model gave better predictions of the gasification temperature and syngas composition in comparison with the experimental date and Giltrap’s model. Liang et al. developed a new numerical model based on the kinetic theory of granular flow and complicated reactions [24]. The relationship between syngas composition at different heights of the gasifier and the distributions of gas velocity were discussed to give insights about gasifier design.

Although kinetic models provide essential information on mechanisms and rates, they are computationally intensive and require comprehensive experiments to determine the kinetic coefficients involved. As a result, the kinetic models have been primarily used to instruct design, evaluation and improvement of gasifiers by providing essential information on kinetic mechanisms of gasification. On the other hand, equilibrium models based on Gibbs free energy are a more general approach that can effectively predict product composition at different reaction conditions without any experimental data. It can also cover a wide range of operating conditions and rigorously takes into account energy and material balances. Therefore, equilibrium models are the most suitable approach for process studies on the influence of the most important process parameters [29]. The major assumptions in the equilibrium model are [29]:

- All reactants are well mixed, and uniform temperature is achieved for the gasifier.
- Gasification reaction rates are fast enough or residence time is long enough to reach the equilibrium state.
- Tars are not formed.
Equilibrium models have two general approaches: stoichiometric and non-stoichiometric models. The stoichiometric models require selecting the product species that are present in the largest amounts. Based on the selection, specify the reactions and use Gibbs free energy to determine the equilibrium constants of the proposed reactions. In the non-stoichiometric models, the only input is the elemental composition of the feed instead of the reactions taking place or species involved. They are based on the minimization of Gibbs free energy in the gasification system. As shown by various authors, the two kinds of models are essentially equivalent as the Gibbs free energy is used to determine the equilibrium constants in stoichiometric approach and is minimized directly in non-stoichiometric approach.

Several equilibrium models based on the Gibbs free energy have been developed to effectively study the thermodynamic performance of gasification. Baratieri et al. used an equilibrium model based on the minimization of the Gibbs free energy, in order to estimate the theoretical yield and the equilibrium composition of the reaction products of biomass thermochemical conversion processes [14]. Tang et al. developed a thermodynamic model with direct Gibbs free energy minimization to estimate equilibrium composition for supercritical water reforming of methanol, and supercritical water gasification (SCWG) of glucose, cellulose, and real biomass [15]. Shabbar et al. evaluated RTC-coal gasification using Gibbs free energy minimization model under different operating condition including air, air-steam and solar heat (under standard pressure) [16]. Further, Kamath et al. embedded Gibbs model as an inner minimization problem within an outer optimization problem (to minimize the cost). By solving this as a bi-level optimization problem, Kamath et al. was able to minimize Gibbs free energy on one hand and obtain the optimum gasification conditions on the other hand resulting in maximum profitability.

In some circumstances like low gasification temperatures and short residence time, the thermodynamic equilibrium state can hardly be achieved. As a result, the equilibrium models yield great disagreements when validated with experimental date. For this reason, several researchers have developed kinetically modified equilibrium models by incorporating carbon conversion correlations determined experimentally to better simulate gasification in a certain temperature specifically.
Li et al. modified the equilibrium model by imposing the fractional achievement of equilibrium, leading to a modified model in which carbon conversion is correlated with air ratio and temperature from experimental data [27]. Barba et al. devised a new mathematical model, the so-called Gibbs Free Energy Gradient Method Model, which used an Arrhenius type equation to express the dependence of kinetic constants on temperature in two reactions [28]. Through this, the model improved the ability of equilibrium models to fit experimental data, in particular as regards the content of methane, hydrogen and carbon residue. Although this method which integrates kinetics into equilibrium models improves the approaching of theoretical results to experiments, it also makes the models unpredicted, and thus missing the possibility to be employed in the development of process design.

1.4 Heat integration modelling

In a gasification process, the sensible heat recovered from syngas cooling could be integrated with feed preheating and/or steam generation. The optimization of heat integration includes two aspects which are how to best integrate the limited heat and how to design the heat recovery network. The integration options are optimized simultaneously with the gasification process through economic profit comparison. Heat recovery network design is realized through the pinch analysis method which is the most used heat integration technique.

The heat recovery network design problem in process design has received remarkable attention in the literature and various approaches have been developed. The methods can be generally classified as sequential synthesis and simultaneous synthesis. For sequential approach, it decomposes the problem to minimum energy targeting and heat exchange network design and solves them in two successive steps. On the other hand, simultaneous approach can address the original problem without decomposition of the problem.

One of the earliest formulations of simultaneous method was developed by Yuan et al. The major drawback of the model is it could not allow splitting or mixing of the process streams [30]. Floudas and Circic proposed the simultaneous match-network hyperstructure model for optimizing all of the capital cost a once [31]. However, the formulation is still based on temperature interval partitioning of the heat recovery network problem.
Although great efforts have been taken to improve the simultaneous method, it still relies heavily on MINLP formulations subject to various simplifying assumptions. For the heat recovery network design in the gasification optimization, the major problem lies on how to obtain minimum energy targeting. Therefore, the sequential method has better performance and more suitable for the optimization target.

For minimum energy targeting, Linnhoff and Hindmarsh invented pinch analysis method to “best” design the highest degree of energy recovery with a given number of capital items [32]. Cerda and Westerburg presented a method which could linearize cooling/heating curves and partition the problem only at potential pinch points [33]. Papoulias and Grossmann developed a linear programming version that was used for predicting the minimum utility cost, and could handle restricted matches and multiple utilities [34].

What these methods have in common is the heat recovery network problem which these methods applied for has the assumption that flow rates and temperatures of the process streams are fixed values. Hence, these methods can optimize the heat integration only after the process conditions are determined through the gasification optimization. However, flow rates and temperatures are critical variables in both optimization problems. The heat integration should be considered simultaneously with the gasification process.

Duran and Grossmann proposed a model which takes into account the interactions between a process and a heat recovery network by a set of constraints that are based on a pinch analysis method [35]. The model makes the simultaneous optimization possible by allowing for variable flow rates and temperatures. Recently, two novel formulations for the simultaneous optimization of chemical processes with heat integration were developed by Hui [36]. In this work, to handle the process streams with phase changes, a novel set of constraints are developed based on the Duran and Grossmann’s approach. The concepts of simultaneous optimization are employed to the entire gasification process. To minimize Gibbs free energy on one hand, maximize CGE or profitability on the other hand with consideration of heat integration as a set of constraints, has never been investigated before.
1.5 Thesis Outline

The general aim of this thesis is to develop simple yet effective models to solve a simultaneous optimization problem for a heat integrated coal gasification process. The work is organized in five chapters, and presents an outline of each chapter in this section.

We begin with developing an effective model for gasification in Chapter 2. Equilibrium model based on the Gibbs free energy minimization is formulated and converted by KKT algorithm to reduce difficulty solving the non-convex problem. Further, a novel single objective model is developed based on an unusual phenomenon.

In Chapter 3, we presented a heat integration model based on the pinch analysis method. The model expands the pinch candidates to phase change temperatures and contains a special set of temperature expressions. As a result, process streams having variable parameters and phase change can be handled properly.

Chapter 4 aims to solve a practical problem for optimizing a heat integrated coal gasification process. The single objective model and the heat integration model are combined to optimize the economic profit of the overall process. The effectiveness of model is illustrated through three case studies.

Finally, we summarize the work and discuss the future work in Chapter 5.
2.1 Equilibrium model based on the Gibbs free energy minimization

2.1.1 Introduction

As discussed in Chapter 1, the equilibrium approach for modelling gasification process is most suitable for process studies on the influence of the most important process parameters. It is known that, when chemical reactions reach equilibrium state for a given pressure and temperature, the reaction system has two distinctive properties: the total Gibbs free energy $G_{sys}$ has a minimum number (non-stoichiometric) and its differential $dG_{sys}$ is zero (stoichiometric) [37]. The stoichiometric property of setting $dG_{sys}$ to zero to determine the equilibrium state is a conventional criterion which has been described in many textbooks about chemical engineering thermodynamics. However, this approach involves specifying a set of reactions, calculating equilibrium constants for each of them. Therefore, it may not be suitable for gasification process that has too many reactions which would result in convergence issues associated with nonlinear equations involving fugacity ratios [38]. In the following session, the non-stoichiometric property of the total Gibbs free energy reaching its minimum at the equilibrium state is utilized to simulate gasification process that includes a number of simultaneous reactions.

2.1.2 System Gibbs free energy

According to the second law of thermodynamics, all irreversible processes occurring at a given temperature ($T$) and pressure ($P$) proceed in a direction such that the total Gibbs free energy of the system decreases [39]. Thus, the equilibrium state of a system is reached when the minimum Gibbs free energy of reaction products is attained at the given $T$ and $P$. Depending on the amounts of feeds and operating conditions, the gasification may have various products. In this modelling work, only important species are considered. If necessary or to improve the model fidelity, more species can be added without any significant effort.
The products considered in the model are: solid carbon (C), solid sulphur (S), hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), nitrogen (N₂), oxygen (O₂), water (H₂O), hydrogen sulphide (H₂S), carbonyl sulphide (COS), ammonia (NH₃) and nitric oxide (NO). These species are classified as gaseous products (GPROD) or solid products (SPROD).

The total Gibbs free energy of the gasification products then can be expressed as the sum of chemical potential of all possible product species:

\[
G_{sys} = \sum_{i \in GPROD} n_i \mu_i + \sum_{i \in SPROD} n_i \mu_i
\]  

(2.1)

For gaseous products (syngas), \( \mu_i \) is the chemical potential of the \( i \)th syngas species and can be expressed as:

\[
\mu_i = G_i^0 + RT \ln \frac{\dot{f}_i}{\dot{f}_i^0}, \quad \forall i \in GPROD
\]  

(2.2)

\( G_i^0 \) is arbitrarily set equal to zero for all elements in their standard states. Then for compounds,

\[
G_i^0 = \Delta G_{f,i}^0, \quad \forall i \in GPROD
\]  

(2.3)

The fugacity coefficient, \( \hat{\phi}_i \), is defined as the fugacity of a species in the syngas to that of the ideal gas at the standard state

\[
\dot{f}_i = \hat{\phi}_i y_i P, \quad \forall i \in GPROD
\]  

(2.4)

The fugacity coefficient can be set equal to 1 under the normal operating pressures and temperatures of gasification. The standard state for gases is the ideal gas state at the standard state pressure, for which

\[
f_i^0 = P^0, \quad \forall i \in GPROD
\]  

(2.5)

For solid products (C and S), \( \mu_i \) can be expressed as:

\[
\mu_i = \Delta G_{f,i}^0, \quad \forall i \in SPROD
\]  

(2.6)

Substitute Eqs. (2.2), (2.3), (2.4), (2.5) and (2.6) into Eq. (2.1) gives:
\[ G_{\text{sys}} = \sum_{i \in \text{PROD}} n_i \Delta G_{f,i}^0 + \sum_{i \in \text{PROD}} n_i RT \ln(y_iP) - \sum_{i \in \text{PROD}} n_i RT \ln P^0 \] (2.7)

The standard Gibbs free energy of formation, \( \Delta G_{f,i}^0 \), can be calculated using Eq. (2.8) (Gibbs–Helmholtz relation) at a certain temperature, \( T \).

\[ \Delta G_{f,i}^0(T) = \Delta H_{f,i}^0(T) - T \Delta S_{i}^0(T) \] (2.8)

The standard enthalpy of formation of a compound, \( \Delta H_{f,i}^0(T) \), is the change of enthalpy from the formation of one mole of the compound from its constituent elements, with all substances in their standard states. In order to calculate the standard Gibbs free energy of formation for each product, the standard enthalpy of formation and the standard entropy need to be calculated based on Eqs. (2.9) and (2.10).

\[ \Delta H_{f,i}^0(T) = \Delta H_{f,i}^0(298) + \int_{298}^{T} C_{p,i}^0(T)dT - \sum_{j \in J} \alpha_{i,j} \int_{298}^{T} C_{p,j}^0(T)dT \] (2.9)

\[ \Delta S_{i}^0 = S_{i}^0(T) - \sum_{j \in J} \alpha_{i,j} \int_{298}^{T} \alpha_{i,j} S_{j}^0(T) \] (2.10)

where \( \alpha_{i,j} \) is the stoichiometric coefficient which is the corresponding mole of each constituent element (species \( j \)) to form 1 mole of compound (species \( i \)).

2.1.3 Heat balance and elemental balances

The gasification process need to subject to the heat balance. The reactions occurring in a gasifier include both endothermic and exothermic reactions. The heat generated from the exothermic reactions is consumed by the endothermic reactions, and the rest is converted to sensible heat of the syngas generated. Preheating of reactants, if applied, also brings heat to the gasifier, which facilitates the gasification process. With that, the heat balance for the gasification process is expressed as:

\[ nH_{f,fuel} + H_p(T_{in}) + \sum_{i \in \text{REACT}} n_i H_{f,i}(T_0) = \sum_{i \in \text{PROD}} n_i H_{f,a,i}(T_{out}) \] (2.11)

where the outlet gas temperature \( (T_{out}) \) is taken as the gasification temperature; the initial temperature of reactants before preheating \( (T_0) \) is assumed to be 298 K in this work.
As suggested by de Souza-Santos [40], the enthalpy of formation for the solid fuels can be expressed as:

\[ H_{f,fuel} = LHV + \sum_{i \in PROD} H_{f,i}(T_0) \]  \hspace{1cm} (2.12)

where LHV is the lower heating value in kJ/kmol and \( H_{f,i} \) is the enthalpy of formation of the \( i \)th gaseous product of complete combustion of the solid fuel.

The increased enthalpy of reactants through preheating can be expressed as:

\[ H_p(T_{in}) = \sum_{i \in REACT} n_i \int_{T_0}^{T_{in}} C_p,i(T) dT \]  \hspace{1cm} (2.13)

The apparent enthalpy of formation is expressed as:

\[ H_{fa,i}(T_{out}) = H_{f,i}(T_0) + \int_{T_0}^{T_{out}} C_p,i(T) dT \]  \hspace{1cm} (2.14)

In Eqs. (2.9), (2.10), (2.13) and (2.14), the heat capacity, \( C_p(T) \), and entropy, \( S(T) \), are empirical polynomial functions of temperature, which have been validated by experiments [41].

In addition, the minimization of Gibbs free energy subjects to elemental balances which are developed as follows. Let \( a_{i,k} \) be the number of atoms of the \( k \)th element present in each molecule of chemical species \( i \). Then, for each element \( k \),

\[ \sum_{i \in REACT} n_i a_{i,k} = \sum_{i \in PROD} n_i a_{i,k} \]  \hspace{1cm} (2.15)

2.1.4 Model implementation

The Gibbs free energy of gasification products is minimized using a generalized reduced gradient nonlinear method, which leads to an equilibrium state of the gasification reaction. Also, the resulted \( n_i \) (\( i \in PROD \)) satisfy the elemental balances (Eq. (2.15)).

For calculating the reaction temperature, the initial temperature is assumed, and it is employed to calculate \( n_i \) (\( i \in PROD \)) in the part of minimization of Gibbs free energy. As shown in Figure 2.1, the assumed temperature and calculated \( n_i \) (\( i \in PROD \)) are substituted to compute the heat balance. The temperature will be reduced if input heat is less than the output heat and vice versa.
After adjusting the temperature, \( n_i \ (i \in PROD) \) are calculated again. The checking of the heat balance is also done again. Those processes will be repeated until heat balance is satisfied. And the syngas composition and gasification temperature can be obtained for a given set of reactant flow rates.

After knowing syngas composition under an equilibrium state, we should also decide which state gives highest CGE. The method using equilibrium model is an iterative search. This means, the previous convergence cycle has to be put in another cycle to iteratively search for the optimum reactant flow rates (see Figure 2.2). So optimization using equilibrium model is a multi-objective problem which need to minimize Gibbs free energy in the inner level and maximize CGE in the outer level.

Moreover, the minimization of Gibbs free energy is a non-convex optimization problem that may have multiple locally optimal points and it can take a lot of time to identify whether the solution is global [42-43]. In the practice, it requires an additional step to differentiate the global optimum from the local optima.

**Figure 2.1. The calculation procedure of equilibrium model**

![Calculation procedure of equilibrium model](image-url)
2.1.5 Model validation

The model is validated through results comparison with those obtained by work of Shabbar et al. [16] as presented in Figure 2.3. In their study, RTC-coal is gasified with the air at 298 K and 1 atm. The empirical formula and higher heating value (HHV) of the coal are \( \text{CH}_{0.8173}\text{O}_{0.0785}\text{N}_{0.0260}\text{S}_{0.0052} \) and 444,259 kJ/kmol, respectively. With the molar ratio of air to feedstock changing from 0.20 to 1.60, the predicted equilibrium gasification product compositions of the present model are plotted in Figure 2.4. The overall change of the product composition predicted by the model is in good agreement with that presented in Figure 2.3. Slight differences have been witnessed for C (s) and CO, probably because C (s) rather than C (g) is chosen as the product in the literature. Thus, C (s) decreases less sharply on the curve in Fig.1. As reflected by the plotted curves in both figures, the amounts of combustible gases peak up at the air ratio of around 0.51, which gives the highest CGE as well.
Figure 2.3. Variation of equilibrium composition with air for RTC-coal gasification [16]

Figure 2.4. Results of RTC-coal gasification with air for model validation
2.1.6 Optimization results and discussion

The parametric study using the developed equilibrium model is conducted by control variate method. Initially, GFW of 0.3 kmole is used for every kmole of RTC-coal and a parametric study is performed by varying the amount of air input. The results that are plotted in Figure 2.5 show that as the air ratio starts to increase, the residual solid carbon is increasingly converted into CO, CO$_2$ and CH$_4$. At the air ratio of 0.53, almost all solid carbon is converted into gaseous products and CGE also reaches its highest level (73.25%) with the presence of the highest yields of H$_2$ and CO as well as the lowest yield of H$_2$O. The corresponding gasification temperature is 935 K where the productions of H$_2$ and CO achieve the highest ones which are 0.4 and 0.8, respectively. As shown in Figure 2.5, the highest temperature of 2100 K is achieved when the air ratio of 1.1 is used. At this state, the major products of the gasification become steam and CO$_2$. It should be noticed that even at the maximum yields of CO and H$_2$, there are still considerable amounts of CO$_2$ and H$_2$O present in the syngas. The generations of both of them are exothermic reactions and molar percentage of them account for 12% or so. It means that a large amount of fuel is consumed by the gasification process itself to provide the heat to the system.

![Figure 2.5. Results of RTC-coal gasification with 0.3 kmole GFW by varying air](image)
Compared with the results provided in the model validation, the air ratio corresponding to the highest CGE moves from around 0.51 to 0.53 due to the extra 0.3 kmole GFW fed to the system. It is calculated that CGE of the case with GFW is 73.25% which is almost 3% lower than former case. In addition, as indicated by the H$_2$ trends in both figures, the case with GFW feed produces more H$_2$. Especially at the point corresponding to the highest CGE, the production of H$_2$ reaches 0.55 kmoles rather than 0.35. As a result, more CO$_2$ is formed from flammable CO to provide adequate heat for the exothermic reactions to generate H$_2$. The largest gap of CO content which is 0.22 kmoles appears at the air ratio of 0.4. What’s more, the gasification temperatures corresponding to the two cases are quite different as well. The case without GFW feed has its highest CGE at 1020 K while the case with 0.3 kmole GFW per kmole RTC coal reaches the highest efficiency at around 935 K. The feed of GFW significantly decreases the gasification temperature as the H$_2$ production from GFW requires a lot of heat.

Figure 2.6. Results of RTC-coal gasification with 0.6 kmole air by varying GFW

![Graph showing gasification results with varying GFW ratio](image-url)
Further, the air of 0.6 k mole is used for every k mole of RTC-coal and a parametric study is performed by varying the amount of GFW input. Unlike previous cases, the results obtained in this are quite straightforward. As shown in Figure 2.6, only the trend of the amount of CO production goes down whereas the amounts of H₂, H₂O and CO₂ increase as the GFW ratio increases. CGE of the gasification process also decreases from 66.54% to 61.98% with increasing GFW ratio from 0 to 1. Compared with varying air ratio in former two cases where CGEs fluctuate below 73.25% and 76% in correspondence to the change of air ratio of 1.6, it is obvious that gasification performance is more sensitive to the oxidant feed. Based on three cases, GFW feed plays a negative role in RTC-coal gasification. The optimum operating condition is that RTC-coal is gasified with air ratio of 0.51 at 1020 K.

As mentioned in Subsection 2.1.4, the local solutions to the non-convex problem of minimizing Gibbs free energy can be easily obtained and need extra steps to eliminate them. These solutions at one operating condition are given in Table 2.1 where there are 3 local solutions in addition to the global solution (Solution 1). It can be observed that Gibbs energy in Solution 4 which is closest to the one in Solution 1 does not give closest results of component ratios. The local solutions would lie out of the trend if a series of solutions to different conditions are generated, and they can be identified accordingly.

<table>
<thead>
<tr>
<th>Components</th>
<th>Component flow rates in 4 cases (Kmoles)</th>
<th>Solutions to Gibbs free energy minimization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air ratio = 0.7, GFW ratio = 0.3</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.00 0.00 0.11 0.00</td>
<td>Solution 1  Solution 2  Solution 3  Solution 4</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.39 0.25 0.00 0.67</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00 0.00 0.00 0.00</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.28 0.42 0.66 0.00</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.61 0.67 0.00 0.89</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.39 0.33 0.89 0.11</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>0.01 0.01 0.01 0.00</td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td>0.00 0.00 0.00 0.01</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>0.03 0.03 0.03 0.03</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1398 1156 1577 1343</td>
<td></td>
</tr>
<tr>
<td>System Gibbs free energy (kJ)</td>
<td>-407765 -355847 -385558 -397682</td>
<td></td>
</tr>
</tbody>
</table>
2.1.7 Conclusions

In this section, an equilibrium model is developed to simulate the gasification process. The model consists of an objective function aiming at minimizing Gibbs free energy and two sets of equality constraints including heat balance and elemental balances. The model is validated with literature and results show good agreement with the data of RTC-coal gasification. In addition to the air gasification case in the model validation, a case of GFW gasification with varying air ratio is performed using developed equilibrium model. CGEs of two cases are calculated and the maximum CGEs reach 76.24% and 73.25%, respectively, which means the extra GFW feed cannot benefit the gasification performance. Further, the case in which GFW is varied with fixed air ratio is performed. The results indicate that CGE decreases with increasing GFW ratio. Therefore, the optimum operating conditions should be RTC-coal is gasified with the air ratio of 0.51 at 1020 K.

Although the optimum condition is obtained eventually via iterative search, it should never be overlooked that the method requires complex calculations and can be easily trapped in a local minimum. The optimum condition is identified through detailed comparisons and analyses of syngas trends. To avoid such tedious work, a more direct procedure which integrates an advanced algorithm and Gibbs free energy minimization is proposed as follows.
2.2 Equilibrium model with KKT conditions

2.2.1 Introduction

In Section 2.1, the syngas flow rates are optimized to have a minimum value of the gasification system Gibbs free energy. Based on this, an equilibrium model is developed to predict the gasification products. However, the main purpose of modelling is to decide the optimum parameters for the operating condition in measurement of CGE or economic profit. This means to optimize variables to achieve the optimum for minimizing Gibbs free energy on one hand and maximize CGE or profit on the other hand in the gasification process. Because Gibbs free energy of products is totally independent of CGE or economic profit of a gasification process, the optimization of the gasification process is theoretically a multi-objective problem, i.e., an inner optimization problem (minimize Gibbs free energy of gasification system) embedded with in an outer optimization problem (maximize CGE or economic profit of gasification process) [44].

The Karush-Kuhn-Tucker (KKT) and Lagrange Multipliers are two efficient methods to convert the problem of finding the extremum into a set of constraints (KKT conditions) [45]. By this way, the iterative search for a multi-objective optimization problem as shown in Figure 2.1 can be avoided. In this work, KKT algorithm is utilized to find the solution for Gibbs free energy minimization constrained to more than one equalities and inequalities.

2.2.2 KKT algorithm

For a minimization problem as

\[ \text{Min } f(x) \]

Subject to \( l_i(x) = 0, \forall i = 1, ... n \)

\( h_i(x) \leq 0, \forall i = 1, ... m \)

In words, find the solution that minimizes \( f(x) \), as long as all equalities \( l_i(x)=0 \) and all inequalities \( h_i(x)\leq0 \) hold. Put the cost function as well as the constraints in a single minimization problem, but multiply each equality constraint by a factor \( \lambda_i \) (the Lagrange multiplier) and each inequality constraint by a factor \( \mu_i \) (the KKT multiplier). The problem defined as above has \( m \) inequalities and \( n \) equalities. Hence, the problem is converted into below function.
\[ F = f(x) + \sum_{i=1}^{n} \lambda_i l_i(x) + \sum_{i=1}^{m} \mu_i h_i(x) \]

The constraints in the function will make \( x \) depend on \( \lambda \) and \( \mu \). The number of variables equals to the elements in \( x \) (say \( k \)) plus the number of multipliers \((m+n)\). However, only \( k \) equations coming from the gradient with respect to \( x \) are available.

Then differentiate the function with respect to each Lagrange multiplier \( \lambda_i \) to get \( n \) more equations. These equations guarantee the set of solutions can meet the equality constraints.

\[ \nabla_{\lambda} f(x) + \sum_{i=1}^{n} \nabla_{\lambda} \lambda_i l_i(x) + \sum_{i=1}^{m} \nabla_{\lambda} \mu_i h_i(x) = 0 \]

Similarly, \( m \) equations from inequalities can be obtained as well. The reason that inequalities can be processed the same way as the equalities lies in the meaning of the feasible solution region. If the extremum of the original function is in \( h_i(x)<0 \), then this constraint will never play any role in changing the extremum compared with the problem without the constraint. Therefore, its factor \( \mu_i \) can be set equal to zero. If, on the other hand, the new solution is at the border of the constraint, then \( h_i(x)=0 \). In both situations, the equations derived accordingly are necessary for the solution to the optimization problem. They can be written as

\[ \mu_i h_i(x) = 0 \]

Therefore, \( m \) equations from the inequalities are got. The coefficients \( \lambda_i \) can have any value. However, the coefficients \( \mu_i \) are limited to non-negative values [46]. The fully converted KKT conditions according to the algorithm then are

Stationarity

\[ \nabla_x f(x) + \sum_{i=1}^{n} \nabla_x \lambda_i l_i(x) + \sum_{i=1}^{m} \nabla_x \mu_i h_i(x) = 0 \]
Equality constraints
\[ \nabla_\lambda f(x) + \sum_{i=1}^{n} \nabla_\lambda \lambda_i l_i(x) + \sum_{i=1}^{m} \nabla_\lambda \mu_i h_i(x) = 0 \]

Complementary slackness condition (inequality constraints)
\[ \mu_i h_i(x) = 0, \forall i = 1, \ldots, n \]

Primal feasibility
\[ l_i(x) = 0, \forall i = 1, \ldots, n \]
\[ h_i(x) \leq 0, \forall i = 1, \ldots, m \]

Dual feasibility
\[ \mu_i \geq 0, \forall i = 1, \ldots, m \]

2.2.3 KKT conditions of minimizing Gibbs free energy

As derived in Section 2.1, the system Gibbs free energy is expressed as Eq. (2.7). As the temperature is converged separately to fulfill the heat balance, this objective function is constrained by one set of equalities (elemental balances) and one set of inequality \((a \leq n_i \leq b)\). Hence, the expression for system Gibbs free energy is converted to below function by multiplying the Lagrange multipliers and KKT multipliers with equalities and inequalities, respectively.

\[ F = G_{sys} + \sum_{k=1}^{m} \lambda_k \left( \sum_{l \in REACT} n_l a_{l,k} - \sum_{l \in PROD} n_l a_{l,k} \right) + \mu_i (a - n_i) + \delta_i (n_i - b) \quad (2.16) \]
Referred to the KKT algorithm, the minimum value of $F$ is found when the partial derivatives of $F$ with respect to $n_i$ are set equal to zero:

$$
\left( \frac{\partial F}{\partial n_i} \right)_{T,P,n_j} = \left( \frac{\partial g_{sys}}{\partial n_i} \right)_{T,P,n_j} + \sum_{k=1}^{n} \lambda_k a_{i,k} - \mu_i + \delta_i = 0 \tag{2.17}
$$

where $n_j$ signifies that all mole numbers are held constant except $i$th. The first term on the right is the definition of the chemical potential. Substitute Eq. (2.7) into above formulation, two stationarities for gaseous and solid products are given by

$$
n_i \left[ \Delta G_{f,i}^0 + RT \ln \left( \frac{y_i P + \epsilon}{P_0} \right) + \sum_{k=1}^{n} \lambda_k a_{i,k} - \mu_i + \delta_i \right] = 0, \forall i \in GPROD \tag{2.18}
$$

$$
n_i (\Delta G_{f,i}^0 + \sum_{k=1}^{n} \lambda_k a_{i,k} - \mu_i + \delta_i) = 0, \forall i \in SPROD \tag{2.19}
$$

where $\epsilon$ is a sufficiently small value that is used to avoid calculation mistakes of natural logarithm. In some circumstances, the amount of product is calculated to be zero, which would lead to the error of the natural logarithm term. Therefore, the stationarities multiply corresponding mole numbers to avoid such errors which would terminate the calculation.

For the equality constraints,

$$
\left( \frac{\partial F}{\partial \lambda_k} \right)_{T,P,n_i} = \left( \sum_{i \in REACT} n_i a_{i,k} - \sum_{i \in PROD} n_i a_{i,k} \right) = 0 \tag{2.20}
$$

For complementary slackness condition (inequality constraints),

$$
\mu_i (a - n_i) = 0 \tag{2.21}
$$

$$
\delta_i (n_i - b) = 0 \tag{2.22}
$$

For primal feasibility,

$$
\sum_{i \in REACT} n_i a_{i,k} - \sum_{i \in PROD} n_i a_{i,k} = 0 \tag{2.23}
$$

$$
\mu_i \geq 0, \delta_i \geq 0 \tag{2.24}
$$
The above formulations describe the final optimality conditions for the gasification model that is to be embedded in the outer optimization problem. If \( i \)th species is an element substance, \( \Delta G_{f,i}^0 \) is arbitrarily set equal to zero. There are \( i \) equilibrium equations, \( i \) equations from complementary slackness and \( k \) equations from material balances – a total of \((2i+k)\) equations. The variables in these equations are the \( n_i, \mu_i \) and \( \lambda_k \) – a total of \((2i+k)\) variables. Thus, the number of equations is sufficient for the determination of all unknown variables.

If maximizing CGE is the objective of a coal gasification process, the optimization problem is:

Maximize CGE 

Subject to:

- Stationarities, Eqs. (2.18) and (2.19)
- Equality constraints, Eq. (2.20)
- Inequality constraints, Eq. (2.21)
- Primal feasibility, Eqs. (2.22), (2.23) and (2.24)
- Heat balance, Eq. (2.13)

2.2.4 Example

Using the same feedstock defined in Section 2.1, a direct optimization for finding the optimum feed flow rates via the equilibrium model with KKT conditions is conducted. Both \( n_i \) (\( i \in PROD \)) and \( n_i \) (\( i \in REACT \)) are variables in this optimization, but \( n_{air} \) is limited to vary between the air ratio of 0.2 and 1.5 as the case in Subsection 2.1.6.
As shown in Table 2.2, the optimization results are in good agreement with ones found by control variant method in Subsection 2.1.6. The Gibbs free energy is minimized to be -244289.49 kJ for the gasification system.
In the calculation, the cases of local optima also occur and one set of the results is shown in Table 2.3 for comparison. The Gibbs free energy is -241522.31 kJ which is a bit higher. The product composition, however, contains majorly H₂ and CO₂, which is quite different from the global optimum.

Table 2.3. Optimization results of one local minimum Gibbs free energy

<table>
<thead>
<tr>
<th>Reactant (mole/hr)</th>
<th>Product (mole/hr)</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1000.00</td>
<td>444.65</td>
<td>N/A</td>
</tr>
<tr>
<td>H 817.30</td>
<td>0.00</td>
<td>N/A</td>
</tr>
<tr>
<td>RTC-coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N 26.00</td>
<td>0.00</td>
<td>N/A</td>
</tr>
<tr>
<td>S 5.20</td>
<td>0.00</td>
<td>N/A</td>
</tr>
<tr>
<td>O 78.50</td>
<td>0.00</td>
<td>N/A</td>
</tr>
<tr>
<td>Air 512.10</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>H₂O 0.00</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>CH₄ 0.00</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>H₂ 0.00</td>
<td>364.45</td>
<td>12.60%</td>
</tr>
<tr>
<td>CO 0.00</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>CO₂ 0.00</td>
<td>555.35</td>
<td>19.20%</td>
</tr>
<tr>
<td>H₂S 0.00</td>
<td>5.20</td>
<td>0.18%</td>
</tr>
<tr>
<td>COS 0.00</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>NH₃ 0.00</td>
<td>26.00</td>
<td>0.90%</td>
</tr>
<tr>
<td>NO 0.00</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>CGE</td>
<td></td>
<td>19.69%</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1642.93</td>
<td></td>
</tr>
<tr>
<td>Gibbs free energy (kJ)</td>
<td>-241522.31</td>
<td></td>
</tr>
</tbody>
</table>

2.2.5 Conclusion

In this section, KKT algorithm is utilized to convert the problem of finding an extremum (Gibbs free energy minimization) into solving a set of constraints. KKT conditions significantly reduce the calculations and shorten the convergence time. When using equilibrium model with KKT conditions, the operating condition is optimized in measurement of CGE directly instead of conducting iteration.
The KKT conditions are necessary to find an optimum, but may not be sufficient. This is because the objective function is not continuously differentiable and convex [47]. Therefore, KKT algorithm only reduces the calculations of minimizing Gibbs free energy rather than avoid obtaining the local optima.

In essence, what makes this model different from the one developed in Section 2.1 is one of the objectives is guaranteed by a set of constraints. Strictly speaking, the equilibrium model with KKT conditions still have multi-objective. In the following section, a novel mathematical model is developed based on the observations at high temperatures. As a result, a single objective model is formulated accordingly.
2.3 Single objective model

2.3.1 Introduction

The developed equilibrium models have offered an iterative approach to optimize the operating parameters of gasification for maximizing CGE, but the optimization process requires special modelling techniques or huge amounts of calculations. Also, the process can be easily trapped at a local optimum, which requires an additional step to differentiate the global optimum from the local optima. To solve this problem, a novel mathematical model has been developed in this section, which converts the multi-objective problem (Gibbs free energy minimization and CGE maximization) into a single objective problem of CGE maximization.

Thus, with this model, the reactant (carbonaceous feedstock, GFW and O\textsubscript{2}) supply, the reaction temperature, and the heat integration of a gasification process to be considered can be simultaneously optimized for maximum economic profit in a selected way of syngas utilization, rather than using an iterative approach. Instead of setting the coal as the feedstock, the carbon which accounts for more than 80% in high quality coal is considered first.

2.3.2 Target function development

CGE which is the ratio of LHV of feedstock to LHV of syngas is often used as an indicator of the performance of the gasification [26-27]. Table 2.4 lists LHVs of the major gas components in the syngas. The composition of the syngas determines the heating value of the gas and is determined by the feeding ratios (e.g. O/C, Steam/C) and the reaction conditions. To evaluate how reactants and temperature would influence the equilibrium products composition, equilibrium constant is used in the following analyses.

The equilibrium constant of a chemical reaction is the value of the reaction quotient when the reaction has reached equilibrium. An equilibrium constant value is independent of the analytical concentrations of the reactant and product species in a mixture, but depends on temperature. Known equilibrium constant values can be used to indicate the proportion of reactants and products for reversible reactions at equilibrium.
Table 2.4. LHV of gases

<table>
<thead>
<tr>
<th></th>
<th>LHV (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>240</td>
</tr>
<tr>
<td>CO</td>
<td>282.80</td>
</tr>
<tr>
<td>CH₄</td>
<td>800.80</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
</tr>
</tbody>
</table>

Gasification of carbon consists of several major reactions [28]: partial and complete combustion (Eqs. (2.26) and (2.27)), carbon-steam (Eq. (2.28)), boudouard (Eq. (2.29)), methanation (Eq. (2.30)) and water-gas shift reactions (Eq. (2.31)).

\[
C + 0.5O₂ = CO \quad (ΔH^° = -110.5 \text{ kJ/mol}) \quad (2.26)
\]

\[
CO + 0.5O₂ = CO₂ \quad (ΔH^° = -283.0 \text{ kJ/mol}) \quad (2.27)
\]

\[
C + H₂O = CO + H₂ \quad (ΔH^° = 131.3 \text{ kJ/mol}) \quad (2.28)
\]

\[
C + CO₂ = 2CO \quad (ΔH^° = 172.5 \text{ kJ/mol}) \quad (2.29)
\]

\[
C + 2H₂ = CH₄ \quad (ΔH^° = -74.9 \text{ kJ/mol}) \quad (2.30)
\]

\[
CO + H₂O = CO₂ + H₂ \quad (ΔH^° = -41.0 \text{ kJ/mol}) \quad (2.31)
\]

The equilibrium mixture of the reversible reactions can be determined by the equilibrium constant, \( K \). As indicated by Eq. (2.32), the calculation of \( K \) relates the standard Gibbs free energy with the temperature.

\[
K = exp \left( - \frac{ΔG^°_f,i}{RT} \right) \quad (2.32)
\]
Table 2.5 shows the calculated equilibrium constants of these reversible reactions at different reaction temperatures. As the gasification temperature increases, the equilibrium constants for the reactions change and at high temperatures only productions of $H_2$ and CO are favored. The decrease of equilibrium constant ($K$) value for the reaction in Eq. (2.27) indicates that with adequate supply of oxygen, carbon tends to be partially oxidized to CO instead of $CO_2$. In Eq. (2.30), the methanation reaction, the value of $K$ approaches zero at temperature above 1300 K, almost no $CH_4$ will be produced. At temperature below 1000 K, the conversion from carbon tends to be low thus leads to incomplete conversion of carbon. These observations lead to the following conclusions:

(1) Carbon gasification is in favor of high temperatures to promote complete conversion of carbon.

(2) With sufficient supply of oxygen, the reactions tend to produce more CO than $CO_2$.

(3) At reaction temperature above 1300 K, $CH_4$ production can be eliminated.

Table 2.5. Equilibrium constants for the six major reactions.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Eq.(2.26)</th>
<th>Eq.(2.27)</th>
<th>Eq.(2.28)</th>
<th>Eq.(2.29)</th>
<th>Eq.(2.20)</th>
<th>Eq.(2.21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.43E+16</td>
<td>1.05E+25</td>
<td>0.00</td>
<td>0.00</td>
<td>2181</td>
<td>137.26</td>
</tr>
<tr>
<td>800</td>
<td>8.09E+11</td>
<td>8.18E+13</td>
<td>0.04</td>
<td>0.01</td>
<td>1.35</td>
<td>4.22</td>
</tr>
<tr>
<td>1000</td>
<td>2.89E+10</td>
<td>1.65E+10</td>
<td>2.52</td>
<td>1.75</td>
<td>0.10</td>
<td>1.44</td>
</tr>
<tr>
<td>1200</td>
<td>3.04E+09</td>
<td>57535774</td>
<td>38.43</td>
<td>52.75</td>
<td>0.02</td>
<td>0.73</td>
</tr>
<tr>
<td>1300</td>
<td>1.26E+09</td>
<td>6560274</td>
<td>109</td>
<td>193</td>
<td>0.01</td>
<td>0.57</td>
</tr>
<tr>
<td>1400</td>
<td>5.94E+08</td>
<td>1023261</td>
<td>268</td>
<td>580</td>
<td>0.00</td>
<td>0.46</td>
</tr>
<tr>
<td>1600</td>
<td>1.72E+08</td>
<td>50350</td>
<td>1141</td>
<td>3424</td>
<td>0.00</td>
<td>0.33</td>
</tr>
<tr>
<td>1700</td>
<td>1.03E+08</td>
<td>14618</td>
<td>2069</td>
<td>7055</td>
<td>0.00</td>
<td>0.29</td>
</tr>
<tr>
<td>1800</td>
<td>65142596</td>
<td>4879</td>
<td>3505</td>
<td>13352</td>
<td>0.00</td>
<td>0.26</td>
</tr>
<tr>
<td>1900</td>
<td>43050378</td>
<td>1831</td>
<td>5605</td>
<td>23510</td>
<td>0.00</td>
<td>0.24</td>
</tr>
<tr>
<td>2000</td>
<td>29551038</td>
<td>759</td>
<td>8527</td>
<td>38921</td>
<td>0.00</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Based on the above analysis, assuming carbon conversion is 100% and sufficient O\textsubscript{2} is fed, the reaction will always be proceeded at a high temperature (e.g. T > 1400 K) and produce mainly CO, CO\textsubscript{2} and H\textsubscript{2} at the syngas. The product gas may contain certain amount of CO\textsubscript{2} since the oxidation of carbon or CO to CO\textsubscript{2} generates heat for maintaining a high reaction temperature. Although CH\textsubscript{4} has the highest LHV among other gases, its production is prohibited at high temperature. The product gas may also contain a certain amount of unreacted water or oxygen. However, when CGE is to be maximized, this unreacted water or oxygen will be minimized.

With these considerations, the question is whether the Gibbs free energy of the product gases can be simultaneously minimized while maximizing CGE. In order to ascertain this, Eq. (2.7) is removed from the equilibrium model to form a new model (single objective model). The single objective model is used to maximize CGE at a specific reaction temperature between 1000 K and 1800 K by varying oxygen and steam feed at the pressure of 1 bar. The reaction pressure is fixed since it should not have a strong influence to the product yield or composition. The elevated pressure in commercial gasifiers is mainly for reducing equipment size [48].

This validation procedure could be referred to Figure 2.7 for details. In the single objective model, the CGE function is maximized with all constraints of heat and elemental balances directly. A series of optimum reactant flow rates at temperatures from 1000 to 1800 K and the corresponding product compositions of gasification have been obtained. Then, in the equilibrium model, by using the optimum reactant flow rates under a certain temperature which is obtained in the single objective model, the corresponding equilibrium reaction temperature and product composition of minimum Gibbs free energy are determined. Record the results of temperature and syngas composition and make a comparison. The results of gasification temperature are plotted in Figure 2.8.
As shown in Figure 2.8, when the gasification temperature is above 1400 K, the equilibrium temperature of minimum product Gibbs free energy equals to the temperature where the optimum reactant flow rates have been determined with maximum CGE, so as the product composition. This means, at above 1400 K, operating conditions that maximize CGE automatically satisfy the constraints of minimized Gibbs free energy. Actually, in gasification economic profit is equivalent with CGE as both objectives aim to get the highest yields of combustible gas in the gasification products. Thus, the multi-objective problem can be converted to a single objective optimization problem of maximizing CGE or economic profit at above 1400 K, in which all the variables can be optimized at a single step. In fact, this is also the temperature range (1473 - 1873 K) that the latest commercial entrained-flow coal gasifiers are operated at [49].
Based on this unusual phenomenon, the optimization problem of a carbon gasification process is simplified to be

\[
\text{Maximize Profit or CGE} \quad \text{Objective}
\]
\[
s.t.
\]
\[
\text{Heat balance, Eq. (2.9)}
\]
\[
\text{Elemental balances, Eq. (2.13)}
\]

\[
\begin{align*}
\text{Constraints}
\end{align*}
\]

2.3.3 Example

In the example, the feed flow rates for carbon gasification at 1773 K are optimized through the single objective model as well as the conventional approach. For the sake of simplicity in the presentation, \(O_{O_2}/C\) and \(O_{GFW}/C\) which stand for the ratio of oxygen atom from oxygen gas to carbon and the ratio of oxygen atom from GFW to carbon, respectively, are used instead of the flow rates.
O_{O2}/C and O_{GFW}/C are optimized to be 0.41 and 0.19, respectively, via single objective model. CGE can reach 83.25% at 1773 K. The calculations converge quickly and seldom stop at the local optima. The conventional approach which embeds the Gibbs free energy minimization within the maximization of CGE to form a multi-objective optimization is used to validate the obtained results. The corresponding results are plotted in Figure 2.9. As shown in the figure, the O_{O2}/C and O_{GFW}/C need to be varied together to keep gasification at 1773 K. First, CGE increases with the GFW and oxygen flow rates. After CGE peaks up at 83.29% with O_{O2}/C of 0.41 and O_{GFW}/C of 0.19, more O_2 and GFW bring negative effects to the gasification performance. The results from the single objective model are almost identical with the ones got via conventional approach.

It can be seen that CGE has a steeper tend before the peak and so does oxygen feed. This is because as O_{O2}/C starts to increase, the residual solid carbon is increasingly converted into CO, CO_2 and CH_4 until the carbon is fully converted and CGE reaches the highest level. After that, more oxygen is fed in order to provide heat for excessive GFW feed to keep gasification temperature at 1773 K. So oxygen is only need to form CO_2 after the peak. The graph again proves that the highest CGE occurs when carbon happens to be entirely converted.

Figure 2.9. The results of conventional approach by iterative searching
2.4 Conclusions

In Chapter 2, three approaches are developed for gasification modelling and optimization. They are the equilibrium model based on the Gibbs free energy minimization, the equilibrium model with KKT conditions and the single objective model. Although it is straightforward to minimize the Gibbs free energy directly in the equilibrium model, finding the global minimum requires complex calculations and can be easily trapped in a local minimum. In the example, the optimization is done through detailed comparisons and analyses of syngas trends. To avoid such tedious work, a more direct procedure which integrates KKT algorithm and Gibbs free energy minimization is proposed in Section 2.2. The equilibrium model with KKT conditions only need to solve the equality and inequality constraints instead of finding an extremum, which greatly simplifies the optimization problem. However, for non-convex problem to be addressed by the gasification model, the KKT conditions are necessary to find an optimum, but not necessarily sufficient. Therefore, despite KKT algorithm reduces the calculations greatly, how to avoid the local optima still should be taken carefully.

In Section 2.3, it is found that, at above 1400 K, the operating conditions that maximize CGE automatically lead to minimized Gibbs free energy of products. Thus, the complicated multi-objective problem of CGE optimization (CGE maximization and Gibbs free energy minimization) is simplified to a single objective problem of CGE maximization, and the model can be developed accordingly. Therefore, the reactant (carbonaceous feedstock, GFW and O₂) supply, the reaction temperature, and the heat integration of a gasification process to be considered can be simultaneously optimized for maximum CGE. Actually, in gasification, economic profit is equivalent with CGE as both objectives aim to get the highest yields of combustible gas in the gasification products. Therefore, either CGE or economic profit could be maximized in the objective function and the results should be the same.
NOMENCLATURE

\[ G_{\text{sys}} \] the Gibbs free energy of system, kJ

\[ n_i \] molar flow rate of species \( i \), kmol/h

\[ \Delta G^0_{f,i} \] standard Gibbs free energy of formation for species \( i \), kJ/kmol

\( P, T \) total pressure and temperature of the system, bar and K

\( R \) universal gas constant, 8.314 kJ/kmol K

\[ y_i \] mole fraction of species \( i \)

\[ \Delta H^0_{f,i} \] standard enthalpy of formation of \( i \)th compound, kJ/kmol

\[ H_{f,\text{fuel}} \] enthalpy of formation of fuel, kJ/kmol

\( H_p \) preheating heat and sensible heat of syngas, kJ/kmol

\( H_{f,i} \) enthalpy of formation of \( i \)th species, kJ/kmol fuel

\( H_{fa,i} \) apparent enthalpy of formation, kJ/kmol

\( C_p \) constant pressure heat capacity, kJ/kmol K

\( S \) entropy, kJ/(kmol K)

\( a_{i,k} \) the number of atoms of the \( k \)th element present in each molecule of chemical species \( i \)

\( K \) equilibrium constant

\( \nu_i \) stoichiometric number of species \( i \) in the reaction

\( \lambda_i \) Lagrange multiplier

\( \mu_i \) KKT multiplier

\( O_{O2} \) oxygen atom from oxygen gas

\( O_{H2O} \) oxygen atom from \( H_2O \)

CGE cold gas efficiency

GFW gasification feed water

HP high pressure

LHV lower heating value, kJ/kmol

HHV higher heating value, kJ/kmol

Subscripts

\( i \) \( i \)th component species

\( j \) \( j \)th constituent chemical substance
\( k \) \( k \)th chemical element

Set

\( REACT \) reactants in the gasification

\( GPROD \) gaseous products in the gasification

\( SPROD \) solid products in the gasification

\( PROD \) products in the gasification
CHAPTER 3

HEAT INTEGRATION MODEL FOR VARIABLE STREAM CONDITIONS AND PHASE CHANGE

3.1 Introduction

As discussed in Section 1.2, syngas product of a gasification process has energy in two forms which are the calorific value and the sensible heat. Most of the gasification studies tend to exploit CGE potential and often ignore efficient utilization of sensible heat to improve the overall gasification process. So far, we have established a gasification model to determine the highest CGE scenario in Chapter 2. And then optimizing the utilization of sensible heat is second target and can be realized in this integration model in this chapter.

The major aim of the heat integration model is to ensure the feasible heat exchange and determines the maximum recovery of sensible heat. However, in a gasification process, sensible heat can be integrated with feed preheating and steam generation. If feed preheating is applied, it will influence the gasification heat balance and further change the flow rates and temperature of syngas components, which in turn affect both the operating condition of the gasification process and heat integration. Therefore, in such circumstances where there exists a strong interaction between the chemical process and the heat recovery network, the heat integration problem should be considered simultaneously with the overall optimization problem instead of being optimized sequentially [50]. As a result, the heat integration model not only need to ensure the feasible heat exchange and determines the maximum heat recovery, but also must be able to handle variable parameters of process streams.

To achieve that, the pinch analysis method where minimum heat transfer temperature is defined is utilized to ensure the feasible heat exchange. The heat recovery is maximized via a set of constraints which describe a feature in the composite curves. In order to deal with variable temperatures and flow rates of process streams, the expressions of temperature differences proposed by Duran and Grossmann are applied [35], which can automatically exclude the irrelevant portion of heat contents.
What’s more, phase change that involves a large amount of latent heat without temperature variation may affect the feasibility of heat transfer [51]. In this study, a set of piecewise functions is formulated to make sure the temperature of phase transition is included in the pinch design method. Two examples are presented to illustrate the optimization procedures.

3.2 Heat integration modelling

3.2.1 Pinch analysis

In a general heat recovery network, any flow which requires to heat or cool down, but does not change in composition, is defined as a process stream. The flow which starts cold and needs to be heated up is known as a cold stream. Conversely, the flow which must be cooled down is called a hot stream. The enthalpy change corresponding to the temperature change of each stream in the network can be plotted on a temperature-enthalpy (T-H) diagram. By adding together the enthalpy change of all cold streams over a certain temperature range, a single curve representing all cold streams can be obtained, known as cold composite curve. A single curve of all hot streams can be formed in a similar way, known as hot composite curve. The calculations and methods of drawing them can refer to the textbook for details [52].

As shown in Figure 3.1 which is a graphic example, two curves provide a counter-current picture of heat transfer and can be used to indicate the maximum heat recovery for the process. These curves can be brought together as close as possible via horizontal displacement, but without violating the minimum driving force ($\Delta T_m$) for heat exchange. In general, $\Delta T_m$ occurs at only one point of closest approach, which is called the pinch [32].

The temperature pair ($T_p, T_p - \Delta T_m$) separates the system into two parts. While the part above the pair requires only cooling, the part below it requires only heating. As indicated by Figure 3.1, the problem of maximizing heat recovery can be converted to the minimization of ($H_{hd} + H_{cd}$). The heating and cooling demands must satisfy heat balance involving heat flow of entire system which is

$$H_h - H_c + H_{hd} - H_{cd} = 0$$  \hspace{1cm} (3.1)

where $H_h$ and $H_c$ represent heat duty of hot streams and cold streams, respectively. They are given by the expressions
\[ H_h - H_c = \sum_{i \in H} n_i[H(T_{i,4}) - H(T_{i,1})] - \sum_{i \in C} n_i[H(T_{i,4}) - H(T_{i,1})] \]  

(3.2)

Figure 3.1. Graphic determination of pinch point and definitions

Pinch analysis method assumes the heat capacities of all process streams are constant [52]. With that, the pinch candidates \((p, p \in P)\) can only occur at the inlet temperatures and phase change temperatures of the process streams, because these temperatures correspond to corner points where a decrease in slope appears in the direction of the composite curve. Obviously, there is only one temperature pair \((T_p, T_p - \Delta T_m)\) among all the pinch candidates that can ensure the feasible heat transfer with non-negative heating and cooling demands. Therefore, the minimum cooling and heating demands \((H_{hd}, H_{cd})\) that are physically attainable in a network can be determined by locating those pinch points that feature the maximum of both heating, \(H_{hd}^p\), and cooling, \(H_{cd}^p\), requirements among all pinch candidates \((p)\).
As composite curves reflected, heating and cooling demands in the system can be interpreted respectively as the heating and cooling sections identified for each pinch candidate. To evaluate the corresponding sections, following associated terms are defined as shown in Figure 3.1:

- Heat source above the pinch, $H_{ha}^p$, which accounts for the contributions from hot streams to the available heat above the pinch candidate.
- Cooling source above the pinch, $H_{ca}^p$, which accounts for the heating requirements above the pinch candidate in order to help cold streams to reach their outlet temperatures.
- Heat source below the pinch, $H_{hb}^p$, which represents the heat below the pinch candidate that hot streams must exchange to reach their outlet temperatures.
- Cooling source below the pinch, $H_{cb}^p$, which represents the heat amount below the pinch candidate that cold streams can accept.

The criteria of minimum heating and cooling demands for each pinch candidate then can be formulated as

$$H_{ha} = \max_{p \in P} (H_{ha}^p) = \max_{p \in P} (H_{ca}^p - H_{ha}^p) \quad (3.3)$$

$$H_{cd} = \max_{p \in P} (H_{ca}^p) = \max_{p \in P} (H_{hb}^p - H_{cb}^p) \quad (3.4)$$

Since the pinch separates the system into two independent parts that are in full heat balance, one of the Eqs. (3.3) and (3.4) is redundant and Eq. (3.3) is selected in this study. So far, the constraints given by Eqs. (3.1) and (3.3) have been obtained based on pinch analysis method to ensure the feasible heat exchange and determine the maximum heat recovery.

3.2.2 Mathematical formulations of temperature difference and phase change

The developed two constraints cannot have real function until they are able to handle variable stream data. To realize that, the mathematical formulations of temperature difference ($\Delta T$) corresponding to different pinch candidates and heat capacity or enthalpy with respect to temperature are needed. For example, to calculate the cooling demand according to Eq. (3.3), we have

$$H_{ca}^p - H_{ha}^p = \sum_{COLD} nC_p \Delta T_c^p - \sum_{HOT} nC_p \Delta T_h^p \quad (3.5)$$
where $C_p$ is heat capacity, $\Delta T_c^p$ and $\Delta T_h^p$ represent the temperature difference for a cold stream and a hot stream under pinch candidate $p$, respectively. The heat capacity for every common substance has empirical polynomial function of temperature, which has been validated by experiments. Nevertheless the temperature difference of each stream above the pinch changes with the pinch candidate. To handle this, a set of max() expressions was developed to automatically include only the relevant portion of the temperature difference according to different pinch candidates.

$$\Delta T_c^p = \max[0, T_{out} - (T_p - \Delta T_m)] - \max[0, T_{in} - (T_p - \Delta T_m)] \quad (3.6)$$

$$\Delta T_h^p = \max(0, T_{in} - T_p) - \max(0, T_{out} - T_p) \quad (3.7)$$

It should be noticed that the max() expressions of temperatures in Eqs. (3.6) – (3.7) have the global effect of including only the relevant portion of the heat content of each stream. For example, the below expression used for heat source of cold streams below the pinch candidate ($H_{hb}^p$) can be reduced according to different circumstances.

$$\max[0, T_{out} - (T_p - \Delta T_m)] - \max[0, T_{in} - (T_p - \Delta T_m)] \quad (3.8)$$

- If a cold stream is located entirely above the pinch candidate, this indicates $T_{out} > T_{in} > (T_p - \Delta T_m)$, which reduces Eq. (3.8) to $(T_{out} - T_{in})$. This means all the heat content of $i$th cold stream is calculated to be heat source above the pinch.
- If a cold stream crosses the pinch candidate, this indicates $T_{out} > (T_p - \Delta T_m) > T_{in}$, which reduces Eq. (3.8) to $[T_{out} - (T_p - \Delta T_m)]$. This means only a fraction of the heat content of $i$th cold stream contributes to heat source above the pinch.
- If a cold stream is located entirely below the pinch candidate, this indicates $(T_p - \Delta T_m) > T_{out} > T_{in}$, which reduces Eq. (3.8) to be 0. This means no heat contributes to heat source above the pinch.
What’s more, the streams with phase change should be treated carefully as neglecting such change may lead to a sub-optimal even infeasible solution. Figure 3.2 (a) shows the composite curves corresponding to an impossible heat transfer network. The flat segment represents the latent heat. If use the linear heat capacity assumption for a whole stream, it becomes a straight line in composite curve and looks feasible as indicated in Figure 3.2 (b), but violates the second law of thermodynamics.

Figure 3.2. Composite curves of heat transfer with phase change in the hot stream

(a) Left. The case considering the phase change.
(b) Right. The case using usual linear heat capacity assumption.

A piecewise function which splits the stream into three sub-streams is developed in this work to avoid such cases. As illustrated in Figure 3.2 (a), for a hot stream with phase change, its 1\textsuperscript{st} and 3\textsuperscript{rd} segment use the same max() expression of a normal stream to formulate the temperature difference. 2\textsuperscript{nd} segment which stands for latent heat does not have temperature change. Since pinch candidates are corner points where a decrease in slope appears in the direction of the composite curve, the pinch cannot form within the flat segment, which means the 2\textsuperscript{nd} segment should be either included or excluded as an entire part in the calculation of heat source above the pinch. To realize this concept, another max() expression for the sub-stream of phase change is developed. The heat source above a pinch candidate of 3 sub-streams can be expressed as

\[ nC_p\Delta T_h^P = n \left[ C_{p,1}\Delta T_{h,1} + h_{\text{latent}} \frac{\max(0, T_{\text{out}}-T_{p}+\epsilon)}{T_{\text{out}}-T_{p}+\epsilon} + C_{p,3}\Delta T_{h,3} \right] \]  

(3.9)
As shown in Figure 3.3, the new \text{max()} expression has the global effect to include or exclude the latent heat according to different pinch candidates.

Figure 3.3. The calculation of heat source above a pinch candidate for a hot stream with phase change

\[
nC_p \Delta T_h^p = nC_{p,3}(T_{in,3} - T_p)
\]

(a) Left. Pinch candidate located at the 3\textsuperscript{rd} segment.

(b) Right. Pinch candidate located at the 1\textsuperscript{st} segment.

Further, the \text{max()} expressions for normal hot streams and hot streams with phase change are integrated into one equation (Eq. (3.10)). So we can have one formulation to include all five cases. As shown in Figure 3.4, they are the normal stream below, crossing and above the pinch candidate as well as the phase change stream below and above the pinch candidate.

\[
H^p_{ha} = \sum_{HOT} nC_p \Delta T_h^p = \sum_{HOT} nC_p \left\{ \left[ \max(0, T_{in} - T_p) - \max(0, T_{out} - T_p) \right] + \frac{\max[0, (T_{out} - T_{in} + \epsilon)]}{T_{out} - T_{in} + \epsilon} \frac{\max[0, (T_{out} - T_p - \epsilon)]}{T_{out} - T_p - \epsilon} \right\}
\]

(3.10)

For phase change sub-streams, \( C_p = h_{\text{latent}} \) and \( \epsilon \) is a sufficiently small number to avoid calculation error. Similarly, for a cold stream, we can formulate an equation (Eq. (3.11)) to include all five cases in the calculation of cooling source above a pinch candidate. As indicated by Figure 3.5, five cases are the normal stream below, crossing and above the pinch candidate as well as the phase change stream below and above the pinch candidate.
$$H_{ca}^p = \Sigma_{COLD} nC_p \Delta T_c^p = \Sigma_{COLD} nC_p \left\{ \max[0, T_{out} - (T_p - \Delta T_m)] - \max[0, T_{in} - (T_p - \Delta T_m)] + \right. \\
\left. \frac{\max[0, (T_{in} - T_{out} + \epsilon)]}{T_{in} - T_{out} + \epsilon} \max[0, (T_{in} - (T_p - \Delta T_m) - \epsilon)]} \right\}$$

(3.11)

Figure 3.4. The calculation of heat source above a pinch candidate for a hot stream

Figure 3.5. The calculation of cooling source above a pinch candidate for a cold stream
3.2.3 The detailed formulations

With heat capacity and the developed mathematical expressions of temperature difference, two constraints can be fully formulated to the functions of temperature and flow rates. In this work, the heat capacity is relaxed to a great extent by using equivalent heat capacity of a single phase which is defined as:

$$C_p = \frac{\Delta H}{\Delta T}$$

where $\Delta H$ is the enthalpy difference over a certain temperature difference ($\Delta T$) in a single phase. The detailed mathematical formulations for the heat integration model then can be formed as follows.

In Eq. (3.3), the total cooling source, $H_{ca}^P$, above the pinch is the sum up of cooling source of each cold stream above the pinch which can be further interpreted to the functions of stream flow rates, temperatures and enthalpy changes of streams as in Eq. (3.12).

$$H_{ca}^P = H_{ca}^P + H_{can}^P$$ \hspace{1cm} (3.12)

where $H_{ca}^P$ and $H_{can}^P$ are the duty of cold streams above a pinch candidate $p$ with and without phase change respectively. The heat duty of cold streams with phase change above a candidate pinch point ($H_{ca}^P$) can be given by

$$H_{ca}^P = \sum_{i \in CV} \sum_{l \in L} n_i \left\{ \frac{H(T_{l,l+1}) - H(T_{l,l})}{(T_{l,l+1} - T_{l,l})} \left[ \max[0, T_{l,l+1} - (T_p - \Delta T_m)] - \max[0, T_{l,l} - (T_p - \Delta T_m)] \right] \right\}$$ \hspace{1cm} (3.13)

For cold streams without phase change (vaporization), their enthalpy change above a candidate pinch point is given by

$$H_{can}^P = \sum_{i \in C} n_i \left\{ \frac{H(T_{l,4}) - H(T_{l,1})}{(T_{l,4} - T_{l,1})} \left[ \max[0, T_{l,4} - (T_p - \Delta T_m)] - \max[0, T_{l,1} - (T_p - \Delta T_m)] \right] \right\}$$ \hspace{1cm} (3.14)

Similarly, the duty of the hot streams above a pinch candidate can be expressed as

$$H_{ha}^P = H_{hac}^P + H_{hanc}^P$$ \hspace{1cm} (3.15)
The non-condensation part of this stream is formulated by multiplying flow rate, equivalent heat capacity and temperature change above the pinch candidates.

\[ H_{hanc}^P = \sum_{i \in H} n_i \frac{H(T_{i,1} - H(T_{i,a}))}{(T_{i,1} - T_{i,a})} \left[ \max(0, T_{i,1} - T_P) - \max(0, T_{i,a} - T_P) \right] \] (3.16)

For hot streams with phase change (condensation), the heat duty above a candidate pinch point \( H_{hac}^P \) can be given by

\[ H_{hac}^P = \sum_{i \in HC} \sum_{l \in L} n_i \frac{H(T_{i,l+1} - H(T_{i,l}))}{(T_{i,l+1} - T_{i,l})} \left[ \max(0, T_{i,l} - T_P) - \max(0, T_{i,l+1} - T_P) \right] \] (3.17)

There is no need to know in advance the relative location of process streams’ temperatures to each pinch candidate. Therefore, for the optimization problem involving variable flow rates and temperatures, the calculation of heat and cooling sources can be done automatically without extra steps. The set of candidate pinch temperatures \( (T_p, p \in P) \) in Eq. (3.18) is given by the assignments

\[ \{T_p \in (T_{c,1} + \Delta T_m) \cup (T_{CV,1} + \Delta T_m) \cup (T_{CV,2} + \Delta T_m) \cup (T_{CV,3} + \Delta T_m) \cup T_{H,1}\} \] (3.18)

To conclude, although there are a few piecewise functions to describe the different parts in composite curves, the optimization problem of minimum utility target could be addressed by solving below two main equations which contain two unknowns \( H_{hd} \) and \( H_{cd} \). The only decision involved in this optimization occurs in Eq. (3.13), where the selection of the heating demand of the largest value among all pinch candidates has to be made.

\[ H_{hd} = \max_{p \in P}(H_{ca}^P - H_{hac}^P) \] (3.19)

\[ H_{cd} = H_h - H_c + H_{hd} \] (3.20)

In a process optimization problem, the flow rates and temperatures of the process streams are not known priori as these are variables whose values will change throughout the optimization procedure. Eqs. (3.19) and (3.20), however, hold for any variable parameters of process streams. Since the heat recovery system normally has limited pinch candidates, the decision could be easily made by comparing the heat demands corresponding to each pinch candidate rather than compute it as a problem of finding extremum.
3.3 Example

3.3.1 Maximum heat recovery with fixed stream parameters

In order to gain some insight into the proposed heat integration model, an optimization of a heat recovery network that has two hot streams and two cold streams with one of them has phase change is shown as follows. The minimum heat transfer temperature is set equal to 10 °C. The stream data of this example is shown in Table 3.1. Except second hot stream which condenses at 100 °C and releases 2260 kW heat, other streams have constant heat capacities.

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>( n\Delta H/\Delta T ) (kW/°C)</th>
<th>( T_{i,1} ) (°C)</th>
<th>( T_{i,4} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>2260 (condense at 100 °C)</td>
<td>240</td>
<td>83</td>
</tr>
<tr>
<td>H2</td>
<td>30.55</td>
<td>230</td>
<td>138</td>
</tr>
<tr>
<td>Cold streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>70.62</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>C2</td>
<td>16.08</td>
<td>116</td>
<td>230</td>
</tr>
</tbody>
</table>

Table 3.1. Data of process streams

The first step of minimum energy target is to identify the pinch candidates. As indicated by Table 3.2, total five pinch candidates consisting of four inlet temperatures and one phase change point should be evaluated. The heat duty of the whole system can also be calculated according to Eq. (3.1). Then based on each pinch candidate, use Eqs. (3.12) – (3.17) to calculate the heat source and cooling source above the pinch candidate for each process stream. The corresponding heat is listed in Table 3.3 in details, from which we can see that only relevant portion of the heat content in each process streams are included with the help of max() expressions.
Table 3.2. Pinch candidates and heat duty

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>n\Delta H/\Delta T (kW/°C)</th>
<th>(T_{i,1}) (°C)</th>
<th>(T_{i,4}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{1,1}</td>
<td>1.85</td>
<td>240</td>
<td>100</td>
</tr>
<tr>
<td>H_{1,2}</td>
<td>4.18</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>H_{1,3}</td>
<td>30.55</td>
<td>230</td>
<td>138</td>
</tr>
<tr>
<td>(H_{1.1})) Condensation (heat duty = 2260 kW)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{1}</td>
<td>70.62</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>C_{2}</td>
<td>16.08</td>
<td>116</td>
<td>230</td>
</tr>
<tr>
<td>(H_h - H_c)</td>
<td>32.36 kW</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3. Calculations of heat demand and cooling demand

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Pinch candidates ((T_p), °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream No.</td>
<td>240 °C</td>
</tr>
<tr>
<td>(H_{ca}^p) (kW)</td>
<td>H_{1,1}</td>
</tr>
<tr>
<td>(H_{ca}^p) (kW)</td>
<td>H_{1,2}</td>
</tr>
<tr>
<td>(H_{ca}^p) (kW)</td>
<td>H_{1,3}</td>
</tr>
<tr>
<td>(H_{ca}^p) (kW)</td>
<td>H_{2}</td>
</tr>
<tr>
<td>(H_{ha}^p) (kW)</td>
<td>C_{1}</td>
</tr>
<tr>
<td>(H_{ha}^p) (kW)</td>
<td>C_{2}</td>
</tr>
<tr>
<td>(H_{ca}^p - H_{ha}^p) (kW)</td>
<td>0</td>
</tr>
<tr>
<td>(H_{hd} = \max_{p \in P}(H_{ca}^p - H_{ha}^p))</td>
<td>175.92 kW</td>
</tr>
<tr>
<td>(H_{cd} = H_h - H_c + H_{hd})</td>
<td>208.28 kW</td>
</tr>
</tbody>
</table>

It can be easily identified that the maximum value of \((H_{ca}^p - H_{ha}^p)\) is the minimum heat duty requirement from hot utility. Correspondingly, 100 °C where the condensation of first hot stream occurs is the pinch point (see Figure 3.6).

If the phase change is not evaluated by the piecewise functions developed in the heat integration model, the temperature corresponding to the second largest number of \((H_{ca}^p - H_{ha}^p)\) will become the pinch (see Figure 3.7). Consequently, that the violation of the minimum heat transfer temperature \(\Delta T_m\) cause the infeasible heat exchange in the recovery network.
Figure 3.6. Composite curves of heat recovery network with fixed stream parameters

Figure 3.7. Composite curves of heat recovery network without considering phase change
3.3.2 Maximum heat recovery with variable stream parameters

Based on the same stream information, the inlet temperatures of a hot stream ($H_1$) and a cold stream ($C_1$) is set to be variables to define a heat recovery network without utility requirements. As shown in Table 3.4, the inlet temperature of $H_1$ and $C_1$ are optimized to be 335.09 °C and 67.05 °C, respectively. The entire heat exchange network is in heat balance, which is reflected by ($H_h - H_c = 0$). The detailed calculation indicates that the pinch point is 100 °C where ($H_{ca}^p - H_{ha}^p$) has the largest number (0). The composite curves with full heat balance are shown in Figure 3.8.

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>$n\Delta H/\Delta T$ (kW/°C)</th>
<th>$T_{i,1}$ (°C)</th>
<th>$T_{i,4}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_{1.1}$</td>
<td>1.85</td>
<td>335.09</td>
<td>100</td>
</tr>
<tr>
<td>$H_{1.2}$</td>
<td>4.18</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>$H_{1.3}$</td>
<td>30.55</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>Condensation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_{2}$</td>
<td>70.62</td>
<td>57.05</td>
<td>110</td>
</tr>
<tr>
<td>Cold streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{1}$</td>
<td>16.08</td>
<td>116</td>
<td>230</td>
</tr>
</tbody>
</table>

$H_h - H_c$ 0.00 kW
Figure 3.8. Composite curves of heat recovery network with variable stream parameters
NOMENCLATURE

\( T_p \)  
\text{temperature of pinch candidate}

\( \Delta T_m \)  
\text{minimum temperature approach}

\( H_{hd} \)  
\text{minimum heating demand}

\( H_{cd} \)  
\text{minimum cooling demand}

\( H_p \)  
\text{heat source above the pinch candidate}

\( H_{ca} \)  
\text{cooling source above the pinch candidate}

\( H_{hp} \)  
\text{heat source below the pinch candidate}

\( H_{cb} \)  
\text{cooling source below the pinch candidate}

\( H_h \)  
\text{heat content of hot process streams}

\( H_c \)  
\text{heat content of cold process streams}

\( H_{cav} \)  
\text{cooling source with vaporization above the pinch candidate}

\( H_{canv} \)  
\text{cooling source without vaporization above the pinch candidate}

\( H_{hac} \)  
\text{heat source with condensation above the pinch candidate}

\( H_{hanc} \)  
\text{heat source without condensation above the pinch candidate}

\( \Delta T \)  
\text{temperature difference}

Subscripts

\( i \)  
\text{ith process stream}

\( l \)  
\text{temperature of a process stream at lth location}

\( c \)  
\text{a certain cold stream}

\( h \)  
\text{a certain hot stream}

Superscript

\( p \)  
\text{index for pinch candidates points}

Sets

\( CV \)  
\text{cold streams with vaporization}

\( C \)  
\text{cold streams without vaporization}

\( HC \)  
\text{hot streams with condensation}

\( H \)  
\text{hot streams without condensation}
\( L \) \quad \text{temperatures of process streams at inlet (1), saturated liquid (2), saturated vapour (3) and outlet (4)}

\( P \) \quad \text{pinch candidate points}
CHAPTER 4

SIMULTANEOUS OPTIMIZATION OF A HEAT INTEGRATED COAL GASIFICATION PROCESS

4.1 Problem Statement

The process flow diagram of the heat integrated coal gasification is illustrated in Figure 4.1. Assuming high quality coal with 100% carbon (C) is fed into the gasifier together with O\textsubscript{2} and GFW for gasification. The syngas produced is then used to generate electricity in a combined cycle. The sensible heat of syngas is recovered and used to preheat the gasification reactants and/or generating steam that can be exported. The optimization target is to maximize the overall profit defined in Eq. (4.1) which is the difference between the cost and revenue of gasification when the syngas is used for preheating reactants, electricity generation and generating steam.

\[
Profit = (n_{coal}LHV_{coal}CGE \eta_e C_e + n_{steam}C_{steam}) - (n_{carbon}C_{carbon} + n_{O2}C_{O2} + n_{H2O}C_{H2O})
\]

where CGE is the ratio of \textit{LHV}	extsubscript{syngas} to \textit{LHV}	extsubscript{coal}. In gasification, the amounts of O\textsubscript{2} and GFW supply directly affect the syngas composition and gasification temperature. As a result, the revenues from electricity generation using syngas and sensible heat recovery change. Meanwhile, the assignment of the sensible heat between preheating of reactants and steam generation also affects the revenue. While using the sensible heat to preheat the reactants reduces the O\textsubscript{2} demand in gasification and increases the CGE, the sensible heat if used to produce steam can also add to the revenue of steam export. Design of the heat integration is mainly affected by the prices of steam and electricity as well as the efficiency of the combined cycle.

Unlike most of the gasification optimization studies that focus on a single operating parameter of gasification [21-23], the problem to be solved in this work is much more complex. The variables including the reactant flow rates, gasification temperature as well as the preheating levels of reactants should be optimized simultaneously to achieve maximum economic profit in electricity generation and steam export.
4.2 Model summary

In order to simultaneously optimize operating conditions and heat recovery network of the gasification process, a model structure that combines the single objective model and heat integration model is proposed accordingly.

The single objective model converts the multi-objective problem (Gibbs free energy minimization and profit maximization) into a single objective profit maximization problem. Hence, it is able to optimize key operating parameter like reactant flow rates, gasification temperature as well as the preheating levels of reactants simultaneously. In addition to satisfying the constraints in the single objective model, the variables also need to be constrained by the heat integration model to ensure the maximum heat recovery as well as feasible heat exchange. In the heat integration, the independent cold stream - HP steam will be optimized for the target of maximum profit as well. The HP steam temperature and enthalpy are fixed by the export requirement. The flow rate of the HP steam will be determined by the constraints in Eq. (3.19) and (3.20). Provided a minimum heat transfer temperature ($\Delta T_m$), the heat integration model, together with the single objective model, will be used for optimizing the profit in Eq. (4.1), using a generalized reduced gradients nonlinear solver.
After above analysis and modelling work, the structure of the model now is developed as

Maximize Profit 

Objective 

s.t. 

Heat balance of the gasification process, Eq. (2.11) 

Constraints 

Elemental balances, Eq. (2.15) 

Heat balance in the heat integration, Eq. (3.13) 

Maximum heat recovery constraint, Eq. (3.14) 

Set 

\[ \text{REACT} \] reactants in the gasification 

\[ \text{GPROD} \] gaseous products in the gasification 

\[ \text{SPROD} \] solid products in the gasification 

\[ \text{PROD} \] products in the gasification 

\[ \text{CV} \] cold streams with vaporization (GFW and HP steam) 

\[ \text{C} \] cold streams without vaporization (oxygen) 

\[ \text{HC} \] hot streams with condensation 

\[ \text{H} \] hot streams without condensation (syngas mixture of H₂, CO, CO₂ and H₂O) 

\[ \text{L} \] temperatures of process streams at inlet (1), saturated liquid (2), saturated vapour (3) and outlet (4) 

\[ \text{P} \] pinch candidate points 

Variables 

\[ n_i \] flow rate of process stream \( i, i \in C \cup CV \cup H \) 

\[ T_{i,l} \] outlet temperature of process stream \( i \) after preheating, \( i \in C \cup CV, l = 4 \) 

\[ T_p \] pinch temperature 

\[ T \] gasification temperature 

Parameters 

\[ T_{i,l} \] inlet temperature of cold streams, \( i \in C \cup CV, l = 1 \)
The temperatures of saturated liquid and vapor, $i \in CV, l = 2, 3$

Outlet temperature of the syngas, $i \in H, j = 4$

Upper limit temperature of process stream $i$ after preheating, $i \in C \cup CV, l = 4$

Minimum heat transfer temperature

Required pressure for HP steam

4.3 Case study

In the following case studies, the flow rate of coal (100% C) is fixed at 10,000 kg/h, which is gasified in the presence of O$_2$ and GFW at 1 bar. The gasifier is allowed to operate under any temperatures from 1673 to 1873 K [53]. The sensible heat of syngas can be used for both reactants preheating and production of HP steam (832 K, 125 bar) for export. The cooled syngas is utilized for electricity generation in a combined cycle. Minimum approach temperature of heat exchange is set at 10 K. In consideration of the reasonable endurance of heat exchanger [54], the temperature limits of each substance are set as shown in Table 4.1. The electricity generation efficiency in the combined cycle is assumed to be 45.7% ($\eta_e$) [55]. The LHVs of different gas components for calculating CGE and the unit prices of coal, O$_2$, GFW and electricity are given in Table 4.2.

Three scenarios are presented. The base case shows the conventional iterative approach to optimize the reactant flow rates and reaction temperature for maximum profit of gasification process. Case 1 illustrates the process of using the single objective model to optimize all the key operating parameters of gasification for maximum profit. Case 2 gives an integrated process of coal gasification with part of the sensible heat of syngas optimized for preheating of reactants. The economic profits from HP steam production and electricity generation using the syngas in all the cases have been calculated.
Table 4.1. Parameters of the heat integrated gasification process

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lower temperature limit (K)</th>
<th>Upper temperature limit (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>298</td>
<td>700</td>
</tr>
<tr>
<td>GFW</td>
<td>298</td>
<td>700</td>
</tr>
<tr>
<td>Gasification temperature</td>
<td>1673</td>
<td>1873</td>
</tr>
</tbody>
</table>

Table 4.2. The data of unit prices and LHV [56]

<table>
<thead>
<tr>
<th>Item</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit Price of coal</td>
<td>79.70 $/t</td>
</tr>
<tr>
<td>Unit Price of O₂</td>
<td>100 $/t</td>
</tr>
<tr>
<td>Unit Price of GFW</td>
<td>5 $/t</td>
</tr>
<tr>
<td>Unit Price of electricity by syngas</td>
<td>0.06 $/kWh</td>
</tr>
<tr>
<td>Unit Price of HP steam</td>
<td>14 $/t</td>
</tr>
<tr>
<td>LHV(_{\text{H₂}})</td>
<td>240 kJ/mol</td>
</tr>
<tr>
<td>LHV(_{\text{CO}})</td>
<td>282.8 kJ/mol</td>
</tr>
<tr>
<td>LHV(_{\text{CH₄}})</td>
<td>802.34 kJ/mol</td>
</tr>
</tbody>
</table>

4.3.1 Base case – Iterative approach for profit maximization

In the base case, a conventional iterative approach is applied to maximize the profit. The optimum reaction temperature is found to be 1673 K. Given the coal feeding rate of 10,000 kg/h, the optimum O₂ and GFW are 10,697 kg/h and 3,030 kg/h, respectively. Under the optimum operating conditions, the CGE can reach 83.88% and the maximum total profit is 322 $/h.

4.3.2 Case 1 – Simultaneous approach for profit maximization

In this case, the O₂ and GFW flow rates and gasification temperature are optimized simultaneously to achieve maximum profit. The sensible heat is used for steam generation only. Preheating of reactants is designed to be absent in this case. According to the single objective model developed in Section 2.3, the operating conditions can be optimized as shown in Figure 4.2. The optimum O₂ supply, GFW supply, and reaction temperature for maximum profit are determined to be 10,666.85 kg/h, 2,999.79 kg/h, and 1673 K, respectively.
The CGE is calculated to be 84.23%. Total 11,006.02 kW sensible heat is recovered through generating 11,669.88 kg/h HP steam and corresponding composite curves are shown in Figure 4.3. The maximum total profit is 330 $/h.

**Figure 4.2. Process flowsheet of Case 1**

**Figure 4.3. Composite curves of Case 1**
4.3.3 Case 2 – Simultaneous approach for profit optimization with heat integration

To exploit the potential for further improvement, the sensible heat of the hot syngas is considered to be used for combined reactant preheating and HP steam production. The optimum operating conditions are shown in Figure 4.4, where 9,863.73 kg/h $\text{O}_2$ and 3,903.29 kg/h GFW should be fed to the gasifier per 10,000 kg/h coal. The $\text{O}_2$ and GFW feed is optimized to be preheated to 700 K. The optimum reaction temperature is at 1673 K, which gives a CGE of 87.95%.

![Figure 4.4. Process flowsheet of Case 2](image)

As shown in Table 4.3, a total amount of 11,525.01 kW sensible heat can be recovered from the syngas, among which 1,070.14 kW and 3,502.16 kW are used to preheat $\text{O}_2$ and GFW feed, respectively. The rest 6,952.71 kW is to generate 7,372.08 kg/h HP steam for export. The composite curves under the optimum operating conditions are shown in Figure 4.5. The total maximum profit is calculated to be 460.15 $/h.

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>Stream type</th>
<th>$T_{in}$ (K)</th>
<th>$T_{out}$ (K)</th>
<th>Heat load (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot syngas</td>
<td>Hot</td>
<td>1673</td>
<td>464</td>
<td>11525.01</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>Cold</td>
<td>298</td>
<td>700</td>
<td>1070.14</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>Cold</td>
<td>298</td>
<td>700</td>
<td>3502.16</td>
</tr>
<tr>
<td>HP steam generation</td>
<td>Cold</td>
<td>298</td>
<td>832</td>
<td>6952.71</td>
</tr>
</tbody>
</table>
Extra capital cost of stainless steel heat exchangers in this case is estimated using heat transfer coefficients in Table 4.4 and Eq. (4.2) \[57\].

\[
\text{Capital cost} = 46500 + 2557.5A^{0.81}
\]

where \(\text{Capital cost}\) is in \$ and \(A\) is exchanger area in \(m^2\).

The heat exchange network is designed as shown in Figure 4.6 and the parameters of the heat exchangers are listed in Table 4.5. The total capital cost of the 3 heat exchangers is 635,463.67 \$ which is equivalent of 7.4 \$/h over a life time of 10 years. This value is much smaller than the increasing of profit through heat integration, and thus, the process design is economically feasible.
In addition, the product composition determined using the simplified single objective model has been validated using ASPEN Plus simulation. With the amount of coal, O₂ and GFW supply optimized in Case 2, the syngas composition given by ASPEN Plus contains 20.62% H₂ and 79.32% CO when the heat duty of the gasifier is zero. This agrees with the assumption that the gasification product should be entirely composed of H₂ and CO at temperatures of above 1400 K when the amounts of O₂ and GFW supply are optimized.

4.3.4 Comparison of the cases

Table 4.6 gives a summary of the results of the case studies. In the base case, the iteration process involves heavy work load of calculation to determine equilibrium product compositions and the CGE values as the amounts of O₂ and GFW supply change under each reaction temperature from 1673 to 1873 K. The results under each temperature are then plotted on an O₂-GFW-CGE diagram to determine the global optimum operating conditions of maximum profit. Some results of locally minimized Gibbs free energy are found during calculation, which are eventually ruled out one by one in separate steps.
Although the optimization results of the base case are basically the same as that of Case 1 using a simultaneous approach, it is worth noticing that the simultaneous approach involves only a single step of using the generalized reduced gradients nonlinear solver to optimize the CGE.

Table 4.6. Summary of the three case study results

<table>
<thead>
<tr>
<th></th>
<th>Base case</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGE</td>
<td>83.88%</td>
<td>84.23%</td>
<td>87.87%</td>
</tr>
<tr>
<td>GFW (kg/h)</td>
<td>3030</td>
<td>3000</td>
<td>3903</td>
</tr>
<tr>
<td>O₂ (kg/h)</td>
<td>10697</td>
<td>10667</td>
<td>9863</td>
</tr>
<tr>
<td>O_GFW/C</td>
<td>0.20</td>
<td>0.20</td>
<td>0.26</td>
</tr>
<tr>
<td>O₂/C</td>
<td>0.80</td>
<td>0.80</td>
<td>0.74</td>
</tr>
<tr>
<td>Recovered heat for feed preheating (kW)</td>
<td>0</td>
<td>0</td>
<td>4572</td>
</tr>
<tr>
<td>Recovered heat for HP steam (kW)</td>
<td>10985</td>
<td>11006</td>
<td>6952</td>
</tr>
<tr>
<td>Feed cost ($/h)</td>
<td>1882</td>
<td>1879</td>
<td>1802</td>
</tr>
<tr>
<td>Electricity Revenue ($/h)</td>
<td>2100</td>
<td>2104</td>
<td>2196</td>
</tr>
<tr>
<td>Water cost ($/h)</td>
<td>58</td>
<td>58</td>
<td>37</td>
</tr>
<tr>
<td>HP steam revenue ($/h)</td>
<td>163</td>
<td>163</td>
<td>103</td>
</tr>
<tr>
<td>Profit ($/h)</td>
<td>322</td>
<td>330</td>
<td>460</td>
</tr>
</tbody>
</table>

In the base case and Case 1, the syngas is not considered for preheating of reactants, and the maximum total profit from HP steam production and electricity generation using the syngas is about 330 $/h. In Case 2, however, when part of the sensible heat of syngas is assigned to reactant preheating, the maximum total profit can reach 460 $/h with an increment of about 40%. This is because, although using part of the sensible heat for reactant preheating reduces the revenue from HP steam production, the expensive O₂ demand is partly replaced by the cheaper oxygen source of GFW as concluded from the increased O_GFW/C value and reduced O₂/C value. This not only directly reduces the feed cost, but also increases the H₂ production so that the CGE is increased which increases the revenue from electricity generation. The additional capital cost for heat exchangers in Case 2 is only about 7.4 $/h with a life time of 10 years, which further confirms the economic feasibility of the designed heat integration process.
Using pure C to represent the coal in the case study leads to an overestimation of the maximum profit. However, this does not affect determination of the optimum reaction temperature. Nor does it affect the fact that the maximum profit is increased with heat integration. The real optimum preheating level of the reactants in a heat integrated process is also independent of the coal composition, as the optimum profit is always achieved when the heat exchangers are used in their full capacity. If permitted, the operating conditions can also be tuned based on the values obtained in the case studies in the real practice on a case by case basis.

4.3.5 Profit with steam price variation

To demonstrate the effectiveness of the model under different product prices, the maximum profit values under different steam prices are generated. Figure 4.7 shows the results of a sensitivity study at steam prices from 15 $/t to 100 $/t. When the steam price is below 45 $/t, the optimum gasification conditions and heat integration design are the same as that in Case 2, and the overall profit increases linearly with the steam price.

Figure 4.7. Profit maximization results with steam price change

![Graph showing profit maximization results with steam price change]

- Maximum profit with steam price below 45 $/t
- Maximum profit with steam price from 45 $/t to 87 $/t
- Maximum profit with steam price above 87 $/t
When the unit price of HP steam is increased to be above 45 $/t but below 87$/t, the maximum profit experiences the first tuning point, indicating that the process design is changed. The process is optimized not to preheat both O₂ and GFW and gasification should be at upper limit (1873K), which lead to more HP steam generation. Moreover, without preheating, the amount of O₂ supply has to be increased to maintain the highest possible reaction temperature. In the meantime, the GFW supply is reduced to maintain the balance of the oxygen atoms. The CO/H₂ ratio of the syngas is reduced from 3.84 in Case 2 to 5.73. Thus, CGE drops from 87.95% to 82.68%. All the sensible heat of the syngas (12,718.06 kW) should be used for HP steam production at a rate of 13,485.19 kg/h.

When the steam price is at 87 $/t or above, the process is optimized to be a complete combustion rather than produce any combustible gas for electricity generation, as the steam price far overweighs the electricity price. The production gas consists of 26.27% CO₂ and 73.73% H₂O. A large amount of H₂O is fed to balance the combustion heat in order to keep the reaction temperature at the upper limit (1873 K). The optimized process eventually generates 57,269.99 kW sensible heat for HP steam production (60,724.40 kg/h).

4.3.6 Profit with variations of combined cycle efficiency and electricity price

Based on Case 2, the preheating is a more efficient utilization of the sensible heat as the electricity production is more profitable. The increase of efficiency and electricity price will drive up the electricity profitability and the optimization will be kept the same. Therefore, only decrease of these two parameters are considered and studied. The results plotted in Figure 4.8 show that the profits have a linear correlation with the decrease of the efficiency and price, which indicates the previous optimization arrangements remain more profitable. The non-profit gasification occurs when the efficiency decreases to 36.20% or the electricity price is only 0.048 $/kWh.
4.4 Conclusions

Based on the research work in Section 2 and 3, a novel mathematical model structure has been developed to simultaneously optimize the gasification temperature, reactant flow rates, and preheating temperatures of the feed for maximum economic profit of a heat integrated coal gasification process.

The model consists of several constraints including the heat balance, elemental balances and feasible heat exchange. Optimum conditions for the maximum profit can be determined from the model using a generalized reduced gradients nonlinear solver. Heat integration described in the model guarantees the feasible heat exchange as the pinch analysis method has been employed. Case studies have been conducted to demonstrate the effectiveness and robustness of the model. The results of the case study also indicate that by assigning part of the sensible heat to preheat the reactants, the profit can be increased by up to 40% compared with that of using sensible heat for HP steam production only.
NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>heat exchanger area, $m^2$</td>
</tr>
<tr>
<td>$W_e$</td>
<td>electricity power, kWh</td>
</tr>
<tr>
<td>$C$</td>
<td>unit price, $/kWh for electricity and $/t for other process streams</td>
</tr>
<tr>
<td>$\eta_e$</td>
<td>combined cycle efficiency</td>
</tr>
</tbody>
</table>

Subscripts

$e$ electricity
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

First, the equilibrium model based on the Gibbs free energy minimization and the equilibrium model with KKT conditions were proposed for gasification modelling and optimization. Although it was straightforward to minimize the Gibbs free energy directly in the equilibrium model, finding the global minimum requires complex calculations and could be easily trapped in a local minimum. In the example, the optimization was done through detailed comparisons and analyses of syngas trends. To avoid such tedious work, a more direct procedure which integrated an advanced algorithm and Gibbs free energy minimization was proposed in Section 2.2. The equilibrium model with KKT conditions only need to solve the equality and inequality constraints instead of finding an extremum, which greatly simplified the optimization problem. However, for non-convex problem to be addressed by the gasification model, the KKT conditions were necessary to find an optimum, but not necessarily sufficient. Therefore, despite KKT algorithm reduced the calculations greatly, how to avoid the local optima still should be taken carefully.

So far, the developed equilibrium models offered an iterative approach to optimize the operating parameters of gasification for maximized CGE but required special modelling techniques and huge amounts of calculations. Also, the process could be easily trapped at a local optimum, which required an additional step to differentiate the global optimum from the local optima. To solve this problem, a novel mathematical model has been developed in Section 2.3, which converts the multi-objective problem (Gibbs free energy minimization and CGE maximization) into a single objective problem of profit maximization.
It was found that when the gasification feed reacted at temperatures above 1400 K, maximizing the economic profit of coal gasification, which was mainly determined by CGE, automatically led to gasification products with minimum Gibbs free energy. Thus, the multi-objective optimization problem could be simply converted to a single objective problem. Based on this observation, a novel model has been developed to simultaneously optimize the gasification temperature, reactant flow rates, and preheating temperatures of the feed for maximum economic profit of a heat integrated gasification process.

Then, in order to evaluate the efficient utilization of the sensible heat, a heat integration model was proposed to optimize the heat recovery network. The model could handle process streams with variable flow rates, temperatures as well as phase change. The method was based on pinch analysis method and included a set of max() expressions so as to ensure the maximum heat recovery. The true pinch point was evaluated among candidates \( p, p \in P \) including the inlet temperatures and phase change temperatures of the process streams, which caused corners on the composite curves. With this model, the heat integration can be simultaneously optimized while performing another process optimization.

A case study later on demonstrated the effectiveness and robustness of the proposed models for optimizing a coal gasifier with options of heat integration. The combination of the single objective model and heat integration model were applied accordingly. Providing the minimum heat transfer temperature \( \Delta T_m \) and the exported steam temperature etc., the novel model maximized the overall profit of the gasification process with considerations of products revenue, feed costs, energy usages and steam export. The results of the case study indicated that by assigning part of the sensible heat to preheat the reactants can increase profit up to 40% compared with that only considered steam production from the sensible heat of hot syngas.
5.2 Future work

Development of the proposed ideas in this thesis together with the fruitful research work in the literature have helped us identify many potential areas for improvement and a number of outstanding issues that need to be investigated [59-60]. Some recommendations for future work are as follows.

The equilibrium model for process study is a non-convex problem and thus, it is hard to find the global optimum. The single objective model can easily converged, however, only applicable to the carbon gasification. The future direction will focus on developing a mixed model in which single objective model handles carbon element in the gasification and the equilibrium model process the other elements. Since the rest elements except for carbon account for minority in the gasification feed, the convergence of the non-convex problem would need much less calculations. Therefore, the mixed model possesses advantages holding for both gasification modelling approaches.

Based on the developed gasification and heat integration modelling, the research work can be extended further to an IGCC plant. An IGCC plant consists of three main processing units, a coal gasifier, an air separation unit (ASU) and a combined cycle (CC) power plant. The ASU provides oxygen for the gasification and its by-product, nitrogen, can be used as a dilution gas in the gas turbine. With additional models for ASU and CC plant, the gasification and heat integration models developed from this work can be applied for integrating three processing units, resulting in better energy efficiency. What’s more, more variables involved when combined three units lead to a more complex optimization problem. How to simultaneously optimize three units along with heat integration is challenging but meaningful.
BIBLIOGRAPHY AND REFERENCES


## APPENDIX A

Formulations of enthalpy, entropy and heat capacity of typical coal gasification components

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature (K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (s)</td>
<td>298 - 3000</td>
<td>14.23258</td>
<td>9.64532</td>
<td>-2.12995</td>
<td>0</td>
<td>0</td>
<td>-6.55364</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>100 - 700</td>
<td>31.32234</td>
<td>-20.2353</td>
<td>57.86644</td>
<td>-36.5062</td>
<td>-0.00737</td>
<td>-8.90347</td>
<td>246.7945</td>
</tr>
<tr>
<td></td>
<td>700 - 2000</td>
<td>30.03235</td>
<td>8.772972</td>
<td>-3.98813</td>
<td>0.788313</td>
<td>-0.7416</td>
<td>-11.3247</td>
<td>236.1663</td>
</tr>
<tr>
<td></td>
<td>2000 - 6000</td>
<td>20.91111</td>
<td>10.72071</td>
<td>-2.0205</td>
<td>0.146449</td>
<td>9.245722</td>
<td>5.337651</td>
<td>237.6185</td>
</tr>
<tr>
<td>O₂</td>
<td>100 - 500</td>
<td>28.98641</td>
<td>1.853978</td>
<td>-9.64746</td>
<td>16.63537</td>
<td>0.000117</td>
<td>-8.67191</td>
<td>226.4168</td>
</tr>
<tr>
<td></td>
<td>500 - 2000</td>
<td>19.50583</td>
<td>19.88705</td>
<td>-8.59854</td>
<td>1.369784</td>
<td>0.788313</td>
<td>0.7416</td>
<td>212.39</td>
</tr>
<tr>
<td></td>
<td>2000 - 6000</td>
<td>35.51872</td>
<td>1.128728</td>
<td>-0.1961</td>
<td>0.014662</td>
<td>-4.55376</td>
<td>-250.881</td>
<td>224.981</td>
</tr>
<tr>
<td>H₂O (l)</td>
<td>298 - 500</td>
<td>-203.606</td>
<td>1523.29</td>
<td>-3196.41</td>
<td>2474.455</td>
<td>3.855326</td>
<td>-256.548</td>
<td>-488.7163</td>
</tr>
<tr>
<td></td>
<td>500 - 1700</td>
<td>30.092</td>
<td>6.832514</td>
<td>6.793435</td>
<td>-2.53448</td>
<td>0.082139</td>
<td>-250.881</td>
<td>223.3967</td>
</tr>
<tr>
<td></td>
<td>1700 - 6000</td>
<td>41.96426</td>
<td>8.622053</td>
<td>-1.49978</td>
<td>0.098119</td>
<td>-11.1576</td>
<td>-272.18</td>
<td>219.7809</td>
</tr>
<tr>
<td>CH₄</td>
<td>298 - 1300</td>
<td>-0.703029</td>
<td>108.4773</td>
<td>-42.5216</td>
<td>5.862788</td>
<td>0.678565</td>
<td>-76.8438</td>
<td>158.7163</td>
</tr>
<tr>
<td></td>
<td>1300 - 6000</td>
<td>85.81217</td>
<td>11.26467</td>
<td>-2.11415</td>
<td>0.13819</td>
<td>-26.4222</td>
<td>-153.533</td>
<td>224.4143</td>
</tr>
<tr>
<td>H₂</td>
<td>298 - 1000</td>
<td>33.066178</td>
<td>-11.3634</td>
<td>11.43282</td>
<td>-2.77287</td>
<td>-0.15856</td>
<td>-9.9808</td>
<td>172.70797</td>
</tr>
<tr>
<td></td>
<td>1000 - 2500</td>
<td>18.563083</td>
<td>12.25736</td>
<td>-2.85979</td>
<td>0.268238</td>
<td>1.97799</td>
<td>-1.14744</td>
<td>156.28813</td>
</tr>
<tr>
<td></td>
<td>2500 - 6000</td>
<td>43.41356</td>
<td>-4.29308</td>
<td>1.272428</td>
<td>-0.09688</td>
<td>-20.5339</td>
<td>-38.5152</td>
<td>162.08135</td>
</tr>
<tr>
<td>CO</td>
<td>298 - 1300</td>
<td>25.56759</td>
<td>6.09613</td>
<td>4.054656</td>
<td>-2.6713</td>
<td>0.131021</td>
<td>-118.009</td>
<td>227.3665</td>
</tr>
<tr>
<td></td>
<td>1300 - 6000</td>
<td>35.1507</td>
<td>1.300095</td>
<td>-0.20592</td>
<td>0.01355</td>
<td>-3.28278</td>
<td>-127.838</td>
<td>231.712</td>
</tr>
<tr>
<td>CO₂</td>
<td>298 - 1200</td>
<td>24.99735</td>
<td>55.18696</td>
<td>-33.6914</td>
<td>7.948387</td>
<td>-0.13664</td>
<td>-403.608</td>
<td>228.2431</td>
</tr>
<tr>
<td></td>
<td>1200 - 6000</td>
<td>58.16639</td>
<td>2.720074</td>
<td>-0.49229</td>
<td>0.038844</td>
<td>-6.44729</td>
<td>-425.919</td>
<td>263.6125</td>
</tr>
</tbody>
</table>
\[ C_p^0 = A + Bt + Ct^2 + Dt^3 + Et^2 \]
\[ H^0 = At + Bt^2/2 + Ct^3/3 + Dt^4/4 - E/t + F^2 \]
\[ S^0 = A*\ln(t) + Bt + Ct^2/2 + Dt^3/3 - E/(2t^2) + G \]

- \( C_p \) = heat capacity (J/mol*K)
- \( H^0 \) = standard enthalpy (kJ/mol)
- \( S^0 \) = standard entropy (J/mol*K)
- \( t \) = temperature (K) \( \div 1000 \)
APPENDIX B

Publications


