Sustainable Steelmaking by Process Integration

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Doctor of Technology Thesis
Thermal and Flow Engineering Laboratory
Department of Chemical Engineering
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To my parents, Marzieh & Reza
with love and gratitude

"We cannot hope to create a sustainable culture with any but sustainable souls."
Derrick Jensen

PREFACE

The work presented in this thesis is a result of my experience in Thermal and Flow Engineering Laboratory at Åbo Akademi University. The work was funded by Fortum Foundation, the Metals Association's Foundation of Finland, and by the Academy of Finland within the GreenSteel and SYMBIOSIS projects. This financial support is gratefully acknowledged.

I would like to express my deepest gratitude to my supervisor, Professor Henrik Saxén, for the opportunity to work in this interesting project. I am extremely grateful for all the guidance and ideas he has given me during all these years.

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Finally, I am very grateful to my family and friends for being constant sources of love, inner peace, and support throughout my life.

Hamid Ghanbari
Turku/Åbo, March 2014

SAMMANFATTNING

Miljöfrågor, inklusive global uppvärmning, är en allvarlig utmaning som har uppmärksammats över hela världen och dessa frågor har blivit speciellt viktiga för järn- och ståltillverkare under de senaste årtiondena. Många anläggningar har lagts ner i utvecklade länder på grund av miljölagstiftning och för att minska skadliga utsläpp. Samtidigt har ett stort antal produktionsanläggningar etablerats i utvecklingsländerna vilket har förändrat järn- och stålekonomin radikalt.

”Hållbar utveckling” är ett begrepp som idag påverkar ekonomisk tillväxt, miljöskydd och sociala attityder och därigenom grunderna för framtida ekosystem. En hållbar utveckling innebär att man försöker bevara naturresurser, återvinna och återanvända material, minska föroreningar, men ändå öka avkastningen och lönsamheten. För att finna hållbara processtekniska lösningar måste flera olika alternativ undersökas, men traditionell ingenjörsteknik kan inte effektivt möta dessa utmaningar. Ett systematiskt verktyg behövs för att underlätta beslutsfattande på basis av en övergripande analys av systemet, där man studerar flaskhalsar och utreder möjliga förändringar som slutligen kan leda till en optimal design och funktion hos systemet.

Sedan åttiotalet har forskare gjort stora framsteg vid utvecklandet av verktyg för vad som idag benämnes processintegrering. Avancerad matematik har använts i simuleringsmodeller för att utvärdera alternativ där olika fysikaliska, ekonomiska och miljömässiga begränsningar har beaktats. Förbättringar i råmaterialegenskaper och -hantering, en konkurrensutsatt marknad, miljöbegränsningar och nordiska stålverks roll som energiproducenter (elektricitet och fjärrvärme) är viktiga motiv för en studie baserad på processintegrering, där utveckling i riktning mot ökad energieffektivitet och minskad miljöpåverkan, dvs. en mer hållbar drift eftersträvas.

I avhandlingen utvärderades framtida utvecklingsmöjligheter för stålframställning med avseende på hållbarhet genom simulering och optimering, med den finska stålsektorn som referens. Forskningen inleddes med en undersökning av möjligheterna att öka energieffektiviteten och minska koldioxidutsläppen genom integrering av stålverket med kemiska anläggningar för bättre utnyttjande av processgaser som uppstår i systemet. Dessa gaser, som kommer från masugnen, konvertrarna och koksverket, består i huvudsak av kolmonoxid, koldioxid, väte, kväve och även metan. De har relativt lågt värmevärde och används för närvarande endast som bränsle inom stålverkets gränser.

Ickelinjära optimeringstekniker användes för att utvärdera en integration av stålverket med en metanolanläggning utnyttjande ny masugnsteknologi (med toppgasåterföring) samt genom att ersätta koks med andra reduktionsmedel, såsom olja, naturgas och biomassa. Tekniska aspekter i anknytning till integreringen och förändringarnas inverkan på masugnsprocessen studerades genom att minimera en ekonomisk målfunktion, där driftkostnader (men inga investeringskostnader) beaktades.

I det fortsatta arbetet modellerades ett system för s.k. polygenerering ("polygeneration system") genom att med en superstruktur beskriva alternativa vägar för behandling och utnyttjande av processgaser för att samtidigt producera elektricitet, fjärrvärme och metanol. Huvudalternativen som beaktades i superstrukturen var vakuumtrycksvängande adsorption, membranteknologi och kemisk absorption för gasseparering, partiell oxidering, metanförgasning genom reformering med koldioxid eller vattenånga, samt gas- och vätskeformig metanolsyntes.

På grund av en hög grad av integration i processyntesen valdes att för optimeringen representera systemet i ekvationsorienterad form. Detta utgör en effektiv strategi i jämförelse med tidigare utnyttjade sekventiella modeller för processanalys. Ett blandat heltals-ickelinjärt problem formulerades och löstes för att studera beteendet hos det integrerade systemet under olika ekonomiska och miljömässiga scenarier.

Nettonuvärdet ("Net Present Value") och det specifika koldioxidutsläppet användes som kriterier för att jämföra ekonomiska och miljömässiga aspekter hos det integrerade systemet för olika alternativa bränslen/reduktionsmedel, implementering av framtida masugnsteknologier och koldioxidutsläppsavgifter. I arbetet gjordes även en känslighetsanalys, en kartläggning av kolfördelningen i systemet samt en utvärdering av inverkan av yttre säsongsberoende energikrav.

Det optimeringsverktyg som utvecklades kan bidra med värdefull information om teknologiska, miljömässiga och ekonomiska aspekter för beslutsfattande och kan användas av ingenjörer och forskare för att uppskatta optimala processvillkor i nuvarande och framtida stålverk under olika scenarier. Arbetets resultat visar att det är möjligt att i framtiden utveckla stålframställningen i en hållbar riktning genom processintegration.

ABSTRACT

Environmental issues, including global warming, have been serious challenges realized worldwide, and they have become particularly important for the iron and steel manufacturers during the last decades. Many sites has been shut down in developed countries due to environmental regulation and pollution prevention while a large number of production plants have been established in developing countries which has changed the economy of this business.

Sustainable development is a concept, which today affects economic growth, environmental protection, and social progress in setting up the basis for future ecosystem. A sustainable headway may attempt to preserve natural resources, recycle and reuse materials, prevent pollution, enhance yield and increase profitability. To achieve these objectives numerous alternatives should be examined in the sustainable process design. Conventional engineering work cannot address all of these substitutes effectively and efficiently to find an optimal route of processing. A systematic framework is needed as a tool to guide designers to make decisions based on overall concepts of the system, identifying the key bottlenecks and opportunities, which lead to an optimal design and operation of the systems.

Since the 1980s, researchers have made big efforts to develop tools for what today is referred to as *Process Integration*. Advanced mathematics has been used in simulation models to evaluate various available alternatives considering physical, economic and environmental constraints.

Improvements on feed material and operation, competitive energy market, environmental restrictions and the role of Nordic steelworks as energy supplier (electricity and district heat) make a great motivation behind integration among industries toward more sustainable operation, which could increase the overall energy efficiency and decrease environmental impacts.

In this study, through different steps a model is developed for primary steelmaking, with the Finnish steel sector as a reference, to evaluate future operation concepts of a steelmaking site regarding sustainability. The research started by potential study on increasing energy efficiency and carbon dioxide reduction due to integration of steelworks with chemical plants for possible utilization of available off-gases in the system as chemical products. These off-gases from blast furnace, basic oxygen furnace and coke oven furnace are mainly contained of carbon monoxide, carbon dioxide, hydrogen, nitrogen and partially methane (in coke oven gas) and have proportionally low heating value but are currently used as fuel within these industries.

Nonlinear optimization technique is used to assess integration with methanol plant under novel blast furnace technologies and (partially) substitution of coal with other reducing agents and fuels such as heavy oil, natural gas and biomass in the system. Technical aspect of integration and its effect on blast furnace operation regardless of

capital expenditure of new operational units are studied to evaluate feasibility of the idea behind the research.

Later on the concept of polygeneration system added and a superstructure generated with alternative routes for off-gases pretreatment and further utilization on a polygeneration system producing electricity, district heat and methanol.

(Vacuum) pressure swing adsorption, membrane technology and chemical absorption for gas separation; partial oxidation, carbon dioxide and steam methane reforming for methane gasification; gas and liquid phase methanol synthesis are the main alternative process units considered in the superstructure.

Due to high degree of integration in process synthesis, and optimization techniques, equation oriented modeling is chosen as an alternative and effective strategy to previous sequential modelling for process analysis to investigate suggested superstructure. A mixed integer nonlinear programming is developed to study behavior of the integrated system under different economic and environmental scenarios.

Net present value and specific carbon dioxide emission is taken to compare economic and environmental aspects of integrated system respectively for different fuel systems, alternative blast furnace reductants, implementation of new blast furnace technologies, and carbon dioxide emission penalties. Sensitivity analysis, carbon distribution and the effect of external seasonal energy demand is investigated with different optimization techniques.

This tool can provide useful information concerning techno-environmental and economic aspects for decision-making and estimate optimal operational condition of current and future primary steelmaking under alternative scenarios. The results of the work have demonstrated that it is possible in the future to develop steelmaking towards more sustainable operation.

APPENDED PAPERS

The present thesis is based on work reported in the following seven appended papers:

I. **Ghanbari, H.,** Helle, M., Pettersson, F., Saxén, H., ***"Optimization Study of Steelmaking under Novel Blast Furnace Operation Combined with Methanol Production"***, Industrial & Engineering Chemistry Research, 2011, 50(21), 12103-12112.

II. **Ghanbari, H.**, Helle, M., Saxén, H., ***"Process Integration of Steelmaking and Methanol Production for Suppressing CO_2 Emissions-A Study of Different Auxiliary Fuels"***, Chemical Engineering and Processing: Process Intensification Journal, 2012, 61:58-68.

III. **Ghanbari, H.,** Helle, M., Pettersson, F., Saxén, H., ***"Steelmaking Integrated with a polygeneration plant for improved Sustainability"***, Chem. Eng. Trans., 2012, 29(2)1033.

IV. **Ghanbari, H.**, Saxén, H., Grossmann, I.E., ***"Optimal Design and Operation of Steel Plant Integrated with a Polygeneration System"***, AICHE J, 2013, 59 (10), 3659-3670.

V. **Ghanbari, H.,** Saxén, H., ***"A Techno-Economic Analysis of Using Residual Top Gases in an Integrated Steel Plant"***, Chem. Eng. Trans., 2013, 35, 169-174.

VI. **Ghanbari, H.**, Pettersson, F., Saxén, H., ***"Optimal Operation Strategy of Integrated Steel Plant by Utilizing Process Top Gases"***, Submitted to Chemical Engineering Research and Design J., 2014.

VII. **Ghanbari, H.**, Pettersson, F., Saxén, H., ***"Sustainable Development of Primary Steelmaking under Novel Blast Furnace Operation and Injection of Different Reducing Agents"***, submitted to Chemical Engineering Science, 2014.

RELATED PUBLICATIONS

I. **Ghanbari, H**., Helle, H., Helle, M., Pettersson, F. and Saxén, H., ***"Sustainable Development of Steelmaking by Optimal Integration of Biomass in the Processes"***, Proceeding of International Symposium on Ironmaking for Sustainable Development, pp. 127-131, 2010, Osaka, Japan.

II. Helle, H., **Ghanbari, H.**, Helle, M., Pettersson, F. and Saxén, H., ***"Optimization of Steel Production Integrated with Methanol Production"***, Proceeding of International Symposium on Ironmaking for Sustainable Development, pp. 76-80, 2010, Osaka, Japan.

III. Helle, H., **Ghanbari, H**., Helle, M., Pettersson, F. and Saxén, H., ***"Analysis of the Economy and Emissions of Blast Furnace Operation with Top Gas Recycling"***, Proceeding of The Iron and Steel Technology Conference and Expedition, PA, USA, 3-6, May 2010.

IV. **Ghanbari, H.**, and Saxén, H. ***"NLP Optimization of Steel and Methanol Production in an Integrated Plant"***, Proceeding of Process Integration Forum for the Steel Industry – 3rd Annual Meeting, September 2010, Lulea, Sweden.

V. **Ghanbari, H**., and Saxén, H., ***"Sustainable Steelmaking by Process Integration"***, CAPD Annual Review Meeting Proceeding, March 2011, Pittsburgh, PA, USA.

VI. **Ghanbari, H.,** Helle, M., Pettersson, F., Saxén, H., ***"Optimization of Blast Furnace Steelmaking Process From a Process Integration Perspective"***, Proceeding of 2011 Annual meeting of AIChE, Minneapolis, MN, USA.

VII. **Ghanbari, H.**, Saxén, H., ***"A Strategy for Suppressing Carbon Dioxide from Blast Furnace Steelmaking"***, the 26th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, July 16-19, 2013, Guilin, China.

VIII. **Ghanbari, H.**, Saxén, H., ***"Perspective Scenarios for Sustainable Development in Primary Steelmaking"***, the 1st International Process Integration Forum for the Steel Industry, June 9-10, 2014, Luleå, Sweden.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

1.1 Aim of Research

The aim of this study is to investigate development and operation of primary steelmaking toward sustainability. Process integration techniques have been applied to provide a pre-engineering feasibility study tool by which one can evaluate optimal operation and design of the system, focusing on analysis of three emerging concepts:

- Blast furnace top gas recycling
- Blast oxygen enrichment
- Carbon capturing and utilization

By the development of the model and different optimization techniques through papers I-VII, an economic and environmental analysis illustrate the feasibility and trade-offs for implementation of some of the best available technologies. The analysis also offers useful information for decision-making.

1.2 Appended Papers Overview

Paper I: ***Optimization Study of Steelmaking under Novel Blast Furnace Operation Combined with Methanol Production***

This paper analyzes the economic potential of using large volumes of off-gases in a steel plant to produce methanol as a valuable by-product in steelmaking. *Conventional blast furnace operation was compared with the option of operating the blast furnace with top gas recycling after carbon dioxide stripping integrated with methanol production.* The optimal integration of the processes was investigated by minimizing the cost of liquid steel production, considering the cost of raw materials and fuels, CO_2 emission and stripping, as well as credits for power, district heat and methanol production. A sequential modular approach is used to develop non-linear model (SSPIv.1) for optimization in MATLAB.

Paper II: ***Process Integration of Steelmaking and Methanol Production for Suppressing CO_2 Emissions-A Study of Different Auxiliary Fuels***

This work studies process economics, carbon dioxide emission and energy flows of a future steelmaking site, which is integrated with a polygeneration plant. The system includes primary steelmaking with conventional or novel ironmaking technologies with top gas recycling and CO_2 stripping, a combined heat and power (CHP) plant and a methanol plant. *Oil, natural gas and biomass are considered as both auxiliary reducing agents in the blast furnace and as fuel in the polygeneration system.*

Previous model is modified (SSPIv.1.1) to consider alternatives and flexibility in polygeneration system.

Paper III: ***Steelmaking Integrated with a polygeneration plant for improved Sustainability***

This study investigates process economics and carbon dioxide emissions from an *Oxygen Blast Furnace steelmaking plant.* The effect of (reductant) injections with lower carbon carrier, such as oil, natural gas and biomass on liquid steel production cost and carbon dioxide emission from the plant is investigated.

Using modified model (SSPIv.1.1) further analysis has done on selected process.

Paper IV: ***Optimal Design and Operation of Steel Plant Integrated with a Polygeneration System***

The work of this paper integrates a *primary conventional steelmaking site with a carbon capture and utilization (CCU) plant as superstructure for process synthesis and analysis*. Using short-cut models and empirical equations for different alternatives unit operation topologies and available technologies for gas separation, methane gasification and methanol synthesis, a mixed integer nonlinear model (SSPIv2) in GAMS is applied to find optimal design of the CCU plant and operational conditions of the proposed superstructure. An equation oriented approach has used for modeling and optimization.

Paper V: ***A Techno-Economic Analysis of Using Residual Top Gases in an Integrated Steel Plant***

This paper evaluates the usage of off-gases in a primary steelmaking site integrated with a carbon dioxide capturing unit and a polygeneration plant. *The results of the analysis illustrate the optimal states and technologies under seasonal external energy demands and different fuel supplies in the polygeneration system*. The previous model has modified (SSPIv2.1) to consider top gas recycling and oxygen enrichment.

Paper VI: ***Optimal Operation Strategy of Integrated Steel Plant by Utilizing Process Top Gases***

The paper studies future perspectives of primary steelmaking with the aim to find ways to increase environmental sustainability. *Options studied are covering different scenarios of preheating, recycling and enrichment of off-gases in the system under seasonal external energy demand.* The previous model modified (SSPIv2.2) to cover use of residual gases under periodic optimization technique to minimize internal energy requirement and maximize the NPV.

Paper VII: ***Sustainable Development of Primary Steelmaking under Novel Blast Furnace Operation and Injection of Different Reducing Agents***

In this paper, an overall model (SSPIv2.3) is presented to investigate sustainable development for primary steelmaking plant. It can cover pre-engineering feasibility studies regarding sustainable process design and operation considering most possible scenarios in superstructure. *The model covers states from conventional BF operation to full top gas recycling, blast oxygen enrichment to oxybf operation, integration with CCU processes and different fuel supplies particularly integration with torrefaction process*. By performing different optimization techniques, one can provide useful techno-environmental and economic information for decision-making.

1.3 Co-author Statement

In paper I-III, the basic blast furnace model earlier developed at Thermal and Flow Engineering Laboratory, Åbo Akademi University was modified by the author to implement further utilization of off-gases available in the system (SSPIv1 in MATLAB). In paper IV-VII, author developed a model based on equation-oriented approach for further process synthesis and analysis and implemented in GAMS (SSPIv2).

The study was carried under the advices of the main supervisor and Professor Frank Pettersson, Dr. Mikko Helle and Professor Ignacio Grossman (Paper IV).

The present author, who also made the analysis and compilation of the results, wrote all the articles. Professor Henrik Saxén provided valuable comments on the study, work and papers.

2 SUSTAINABLE DEVELOPMENT

Sustainability is a familiar word, which the general concept is bringing a better life for present and future generations. Global climate change, increasing population, industrialization, and risk to ecosystems has increased the interest in sustainability during the past decades and brought a desire to balancing among economic growth, environmental protection, and social equity referred to as the triple bottom line: people, planet, and profit (El-Halwagi 2012).

Sustainable development has been defined in many ways, but the most frequently quoted definition is from *Our Common Future*, also known as the Brundtland Report: "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland 1987).

2.1 Sustainable Process Design

The process industries have an important role in the sustainability. Designing more sustainable processes is one of the key challenges for sustainable development of the industry. This is a difficult assignment, as it requires interpreting the theoretical principles of sustainable development into design practice considering all three components of sustainability (economic, environmental, social) which increase the number of decision criteria compared to conventional design. This will extend the system boundaries which effects the level of the design and requires identification of relevant sustainability indicators to analyze the trade-offs among different criteria.

The objective of preventing pollution, conserving resources, increasing productivity, and enhancing profitability are among the top priorities of the process industries. Stricter emissions and waste disposal legislations in one side and need for businesses to remain in a highly competitive market (especially emerging in China and India) are some of the reasons for developed countries to drive toward sustainable process design. On the other hand, pollution prevention and social responsibilities make it attractive for developing countries, too. Hence, the manufacturing sectors must be sustainable in order to preserve the high standard of living achieved by industrialized societies and to enable developing societies to achieve the same standard of living sustainably.

Therefore, there is a need to move beyond the traditional 3R open loop life cycle concept promoting green technology (Reduce, Reuse, Recycle) to a more recent 6R closed loop multi life-cycle concept including Reduce, Reuse, Recover, Redesign, Remanufacture and Recycle (Jayal et al. 2010). The evolution of sustainable manufacturing and closed-loop product life-cycle system in 6R approach are shown in Figure 1.

Industrial processes are in the core of supply chains of the products, so promoting sustainability would include not only reduce, reuse and recycle but also focusing on a broader perspective to recover, redesign and remanufacturing industrial products.

Although this is a global and holistic approach, it can give an insight to evaluate different sectors defined as a system.

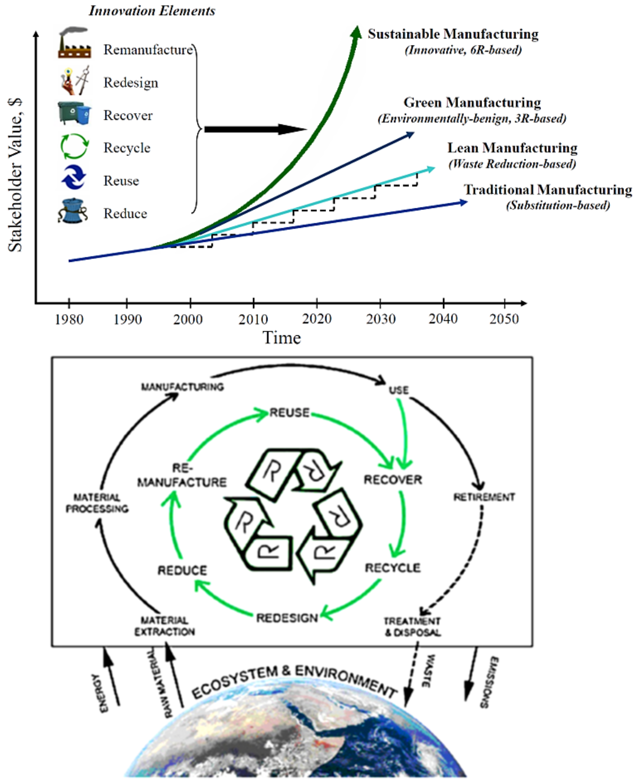

Figure 1 Evolution of sustainable manufacturing and closed-loop product life-cycle system in 6R approach (Jayal et al. 2010).

Key objectives for sustainable process design are (El-Halwagi 2012):

- Resource conservation
- Recycle/reuse
- Pollution prevention
- Profitability enhancement
- Yield improvement
- Capital-productivity increase and debottlenecking
- Quality control, assurance, and enhancement
- Process safety

Considering the complexities involved in sustainability, process integration provides a framework that can effectively apply different techniques to achieve the key objectives for a sustainable design. This approach can help industries to identify potentials and limitations of the whole system and investigate technical insights of process units. On the other hand, it can also deliver useful information for public decision makers.

2.1.1 Process Integration

The process industries are usually a complex network of unit operations connected by material streams and exchange of energy. Improving energy efficiency and technology in one unit may not result in higher efficiency for the whole system. Process Integration (PI) is a holistic approach to process design, where retrofitting, and operation emphasize the unity of the process (El-Halwagi 2012). A sustainable design through the process integration concept may include:

- Task identification: explicitly express the goal as an actionable task.
- Targeting: identification of performance benchmarks ahead of detailed design to determine the potential and opportunities for the process.
- Process synthesis: generate and select alternatives possible solutions to reach the target.
- Process analysis: evaluate the generated alternatives.

A schematic representation of process synthesis and analysis as the two primary pillars for a sustainable process design are depicted in Figure 2 (El-Halwagi 2012).

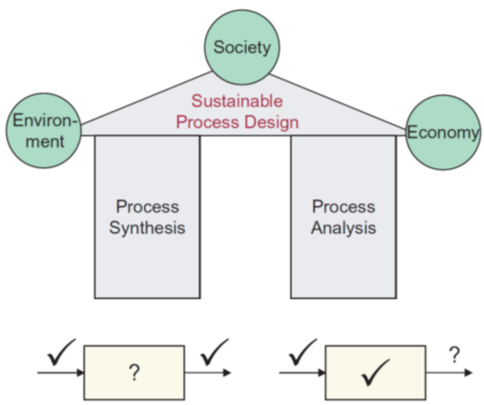

Figure 2 Pillar of sustainable process design (El-Halwagi 2012).

The contributions to this field during past decades can be classified in mass, energy and property integration of a system, which delivers a systematic methodology providing fundamental understanding of distribution of mass and energy and operation of the process units.

2.2 Advances in Process Integration

Process integration supporting process design, integration and optimization have been around more than four decades. Numerous studies have used different aspect of process integration from research and development to industrial implementation (Grossmann, Guillén-Gosálbez 2010, Klemes 2013). The concept of process integration was mainly started by pinch analysis (heat integration) that initially was a graphical approach using thermodynamics insights of the process to find the bottleneck in heat recovery of a heat exchanger network (Linnhoff, Hindmarsh 1983, Linnhoff et al. 1994, Klemes, Varbanov & Kravanja 2013).

Progress in Information Technology (IT) gave new opportunities to exploit process integration and its application in the use of advanced mathematical techniques and computer programming. Mathematical programming, despite the difficulties in effective problem formulation and solution strategies, has been broadly used in different area of research and development known as Process System Engineering (PSE), (Biegler, Grossmann & Westerberg 1997, Grossmann, Guillén-Gosálbez 2010). Mathematical programming applies different optimization techniques to find an optimal solution as a trade-off among economic, environmental and social footprint and indexes. It simultaneously presents the optimality for several interactive subsystems (topologies) such as reaction paths, separations, and auxiliary operations to find optimal property of the system.

Mathematical programming has been used in Supply Chain Management (SCM) and Process Synthesis (PS), which can be expanded to Enterprise Wise Optimization (EWO) problems to reduce the environmental impact of a process over its entire life cycle. It involves optimizing the operations of supply, manufacturing and distribution activities of a company to reduce costs and inventories with a major focus on the optimal operation of manufacturing facilities (Grossmann 2005).

2.2.1 Mathematical Programming Techniques

Sustainable design processes often involve mixed integer optimization, which in the case of nonlinear models gives rise to Mixed Integer Nonlinear Programming (MINLP) problems (Floudas 1995). It applies discrete variables to model assignments and sequencing decisions, and continuous variables to model mass and energy flows and operating conditions.

There are several approaches to solve MINLP optimization problems such as the Branch and Bound (BB), Outer Approximation (OA), Generalized Bender Decomposition (GBD), Extended Cutting Planes (ECP), and Linear/Non-linear Programming (LP/NLP) based branch and bound (Burer, Letchford 2012, Ambrosio, Lodi 2013).

These methods have been developed to become more effective over the years, but there are still limitations in solving problems bigger than few hundreds of integer variables and thousands of continuous variables and constraints.

General Algebraic Modelling System (GAMS) is widely used as modelling system for mathematical programming and optimization (GAMS Development Corporation 2014). It offers multiple solution methods through different solvers such as DICOPT (Viswanathan, Grossmann 1990), SBB (Belotti et al. 2009) and BARON (Sahinidis 1996) which have been used in this study.

General Disjunctive Programming (GDP) is also developed as a modelling technique in terms of Boolean and continuous variables that are involved in constraints in the form of equations, disjunctions and logic propositions (Grossmann 2002). It simplifies the modelling of discrete/continuous problems. Additionally, the logic-base outer approximation for nonlinear GDP problems has the important feature of generating NLP sub-problems where redundant equations and constraints of non-existing units are not included, which improves the robustness of optimization. On the other hand, LOGMIP (Vecchietti, Grossmann 1997) is the only GDP solver and there are challenges to obtain the global optimum solution (Lee, Grossmann 2001). The modeling and optimization of generalized disjunctive programs seem to hold good promise for process synthesis and enterprise-wide optimization problems (Grossmann, Guillén-Gosálbez 2010).

Multi-Objective Optimization (MOO) is a technique by which several conflicting objectives can be simultaneously optimized. In sustainable process design, MOO has often been applied to include environmental aspects as decision-making objectives. There are three approaches to multi-objective optimization:

- Transforming the problem into a single objective optimization
- Non-Pareto approach that use search operators based in the objectives to be optimized
- Pareto approaches that directly apply the concept of dominance

It is important to point out that the methods in process integration can be coupled with single objective MOO approaches such as the epsilon constraint method used in this work (Bhaskar, Gupta & Ray 2000).

A review of software tools in the area of process integration, modelling and optimization in different categories of process integration and retrofit analysis tools; general mathematical modelling using optimization libraries, flow-sheeting simulation and graph-based process optimization tools can be found in (Lam et al. 2011).

3 ADVANCES IN CONVENTIONAL STEELMAKING PROCESS

3.1 Overview

Global crude steel production has been increasing over the years as an essential indicator of development in the world. In 2013, more than 1.5 billion tons of steel were manufactured with China responsible for approximately half of this production. There will be continuing growth in the volume of steel produced, particularly in developing areas such as Latin America, Asia, Africa, and the Indian sub-continent, where steel will be vital in raising the welfare of the developing societies (World Steel Association 2013b).

There are currently four routes available for steel production worldwide (Remus et al. 2013). These routes are shown in Figure 3:

- Blast Furnace/Basic Oxygen Furnace (BF-BOF)
- Electric Arc Furnace (EAF)
- Direct Reduction (DR)
- Smelting Reduction (SR)

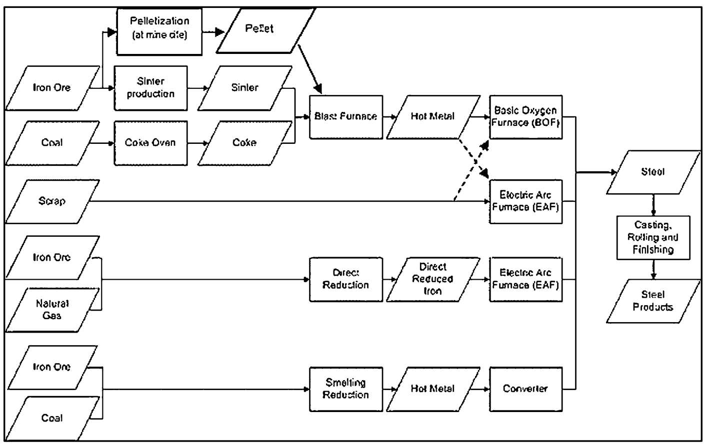

Figure 3 Flow diagram of steel production routes (Hasanbeigi, Arens & Price 2014).

Traditional steelmaking is known as an energy intensive sector and a remarkable source of carbon dioxide emissions among primary industries and it is responsible for more than 65 percent of the steel manufactured worldwide. Electric arc furnace as the second most common steelmaking route accounted for approximately 30 percent of steel production (World Steel Association 2013a). This route is primarily based on scrap, i.e., recycled steel.

In this study, we focus on the BF-BOF route and in this section briefly introduce alternative ironmaking processes, which are the direct reduction and smelting reduction process. The main motivation behind the DR and SR processes compared to the BF is their lower environmental impacts, such as lower carbon dioxide emission, due to reduction by natural gas. Furthermore, these processed do not need a coke oven plant; they give ride to less dust emission and have a better water treatment. However, the economy and operational condition of these processes are the local challenges to compete with conventional steelmaking (Huitu, Kekkonen & Holappa 2009).

3.1.1 Direct Reduction

Direct reduction involves reduction of oxygen from iron ores by using natural gas as reducing agent in a solid-state process. The unit process is carried by shaft furnaces technology such as MIDREX (Klawonn, Siuka 2006) and HYL (Huitu, Kekkonen & Holappa 2009), rotary kilns technology such as the SL/RN Process (Erwee, Pistorius 2012), rotary hearth furnace technology such as Fastmet/Fastmelt (Joyner 2000) and ITmk3 (Tsuge et al. 2002), or fluidized bed reactors technology such as Circofer (Husain, Sneyd & Weber 1997).

3.1.2 Smelting Reduction

An alternative to the BF to produce liquid iron is the smelting reduction process. Like in the DR, there is no longer need of a coke oven plant; hence SR is aimed at using a wide range of coals and iron fines. Smelting reduction has two stages, where firstly iron ore is heated and partially reduced by gases generated in the smelter. In the second stage, the smelter, further iron reduction takes place in liquid state in contact with coal and oxygen. The FINEX process (Eberle et al. 1999), an improved version of the COREX process (Wieder et al. 2009), are the main SR technologies and HISARNA technology has developed under ULCOS programme.

3.2 Conventional Steelmaking

Conventional BF-BOF steelmaking (Figure 4) ranks foremost amongst all the steelmaking processes mainly due to cost, energy efficiency, and high production rate as well as the high degree of heat utilization (Biswas 1981).

This primary steelmaking process is well established and has already evolved to a mature state. Therefore, it is difficult to reduce substantially the energy demand and the emissions especially in the blast furnace, which operates very close to its theoretical minimum in terms of reductants and energy as it has approached its physical limits with respect to energy efficiency (Lungen, Schmöle 2004, Xu, Cang 2010).

In the following section, short descriptions of each process units, formulation and advances in technologies have been provided. In the present work, some of process models for the steelmaking units are simplified linear equations based on historical data from a Finnish steel works. Based on data available for each unit process, efficiency factors and parameters considered for energy recovery and emission.

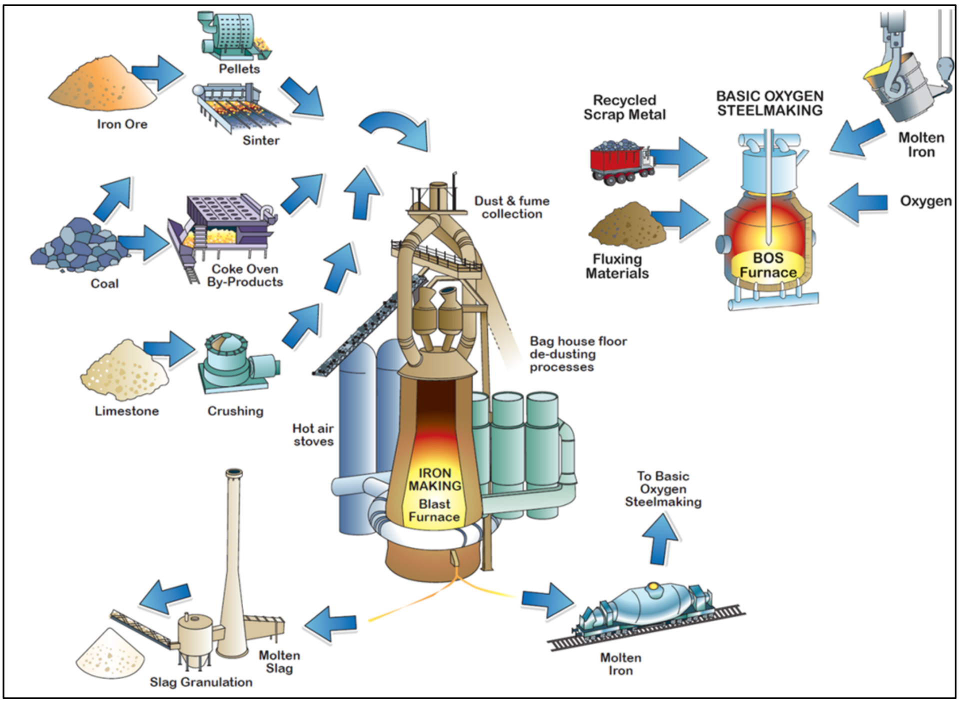

Figure 4 Conventional steelmaking process (Steel Stewardship Forum 2014).

3.2.1 Process Descriptions

3.2.1.1 Sinter Plant

One of the first processes involved in primary steelmaking is the sinter plant (SP), which converts a raw material mixture, with iron oxides as main constituent, into agglomerated particulate form, sinter, which is fed to the blast furnace. A bed of sinter feed mix travels under an ignition hood where hot combustion gases ignite coke blended into the sinter mix to start the sintering process, which is maintained by sucking large volumes of air through the bed from below. Therefore, the process is a source of CO_2 emissions (around 12% of integrated steelmaking) that can be estimated from mass balance of the sinter plant (Ghosh, Chatterjee 2008).

There are potential energy mitigation options for sintering operations. Recovery of heat from the sinter plant can be used to preheat the combustion air for the burners and to produce high-pressure steam. Various systems exist for new plants such as Lurgi emission optimized sintering process. A retrofitted plant in The Netherland has been estimated to have 0.55 GJ per ton sinter fuel saving. A Japanese plant has reported recovery up to 0.25 GJ per ton sinter heat using a waste heat boiler by generating steam. An emission optimized sintering process developed by Outotec company is reported to reduce the off-gas volume by up to 60% through housing the entire sinter strand, recirculating off-gases, and using its carbon monoxide content as an energy source. Reducing air leakage decreases fan power up to 0.014 GJ per ton sinter. Increasing bed depth can lower fuel consumption, improve product quality, and increase productivity slightly. Improving process control, use of waste fuels, improving charging method, improved ignition oven efficiency are also available potentials to increase energy efficiency in sinter plants (EPA 2012, Remus et al. 2013).

In this work, it is assumed that sintering process is fed by only iron ore, coke and limestone as raw materials, given as a function of the produced sinter with constant percentage of heat recovery for a continuous process. In the steelmaking plant studied, the sintermaking capacity was limited, so external iron-bearing materials may be needed in order to reach the desire steel production rate (Helle, Helle & Saxén 2011).
Pellets from an external producer are used, if required, in the system in the range of 0-600 kg/t_{hm}. High pellet to sinter ratio is effective for gas distribution and BF burden operation, which can increase productivity and decrease fuel rate (Eklund et al. 2009, Gupta et al. 2010). 100% pellets charging makes the sinter plant obsolete in conventional steelmaking (Mitra 2011). Charging imported pellet in BF is also reduce amount of emission from the integrated system due to reduce or cut the emission from sinter plant.

3.2.1.2 Coke Plant

In the Coking Plant (CP) operation, coal is dry-distilled to coke, which is a strong particulate matter of low reactivity at moderate temperatures suitable as a feed to the blast furnace. Cokemaking products are coke, Coke Oven Gas (COG), tar and residual fuel oil. The main part of the coke goes to the blast furnace, while a smaller amount of coke breeze goes to the sinter plant (Ghosh, Chatterjee 2008).

COG as a byproduct of the coking plant is a hydrogen-rich gas and appoint of high interest to enhance energy efficiency and reduce Green House Gas (GHG) emissions (Wang et al. 2008). It can be used as fuel in different processes in steelmaking such as coke oven, in reheating furnaces, as reducing agents in the BF (Richlen 2000), in power plants (Modesto, Nebra 2009) or feedstock to other chemical and metallurgical plants such as methanol (Arvola et al. 2011, Bermúdez et al. 2013, Guo et al. 2013b) and DRI (Johansson, Söderström 2011) production. The waste heat from the COG can also be used to dry the coal used for cokemaking, which may reduce the fuel consumption up to 0.3 GJ/t.

The following is some of the potential energy saving options, which has been studied: programmed heating may reduce fuel consumption by 10 percent (EPA 2012). Coke dry quenching (Bisio, Rubatto 2000) can increase the energy efficiency by recovery of steam up to 0.55 GJ per ton coke. In Nippon Steel, it was reported to reduce the amount of coke consumption in the blast furnace by 0.28 GJ per ton molten iron. Single chamber system coking reactors (Hein, Kaiswe 2012) may improve thermal efficiency up to 70 percent (EPA 2012) in comparison with multi-chamber reactors (Hasanbeigi, Price & Arens 2013).

From the modeling perspective, a linear relation between the mass flow rate of feed coal and the volume flow rate of purified COG with the mass flow rate of the coke is assumed in the present work. For practical reasons the capacity of the coke production was considered to be fixed at an upper limit (55 t/h), so any deficit/excess of coke (after the requirement of the sinter plant and blast furnace) will be bought/sold (Helle, Helle & Saxén 2011). COG was considered to distribute between the polygeneration system and as reducing agent in blast furnace.

3.2.1.3 Blast Furnace

Figure 5 shows the evolution of hot metal production in the blast furnaces reporting to the European Blast Furnace Committee (EBFC) since 1990. It shows that the average production per blast furnace has increased by approximately 48% while the average working volume of the furnace increased only by 26.6 percent. This demonstrates that apart from the enlargement of the furnaces also the measures to increase furnace productivity enabled the required hot metal production with fewer furnaces (Luengen, Peters & Schmöle 2012).

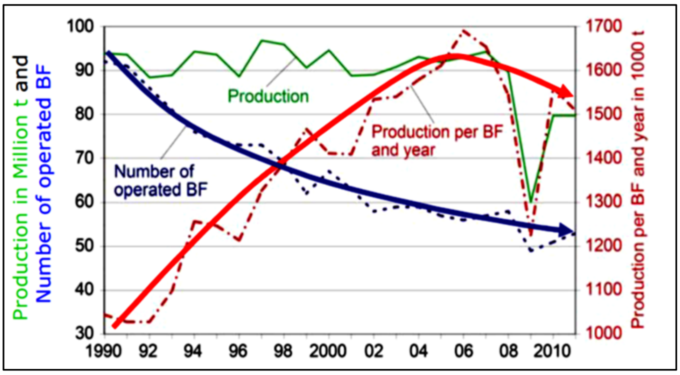

Figure 5 Evolution of hot metal production in the EBFC (Luengen, Peters & Schmöle 2012).

The blast furnace as the heart of the steel plant acts as a large shaft-like counter-current heat exchanger and chemical reactor, where the agglomerated iron-bearing burden is charged with coke in alternate layers. The combustion of coke, which is maintained by the supply of preheated air (blast), provides CO to reduce iron oxides to iron and provides energy to heat and melt the iron and impurities. The molten iron and the by-product, slag, are tapped intermittently through tap-holes from the lower furnace, while the top gas leaves the furnace top through uptakes.

The main improvement in the BF operation is regarding reducing agents and top gases utilization, which is presented in subsection 3.2.2 and in section 4, respectively. Other potential energy mitigation options for the blast furnace are charging carbon composite agglomerates, application of top pressure recovery turbines, improvement of blast furnace control system (up to 0.4 GJ/t_{hm}) and slag heat recovery (up to 0.35 GJ/t_{hm}) (EPA 2012).

The blast furnace process has been extensively studied and numerous attempts have been made to model the BF process, including the following:

1) Mathematical models such as Discreet Element Method and Computational Fluid Dynamics (Nogami, Chu & Yagi 2005, Ueda et al. 2010, Rocha et al. 2013, Nogami, Kashiwaya & Yamada 2014);
2) Black box models based on data mining methods such as Statistic Algorithms (Chu, Gao 2014), Evolutionary Algorithms (Pettersson, Chakraborti & Saxén 2007, Pettersson, Saxén & Deb 2009), Neural networks (Helle et al. 2006) and Support Vector Machine algorithms (Ghosh, Majumdar 2011); and,
3) Thermodynamic models based on equilibriums (Kulinich 2007, Jak, Hayes 2012, Harvey, Gheribi 2014), mass and energy balance (Helle, Helle & Saxén 2011).

In this study, a thermodynamic first-principles model (Saxén et al. 2001, Pettersson, Saxén & Deb 2009, Helle, Helle & Saxén 2011) which is based on the approach behind the Rist diagram (Rist, Meysson 1967) is used. The process is divided into two main control volumes, with thermal and chemical equilibrium approached on the boundary — the reserve zone — between these. Given blast parameters and specific injection rates of auxiliary reductant, the model calculates the energy input through the tuyeres as well as the raceway adiabatic flame temperature and bosh gas volume. With this information, material and energy balance equations for the lower main control volume (elaboration zone) yield the hot metal production rate and the coke rate, as well as the flow rate and composition of the gas at the thermal/chemical reserve zone, where the temperature and fractional approach to equilibrium are user-specified parameters. Since the upper boundary conditions of the lower zone are identical with the lower boundary conditions of the upper zone, the equations for the upper control volume (preparation zone) next yield the flow rate, temperature and composition of the top gas (Helle, Helle & Saxén 2011).

3.2.1.4 Hot Stoves

Hot stoves (HS), also known as cowpers are used to preheat air (blast) required for combustion of coke in the BF. They work as a counter current regenerative heat exchanger. Low cost and low calorific value residual gases from the BF operation with small amount of other fuels, such as COG or natural gas, are commonly used in the stoves to increase the hot blast temperature up to 1523 K. It is known that the coke consumption decreases by 10-15 kg/t_{hm} with an increase of 100 K in the hot blast temperature (Moon, Kim & Sasaki 2014).

Many BFs have three hot stoves. While two of them are being heated, the blast passes through the regenerative chamber of the third stove on its way to the blast furnace. Hot stove automation can reduce energy consumption by optimal operational condition up to 17 percent. Another potential for energy saving is by heat recovery from flue gases for preheating of air. This concept can reduce fuel consumption by 0.085 GJ/t_{hm} and yield energy savings of up to 0.35 GJ/t_{hm}. Improvement of combustion condition through more efficient burners can lead to energy saving up to 0.04 GJ/t_{hm} (EPA 2012).

In order to reduce overall fuel consumption in industrial heating, oxygen enrichment of combustion air can be very effective. The application of oxygen enrichment in hot stoves will lead to lower fuel rate and increasing hot blast stoves efficiency (Bisio, Bosio & Rubatto 2002, Wang et al. 2011b, Wang et al. 2011a, Sandberg, Wang & Larsson 2013). In this study, an upper bound of 32% enrichment was considered in hot stoves due to physical restriction.

3.2.1.5 Basic Oxygen Furnace

The Basic Oxygen Furnace (BOF) process converts the molten iron from the blast furnace with limestone and up to 30% steel scrap by injecting oxygen at supersonic speed, resulting in oxidation of carbon and impurities, producing liquid crude steel with typically 0.1-0.5 weight-% of carbon. High purity oxygen is blown through the molten bath to lower carbon, silicon, manganese, and phosphorous content of iron, while various fluxes are used to reduce the sulfur and phosphorus level.

BOF can operate either in open-hood or closed-hood vessels. This makes opportunities to recover heat or fuel from off-gases, which is rich in CO. Closed-hood BOF offers the best potential for both. This technology has been extensively implemented in Western Europe and Japan. This technology would reduce unavoidable CO_2 generation up to 0.16 ton per ton liquid steel, resulting in energy saving in the range of 0.53-0.92 GJ/ton liquid steel. On the other hand, due to batch processing, the volume of off-gases varies widely so installing variable-speed drives on ventilation fans can reduce the energy consumption. Improvement of process control and optimal operation of ladle heating may be other potentials to improve efficiency. At the Burns Harbor steelmaking facility, these modifications reduced energy use at the BOF by 50% and reduced operation and maintenance expenses (EPA 2012).

In the present work, a general mass balance is used based on known hot metal flow rate, considering constant composition of top gases (mainly CO and CO_2) and 50% of the arising gases were assumed to be recovered. For the sake of simplicity, the feed of scrap was assumed to be one fourth of the mass of hot metal in the feed (Helle, Helle & Saxén 2011).

3.2.1.6 Air Separation Unit

In the system, there is a large demand for oxygen to inject in the BF (either as oxygen-enriched blast or as cold pure oxygen) as well as in the BOF. Cryogenic air separation (ASU) is the most efficient way to produce high volumes of oxygen, but it is an energy intensive process. The carbon dioxide emission from the air separation unit is estimated from energy required and available fuel in polygeneration system (Castle 2002).

3.2.2 Reducing Agents Injection

Various reducing agents are available as injectants in the BF. Carbon/hydrogen/ hydrocarbons in the form of granular or pulverized coal, heavy fuel oil, oil residues, used oils, fats and emulsions, animal fats, eco-oil, natural gas, coke oven gas, BOF gas, BF gas, waste plastics, coal tar and biomass products are generally available in sufficient quantities at reasonable cost, however varying greatly between different regions. However, the choice among several reducing agents is determined by cost and operation constraints of the blast furnace. Coke, as the main reductant, also serves as a physical carrier of the bulk column in the BF, without which the BF operation would not be possible (Remus et al. 2013).

Figure 6 shows the evolution of the reductant rates as a weighted average for furnaces within the EBFC. Whilst total reductant consumption slightly increased, the coke rate was decreased by increased coal injection rates. The increase in total reductant comes from the replacement ratio of coal to coke below unity, since coal has lower carbon content (Luengen, Peters & Schmöle 2012).

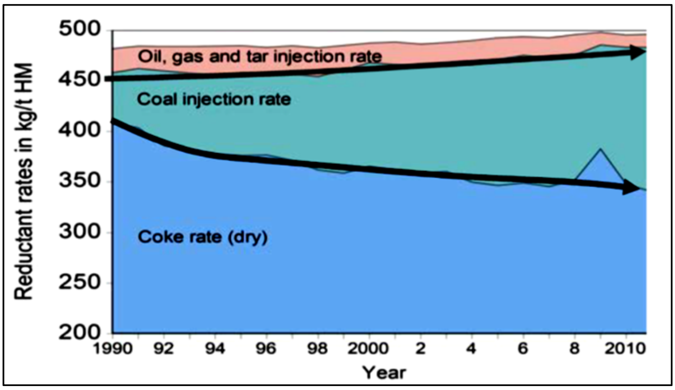

Figure 6 Average weighted reductant rates of the blast furnaces reporting to the EBFC (Luengen, Peters & Schmöle 2012).

3.2.2.1 Coke

Coke is the primary fuel and reducing agents in the BF process. Depending on auxiliary reducing agents used, the coke consumption level is around 350-400 kg/t_{hm} in modern blast furnaces. The metallurgical coke in the blast furnace acts as a reducing agents, energy carrier and support medium for the burden material. By implementation of new concepts of blast furnace operation, the coke consumption may be decreased to 200 kg/t_{hm} (Hooey et al. 2010).

3.2.2.2 Oil Injection

Heavy oil or waste oil has been used as auxiliary reducing agents in the BF to partially replace coke. The main advantage of oil is that it is an effective injectable hydrogen carrying reducing agent, which may lead to reduce CO_2 emissions. During many years, the Finnish steelmaking company Ruukki reported a consumption of about 360 kg/t_{hm} coke and about 100kg/t_{hm} oil (Slaby et al. 2006, Luengen, Peters & Schmöle 2012).

3.2.2.3 Natural Gas Injection

Natural gas injection is an alternative injectant for medium-size furnaces. Its selection depends on the price of natural gas versus coal and its availability. It can be also injected simultaneously with pulverized coal. Increasing the natural gas injection rate may require increased oxygen enrichment to keep the flame temperature and bosh gas volume within bounds.

Along with natural gas injection, the utilization rate of CO is enhanced while that of H_2 decreases. The permeability of blast furnace, H_2 indirect reduction and productivity increases (Guo et al. 2013a). In USA, injection of natural gas up to 155 kg/t_{hm} has been reported (Babich et al. 2002).

3.2.2.4 Pulverized Coal Injection

Pulverized coal is the most used auxiliary reducing agents in the BF process. There is a practical upper limit to the scale of pulverized coal injection, depending on coal types and raw material qualities among other variables. Pulverized coal injection rates above 200 kg/t_{hm} are considered massive and may not be sustained for long periods especially for large furnaces (EPA 2012) even though rates up to 250 kg/t_{hm} have been reported as a monthly average.

3.2.2.5 Off-gases Injection

Large volumes of off-gases from coke plant, blast furnace and basic oxygen furnace (COG/BFG/BOFG) are available in integrated steelmaking. These gases contain mainly CO, CO_2, CH_4, H_2 and N_2, which are used as fuel in the hot stoves, reheating furnaces and power plant. However, the gases also have the potential to be used as reducing agents in BF. This concept has been investigated and implemented in pilot and semi-industrial units (Tseitlin, Lazutkin & Styopin 1994, Zuo, Hirsch 2009). For applying top gas recycling in the BF, a sufficient level of oxygen enrichment is necessary to burn carbon, CO and H_2 in lower part to produce reduction gases at sufficient temperature. By implementation of TGR, the total BF operation fuel consumption is estimated to be around 300 kg/t_{hm} in interchange of top gas utilization unit operation costs (Section 4).

3.2.2.6 Biomass Injection

Biomass as low-carbon or carbon-neutral carrier has been studied to replace fuels in blast furnace. Most of the efforts have been on solid fuel such as Charcoal BioMass (CBM) (Faleiro et al. 2013) and up to 150 kg/t_{hm} has been used in practice in small blast furnaces in Brazil (Babich et al. 2002, Lampreia et al. 2011). The heating value of biomass is low compared to fossil fuels. Thermochemical conversion processes ranging from torrefaction to pyrolysis may enhance the biomass properties to make it useful in the form of solid, liquid and gaseous reducing agents. Some processes may produce valuable byproducts that can be utilized in other chemical and energy sectors (Norgate, Langberg 2009, Suopajärvi, Pongrácz & Fabritius 2013, Suopajärvi, Pongrácz & Fabritius 2014).

Replacement of fossil carbon by renewable biomass-based carbon is an effective measure to mitigate carbon dioxide emission intensity from the blast furnace. Besides the characteristic of the biomass as feasible reductant such as volatile matter and ash contents (Jahanshahi et al. 2014), the availability and economic competitiveness of biomass treatment plays an important role. The possible use of Finnish biomass in the integrated steel plant, particularly as auxiliary reducing agents in the blast furnace, after preprocessing it, decreases the oxygen content and increases the heating value has been investigated (Suopajärvi, Fabritius 2013, Helle 2014, Suopajärvi, Pongrácz & Fabritius 2014).

A key challenge is to develop efficient conversion technology, which can make the product compete with fossil fuels economically, considering the environmental benefit. The availability of large amounts of low temperature gases increases the potential of the torrefaction process, which produces Torrefied BioMass (TBM), compared to higher degree of pyrolysis (e.g., charcoal) (Batidzirai et al. 2013, Saari et al. 2013, Suopajärvi, Pongrácz & Fabritius 2014). The results indicate that based on typical cost of today, biomass products may not be economically competitive compared to fossil fuels (particularly coal). However, introduction of a carbon trading scheme or high carbon tax is expected to increase the motivation and interest in using biomass to partly replace coal in steelmaking (Norgate, Langberg 2009, Fick et al. 2014).

Table 1 shows some properties of reducing agents analyzed in this work. Coke oven gas, heavy oil, natural gas, pulverized coal and biomass products were studied as different reducing agents to be injected in the blast furnace for partial replacement of coke. In the reference plant, up to 17.6 t/h of coke oven gas was assumed to be available according to the coke production limitations. COG, which contains carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen and methane, either can be inject into blast furnace or sent to the polygeneration system. For the sake of simplicity, in the BF all the injectants studied were taken to have an upper limit for the injection rate of 120 kg/t_{hm}.

Table 1 Reducing agents and their composition.

Reducing agents	C	H_2	CH_4	CO	CO_2	N_2	O	HHV (MJ/kg)
PC	73.2	4.7	-	-	-	1	9	29.8
Oil	85.5	11.2	-	-	-	0.8	-	43.1
COG	0	12.3	42.1	17.2	7.8	19.8	-	42.4
NG	1.55	0.35	96.3	-	0.3	1.5	-	54.5
CBM	87.69	3.39	-	-	-	-	9	33.5
TBM	Estimated as f(Temp,time) Ref. PaperVII							

4 CARBON CAPTURING AND UTILIZATION

The considerable contribution of integrated steelmaking to greenhouse gas emissions, particularly of carbon dioxide, has already initiated research and development programs among main iron and steel producers (World Steel Association 2013b, Fu et al. 2014).

Research and development efforts on the conventional BF-BOF steelmaking route have been carried out, e.g., in the Ultra-Low CO_2 Steelmaking (*ULCOS*) programme within EU (Danloy et al. 2009, Zuo, Hirsch 2009), and in the CO_2 Ultimate Reduction in Steelmaking Process by Innovation Technology for Cool Earth 50, which is recognized as the *COURSE50* programme, in Japan (Tonomura 2013, Watakabe et al. 2013).

Carbon dioxide emission reduction methods in conventional steelmaking may be categorized into 1) use of alternative reducing agents such as neutral or low-carbon carriers, and 2) reduction of CO_2 emissions that are inevitable in the process by capturing CO_2 followed by sequestration.

Figure 7 shows a schematic of the blast furnace operation under generalized carbon dioxide emission reduction methods in ULCOS and COURSE50. The main improvement in the technology is recycling CO_2-stripped blast furnace top gases back to the tuyeres. To implement the top gas recycling concept external investment needed to recover and purify the gases, including a capturing unit process and technology for transporting the separated CO_2, utilizing or sequestrating it.

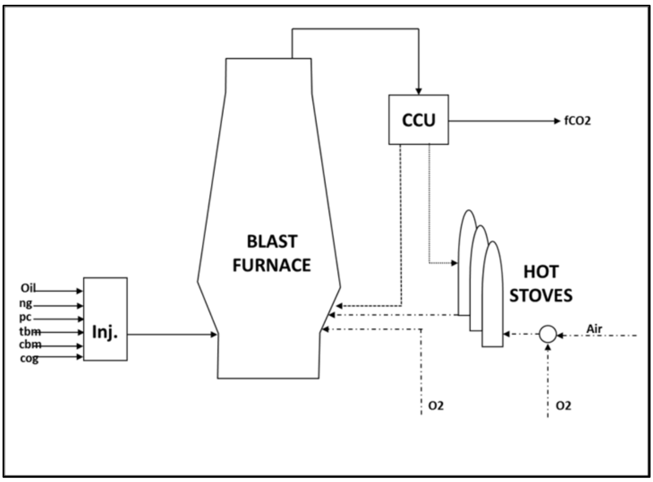

Figure 7 Blast furnace operation under top gas recycling and different reducing agents.

Considerable research has been undertaken in the area of post combustion CO_2 capturing, where exhaust gas from coal or gas-fired power plants is captured and prepared to be sent for geological storage. The most common technologies under development are amine based chemical absorption, pressure swing adsorption and membrane separation (Quintella et al. 2011, Kuramochi et al. 2012, Li et al. 2013).

Off-gases in integrated steel plants have some important differences compared to flue gases from power plants, such as higher CO_2 content, lack of oxygen and different total pressure, which may result in other optimal solutions for off-gas treatment (Oda et al. 2009, Xu, Cang 2010, Kuramochi et al. 2011). These researchers provided comparative case studies for different scenarios of operation. The possibility for further utilization of residual gases in a polygeneration system has been considered by (Liu 2009).

In the present study, the captured CO_2 is assumed to be pressurized and sent out of the system for geological storage (if available) or other emerging options for sequestration such as mineralization to carbonates (Zevenhoven, Fagerlund & Songok 2011).

In the following sections, a brief description of main unit processes available for off-gas utilization in a steel plant integrated with a polygeneration system are presented.

4.1 Unit Processes

Depends on BF operation under different emerging technologies concepts, several gas separation units such as alternative carbon capturing process are considered for off-gas treatment and utilization.

To recover CO and H_2 from the stripped gas streams the most common methods employed are liquefaction, chemical absorption and selective swing adsorption. Liquefaction may not be suitable in the conventional BF operation due to relatively high nitrogen concentration in the blast furnace top gas, as CO and N_2 are very similar in nature, which makes their separation by physical means difficult.

Residual gases can be used for top gas recycling, as fuel in the power plant or to produce chemicals in a chemical plant. COG can be used in the integrated plant either in BF as reductant or in the power plant. Another option would be further separation of COG contaminants to recover methane and to produce syngas through gasification. Syngas, in turn, can be used to produce chemicals such as methanol (Arvola et al. 2011, Bermúdez et al. 2013).

4.1.1 Separation Unit Operations

An integration of carbon dioxide capturing unit with a polygeneration system could be a long-term solution for suppressing CO_2 emissions from steel plants. Already in conventional operation, the blast furnace produces a top gas that contains more than 20 vol-% of carbon monoxide, which could be used to produce high value chemical byproducts, such as methanol. In addition, it contains more than 20 vol-% carbon dioxide, which could be captured and sequestrated.

Figure 8 shows the unit processes for gases treatment from the blast furnace and basic oxygen furnace. Three major units with two different CO, CO_2 and H_2 separation technologies are included.

4.1.1.1 Chemical Absorption

Chemical absorption is a separation technology suited for large volumes of gases. For CO_2 capturing, the development of technology for BF gas has resulted in alternatives with an energy consumption of about 2 GJ/t_{CO2} which is a half of the value required by the conventional chemical CO_2 amine-based solvent process (Hayashi, Mimura 2013).

The CCA process includes gas treatment, CO_2 removal, solvent regeneration, conditioning and compression steps. The lowest consumption of energy per ton carbon dioxide was achieved by combining the 2-amino-2-methyle-1-propanol (AMP) with intercooling (Tobiesen, Svendsen & Mejdell 2007, Hooey et al. 2013).

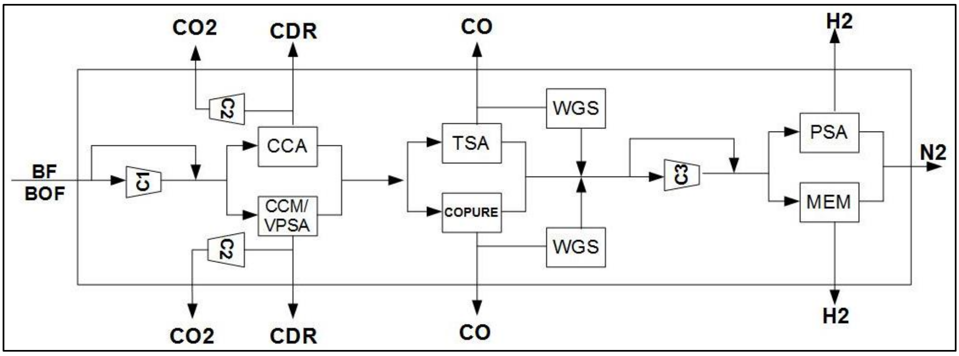

Figure 8 Carbon capturing unit in the superstructure. TSA: Temperature Swing Adsorption, COPURE: Chemical absorption unit, WGS: Water Gas Shift reactor, CCA: CO_2 Chemical Absorption, CCM: CO_2 Capturing membrane, (V)PSA: (Vacuum) Pressure Swing Adsorption, MEM: Membrane separation.

The COPure^{SM} process can be used to apply selective separation of CO from the blast furnace top gas. Low pressure and low temperature operation and noncorrosive solvent make the process economical in terms of capital and operation costs. Reported carbon monoxide recovery and purity exceed 98% and 99%, respectively. The approximate utility requirements, e.g., electrical power, reboiler and cooling duties, steam needed and investment cost used in the present work were provided through private communication with Rockey Costello, R.C. Costello & Assoc., Inc, (Costello 2011).

4.1.1.2 Selective Swing Adsorption

The Vacuum Pressure Swing Adsorption (VPSA) as a technology for CO_2 capturing has been developed and tested in the experimental blast furnace in Lulea, Sweden, under the ULCOS project (Torp 2005, Birat 2009, Danloy et al. 2009).

The Temperature Swing Adsorption (TSA) process may be applied for selective adsorption of CO from gas streams with an adsorbent mass comprising of crystalline zeolite molecular sieves. Pressure is not a critical factor and temperature changes in 273-573 K with a reported CO recovery of 99 %. This process can purify a gas stream containing as little as 10 ppm by volume of carbon monoxide but it is preferred to utilize the process to make bulk separation of CO from gas streams containing at least 5 vol-% (Rabo, Francis & Angell 1977, Roark, White 2004).

An efficient H_2 recovery could be achieved by operating a Pressure Swing Adsorption (PSA) in a high-pressure ratio of the feed over the residue or by a membrane in a high-pressure ratio of the feed over the product, which may result in extra compression costs for both investment and operation (Ruthven, Farooq & Knaebel 1994).

4.1.1.3 Membrane Technology

For CO_2 recovery (CCM), a fixed carrier site membrane with amine groups is suggested to selectively separate CO_2 from the blast furnace top gas. In this process, water in the feed gas is an advantage rather than a problem since the membrane should be humidified during the operation, which makes it a proper choice after sulfur scrubbing of the feedstock. The process is in two stages with low temperature feedstock and carbon dioxide is after compression sent to the pipeline at 110 atm (Lie et al. 2007).

For H_2 recovery, a Prism^{TM} separator system developed by Air Product and Chemical Inc, is chosen. The unit is controlled by pressure and flow adjustment of gas streams. The separator utilizes the principle of selective permeation through a gas permeable membrane that has specially designed hollow fibers. Permeability coefficients of gases through a multicomponent membrane are used to estimate the flow rate and operational pressure of the system (Henis J.M.S., Tripodi 1980, Porter 1990).

4.1.2 Gasification Unit Operations

The composition of the coke oven gas is assumed constant and it contains high amounts of hydrogen and methane, which can be used directly in the BF, polygeneration system or as feedstock to the gas reforming plant.

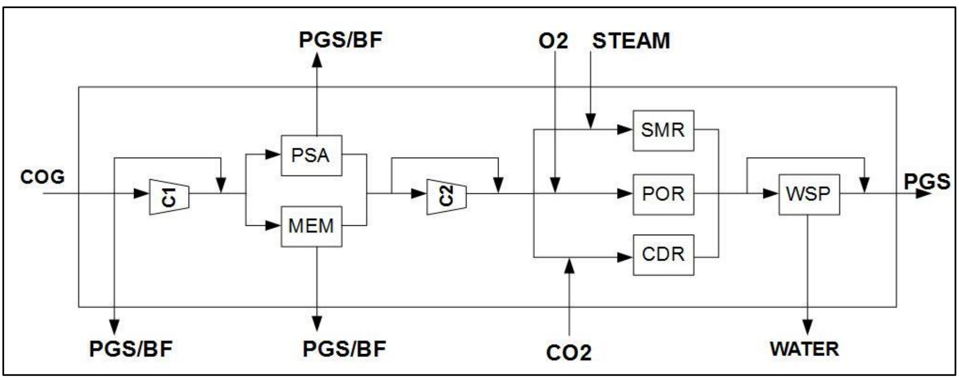

Figure 9 Methane gasification units in superstructure. PSA: Pressure Swing Adsorption, MEM: MEMbrane adsorption, SMR: Steam Methane Reforming, POR: Partial Oxidation Reforming, CDR: Carbon Dioxide Reforming, PGS: PolyGeneration System, WSP: Water Separation unit.

Figure 9 shows the alternative unit processes for the gasification route. Pressure swing adsorption and membrane technologies are used to separate mainly hydrogen from methane and Steam Methane Reforming (SMR), Carbon Dioxide Reforming (CDR) and Partial Oxidation Reforming (POR) technologies are applied for methane gasification to produce more hydrogen.

In the gas reforming units, the optimal values of the critical parameters (temperature, pressure and reactant ratio) have been taken from literature based on standalone processes.

4.1.2.1 Steam Methane Reforming

Production of synthesis gas from methane can be realized through steam methane reforming. This process is highly endothermic, but has low carbon deposition and high H_2/CO ratio, which makes it suitable for methanol synthesis. The steam-methane reaction takes place with the water gas shift reaction

$$CH_4 + H_2O = CO + 3H_2 \quad (1)$$
$$CO + H_2O = CO_2 + H_2 \quad (2)$$

The feedstock to the SMR unit is mixed with saturated steam in a methane-to-steam ratio of 3.681 kmol H_2O/kmol CH_4, and the reaction takes place at 20 bar and 1153-1300 K. The conversion of CH_4 and CO is considered to be $x_{CH_4}^{SMR}$=81.5% and x_{CO}^{SMR}=40.2% (Van Dijk, Solbakken & Rovner 1983). The heat of reaction at typical reformer operating conditions for the steam-methane reaction and water-gas shift reaction are 234.7 kJ/mol and -34.6 kJ/mol, respectively.

4.1.2.2 Carbon Dioxide Reforming

Carbon dioxide reforming (CDR) of methane can be expressed as

$$CO_2 + CH_4 = 2\,CO + 2\,H_2 \quad (3)$$

and has a great potential to be used in chemical industry to gain more environmental benefits by suppressing carbon dioxide emissions. It has been shown that the optimal operating condition would be 1143-1313 K at a pressure of 1 bar, equal ratio of methane to carbon dioxide and the conversion of methane in the reaction is $x_{CH_4}^{CDR}$= 0.90. The heat of reaction has been reported as 247 kJ/mol at 298 K (Wang, Lu & Millar 1996).

4.1.2.3 Partial Oxidation Reforming

The third alternative technology for synthesis gas formation is the exothermic methane partial oxidation reaction with standard heat of reaction of -35.9 kJ/mol and is expressed as

$$CH_4 + 0.5\,O_2 = CO + 2\,H_2 \quad (4)$$

This process shows a high yield of hydrogen, but the oxygen stream makes it costly. It has been determined that by increasing temperature, the selectivity of carbon monoxide and hydrogen increases but pressure has a negative effect on methane conversion and hydrogen production. The investigators (Zhu, Zhang & King 2001) also showed that a CH_4/O_2 ratio of 2, a temperature between 1073-1473 K at 1 bar are ideal conditions for an oxy-reforming reaction to get a high yield of the synthesis gas. The conversion of methane is considered to be $x_{CH_4}^{POR}$= 0.95.

4.1.3 Torrefaction Unit

Biomass as energy source has some characteristics such as potential contaminants that make it a complicated fuel in terms of wide range of resource and waste streams. Furthermore, it has a low volumetric heating value and its moisture content may vary considerably. A key challenge is to develop efficient conversion technology, which can make biomass compete with fossil fuels economically, preserving the benefits regarding environmental aspects. Availability of large volumes of low temperature gases as source of heat increases the potential of the torrefaction process in comparison with a higher degree of pyrolysis. In this study, a torrefaction process, including dryer, torrefaction, cooling and grinding were added to the system to find optimum operational condition for the torrefaction process in this environment (Batidzirai et al. 2013).

Mass and energy yield, *MY* and *EY*, on a dry ash-free basis is represented by correlations as function of temperature and time. The residence time of the torrefaction process considered was between 0.2-1 h and temperature of torrefaction may vary between 200 ℃ and 300 ℃ (Saari et al. 2013). Mass and energy balance for the torrefaction reactor can be estimated from its Moisture Content *(MC)*, High Heat Value (HHV), torrefied biomass composition and energy required for grinding are given as a function of torrefaction temperature (Phanphanich, Mani 2011).

4.1.4 Other Available Units

4.1.4.1 Water-Gas Shift Reactor

Water-gas shift reaction (WGS) is an important industrial reaction that is used in the manufacturing of ammonia, hydrocarbons, methanol, and hydrogen. The WGS reactor is considered to provide a carbon monoxide to hydrogen ratio required for methanol synthesis. It provides a source of hydrogen at the expense of carbon monoxide.

$$CO + H_2O = CO_2 + H_2 \quad (5)$$

It is assumed that the reaction takes place at 473 K with CO conversion greater than 0.9 and heat of reaction of -41.2 kJ/mol (Cheng, Kung 1994).

4.1.4.2 Water Separation Unit

The produced syngas, depending on the gasification units, may pass through heat exchangers to be cooled and then be sent to a water removal column. The operational conditions considered are the blow dew point of water and complete condensation of water occurs. It is assumed that a small amount of carbon particles produced in the syngas generator due to coking are removed with the water, and the dry syngas is sent to the polygeneration plant.

4.2 Polygeneration System

Integrated steel plants in the EU have often an on-site power plant where the process gases, such as BF, BOF and COG are used to produce heat and power. Investigations have shown (Figure 10) that there is high potential of energy saving in these sectors by considering the Best Available Technologies (BATs) and state of the art power plant (Moya, Pardo 2013).

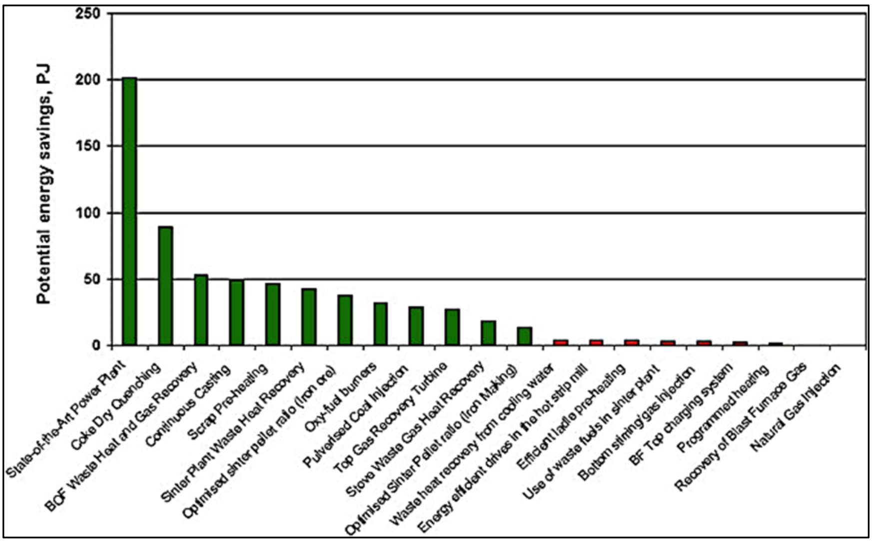

Figure 10 Ranking of the potential energy savings for BATs (Moya, Pardo 2013).

It has been proposed that the primary steelmaking should be integrated with a polygeneration system to solve the problems of utilizing energy efficiency and to reduce emissions. An idea would be to remove carbon dioxide and use the residual gases as feedstock to a polygeneration system to produce district heat, electricity and methanol.

Polygeneration systems are claimed to be more energy efficient than standalone processes, as they have higher flexibility to switch between different forms of energy products depending on regional and seasonal demands. The benefit of liquid methanol in comparison with other forms of energy is its higher volumetric heating value and the fact that it can be stored and used as a substitution for traditional energy carriers or as a feed material for small-to-medium scale chemical industries. Additionally, the steel plant could avoid paying for emission or sequestration of CO_2 by converting the residual carbon to methanol, which extends the life cycle of carbon. However, the energy required for this upgrading must be considered carefully.

There have been several studies on optimal design of polygeneration systems. Liu (Liu 2009) studied a system with different feed-stocks and technologies that coproduce electricity and methanol. Their study showed that conversion rate of technologies, price of feedstock, capital investment and the fixed operating cost have strong influence on the net present value. They also presented a multi-objective mixed-integer nonlinear programming formulation of a typical polygeneration process operating over a time horizon, where both profitability and environmental impacts are considered.

Chen (Chen 2012) proposed a coal and biomass polygeneration system to produce power, liquid fuels and chemicals under different economic scenarios using nonlinear programming. They also performed a simultaneous optimization, analyzing the design and the operational decision variables. The results showed that higher net present values could be obtained with increasing operational flexibility.

4.2.1 Methanol Unit Operations

All the syngas from gas utilization units is distributed and used in the polygeneration system to produce methanol, electricity and district heat. Methanol can be produced via two different technologies:

- Gas Phase Methanol (GPMEOH),
- Liquid Phase Methanol (LPMEOH)

In the GPMEOH production, methanol is synthesized in a gas phase reaction over a heterogeneous catalyst from a synthesis gas that consists primarily of hydrogen, carbon monoxide and carbon dioxide. Newer processes focus on the use of CO-rich synthesis gas instead of H_2-rich synthesis gas, thereby utilizing cheaper synthesis gas for the production of methanol. One of the promising technologies utilizing CO-rich synthesis gas is the LPMEOH synthesis process, but the single pass conversion of syngas in the LP reactor is still limited (Vaswani 2000).

Figure 11 shows the methanol production and purification route considered in this study. Main reactions take place in the synthesis of methanol are

$$CO + 2\,H_2 = CH_3OH \quad (6)$$
$$CO_2 + 3\,H_2 = CH_3OH + H_2O \quad (7)$$
$$2CO + 4H_2 = C_2H_6O + H_2O \quad (8)$$

The heat of reaction for the first and the second reaction at standard temperature and pressure are -90.79 kJ/mol and -49.50 kJ/mol, respectively. In addition, the third reaction takes place as a side reaction in the GP, producing dimethyl ether (DME) to a limited extent with a reaction heat of -204.94 kJ/mol at standard conditions.

In the GP reactor carbon monoxide, carbon dioxide and hydrogen are catalytically converted to methanol and dimethyl ether. Typical operating conditions are 50 atm and 533 K and all reactions are exothermic and the excess heat must be removed to maintain optimum operational conditions. The conversion is dependent on temperature, pressure, hydrogen to carbon monoxide ratio, space velocity, catalyst composition and carbon dioxide content.

The overall conversion of the carbon monoxide and carbon dioxide in the syngas to methanol is typically 0.95 and methane and nitrogen are considered as inert. The amount of dimethyl ether produced is 2 wt-% of methanol produced (Van Dijk, Solbakken & Rovner 1983, Vaswani 2000).

The product stream is cooled down to 318 K to condense all methanol, dimethyl ether and water. Unreacted H_2, CO, CO_2, CH_4 and N_2 do not condense at the conditions of the exchanger and must be recovered in a flash drum and sent to utility to be burned or released.

Dimethyl ether can be separated from methanol by extractive distillation at 11.2 atm and a reflux ratio of 20 mol recycled liquid/mol distillate. In this column, almost complete recovery of DEM is assumed which is accomplished as a top product while methanol and water leave at the bottom. DME can be sold to be used as an additive to diesel.

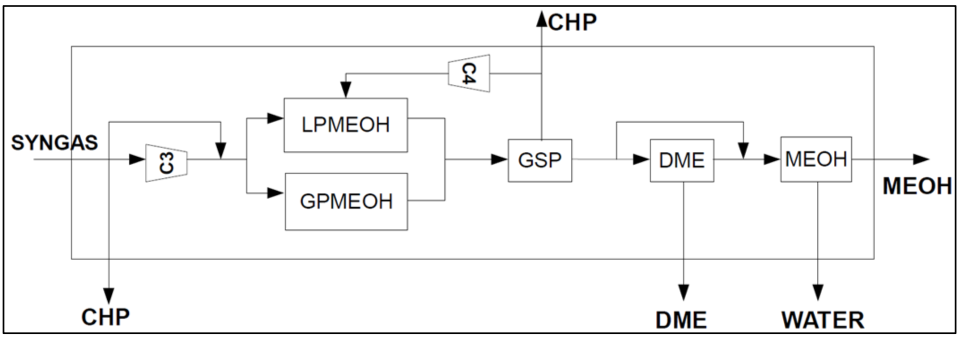

Figure 11 Methanol production units in superstructure. CHP: Combined heat and Power plant, LPMEOH: Liquid Phase methanol reactor, GPMEOH: Gas Phase methanol rector, GSP: Gas Separation unit, DME: Dimethyl Ether purification, MEOH: Methanol purification.

The LPMEOH process has some advantages. Although the operation conditions are similar to the those of the gas phase process, such as ability to control temperature, achieving higher conversion per pass with the same H_2/CO ratio (≥2); heat of reaction can be more effectively used to generate high-pressure steam and catalyst can be added and withdrawn from the system while on stream without the necessity of shut down the process.

However, the conversion per pass in the liquid phase reactor in CO-rich syngas is low and therefore the methanol yield is low.

LPMEOH operational conditions depend on reactor pressure, temperature, composition of the feed syngas, which per pass conversion of syngas to methanol may vary from 15% to as high as 60%. Equations (6-7) are considered as the main reactions and the reactor typically operates at 523 K and 50 atm. The conversion of carbon dioxide in Eq. (7) is assumed to be fixed at 8.9% and carbon monoxide conversion is estimated to be 30.6% (Van Dijk, Solbakken & Rovner 1983, Vaswani 2000).

The product stream is sent to heat exchanger to condense methanol and water from the unreacted gases. In the methanol separator, a simple phase separation takes place, the bottom product is sent to the methanol distillation column, and the unreacted syngas is recovered to be recycled or sent to power generation plant.

At the final stage, in the methanol distillation column water and methanol are separated at 3.4 atm and 318 K with 99.9% of methanol purity as top product at a reflux ratio of 1.5. Water with balance methanol leaves as the bottom product of the distillation column and is sent to a wastewater treatment facility (Van Dijk, Solbakken & Rovner 1983, Vaswani 2000).

4.2.2 Combined Heat and Power Plant

In the combined heat and power plant, the syngas is modeled to be burned to release heat at high temperature to produce high-pressure steam for a turbine, with given efficiency factors in the turbine and in the generator. The low-pressure steam is finally condensed, releasing heat for district heat production. To estimate the amount of electricity and district heat, which could be sold, energy balances for the main processes such as compressor, reactors and purification columns are used to calculate the internal power requirement. The energy used in the compressor calculated by determining the work required for compressing from inlet to outlet pressure.

The reference case of the compressor is assumed to operate isentropically, and the true operation is estimated with adiabatic, motor drive and mechanical efficiencies of η_{ad}=0.9, η_{md}=0.9 and η_{mech}=0.85, respectively.

5 PROBLEM STATEMENT IN THIS THESIS

This work presents several feasibility case studies for conventional primary steelmaking toward more sustainable operation. Economic development, global warming and other environmental issues have direct effects on social behavior and requirements. It has given rise to different regulations and restrictions, such as the international Kyoto protocol, as well as nuclear energy and geological sequestration limitations by countries.

In this work, mathematical modeling and programming have been applied to explore viability of integration of primary steelmaking with some emerging technologies. The model developed covers economic and environmental aspects as well as key operating conditions for the system. The concept of polygeneration system has been applied, which gives more flexible evaluation and utilization of the residual gases and, in consequence, improvements in the energy efficiency of the steel plant.

Papers I-III provide key information regarding implementation of top gas recycling and oxygen enrichment, as well as use of different auxiliary reducing agents in the BF and production of methanol as carbon and energy carrier. Papers IV-VII describe a general tool for further pre-engineering studies regarding sustainable development, proposing a superstructure for process synthesis and analysis under different fuel supplies and emerging BF operation technologies, including estimation of investment and operation cost of development. This also may affect the operation of steel plants, which are examined by multi-objective and multi-periodic optimization methods.

5.1 Superstructure Development

Figure 12 (Papers I-III) and Figure 13 (Papers IV-VII) represent the schematic of the studied system. Due to several options and scenarios, each paper presents selected case studies, gradually developing the superstructure and optimization technique.

Paper I studies the effect of integration of the steel plant with the methanol plant under top gas recycling (TBF) and oxygen (OBF) Blast Furnace operation compared with a conventional BF (CBF). Paper II extends the model to investigate the effect of different fuels, particularly biomass (considering a pyrolysis step) and air separation units. In Paper III the effect of auxiliary reducing agents injection into the BF for OBF has been investigated.

Paper IV introduces a superstructure for off-gas utilization for conventional BF operation. Paper V modifies the model to study the effect of external energy demand on the optimal solution of polygeneration system with different fuel supplies. Paper VI modifies the original model, exploring new technologies of blast furnace operation with different states of preheating in hot stoves and seasonal operation of the system. Finally, Paper VII illustrates the overall model as a general tool that can be used to investigate feasibility for sustainable development of the system by process integration not only from an engineering view (process synthesis and analysis) but also it can provide useful information on different scenarios for decision makers.

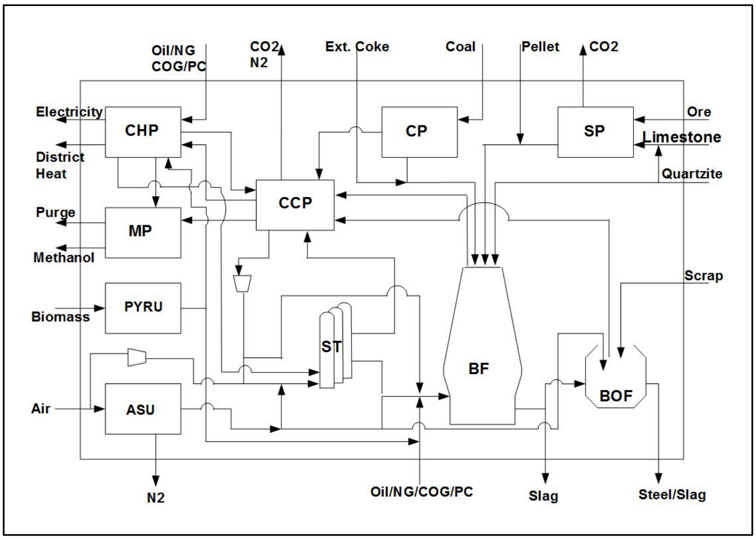

Figure 12 Integrated Steel Plant. CP: Coke Plant, SP: Sinter Plant, ST: Hot Stoves, CCP: CO_2 Capturing Plant, BF: Blast Furnace, BOF: Basic Oxygen Furnace, CHP: Combined Heat and Power Plant, PYRU: PYRolysis Unit, ASU: Air Separation Unit and MP: Methanol Plant.

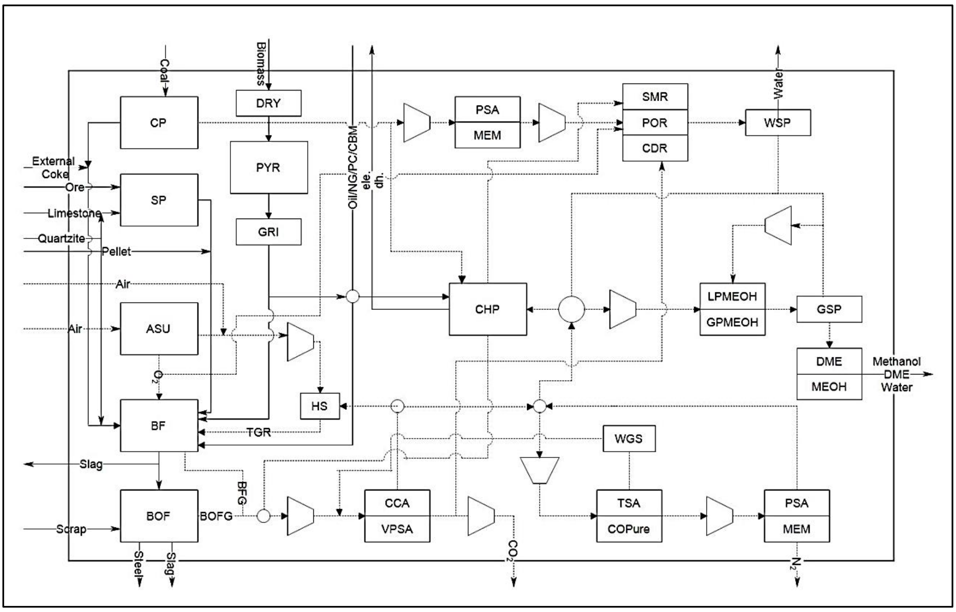

Figure 13 Superstructure for suggested Integrated Steel Plant. Lines depict solid and liquid phase material flow and dash-lines are residual gas network. It includes Coke Plant (CP), Sinter Plant (SP), Hot Stoves (ST), Blast Furnace (BF), Basic Oxygen Furnace (BOF), Combined Heat and Power Plant (CHP), Air Separation Unit (ASU) and available technologies for carbon capturing and sequestration plant which are: Pressure Swing Adsorption (PSA), Membrane adsorption (MEM), Steam Methane Reforming (SMR), Partial Oxidation Reactor (POR), Carbon Dioxide Reforming (CDR), Water Separation (WSP), Liquid phase Methanol reactor (LPMEOH), Gas phase Methanol rector (GPMEOH), Gas Separation unit (GSP), Dimethyl Ether purification (DME), Methanol purification (MEOH), Temperature Swing Adsorption (TSA), Chemical absorption unit (COPURE), Water Gas Shift reactor (WGS), CO_2 Chemical Absorption (CCA), Vacuum Pressure Swing Adsorption (VPSA) and Compressors.

In Papers VI and VII, different states of preheating and scenarios of oxygen enrichment of the blast and top gas recycling rates, in addition to partial replacement of coke with other reducing agents and BF top gases, have been considered. Figure 14 depicts three different input gas-preheating states that have been studied in this work. In State 1, both blast and recycled top gas are pressurized and preheated in two sets of compressors and hot stoves. Therefore, a new set of compressors and hot stoves (650 m^3) must be added, leading to considerable investment costs. In the other states, only the available compressors and hot stoves are used for preheating either the blast (State 2) or the recycled top gases (State 3) up to 1200 °C.

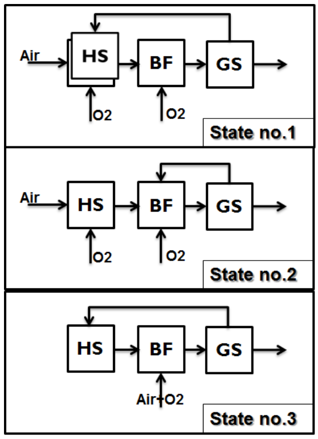

Figure 14 Different states of blast preheating and oxygen enrichment: State 1: preheating TGR+BL in two sets of hot stoves, State 2: preheating BL in one set of hot stoves, and State 3: preheating of TGR in one set of hot stoves. GS indicates the gas separation unit processes.

5.2 Model Development

5.2.1 Mathematical Model

Papers I-III present a Non-Linear Programming (NLP) problem (Floudas 1995) based on a blast furnace model (Helle, Helle & Saxén 2011) which can be expressed as

$$\begin{aligned} &\min_{X} && f_0(X) \\ &S.t. && f_1(X) = 0 \\ & && f_2(X) \le 0 \end{aligned} \qquad (9)$$

where X is a vector of n components $\{x_1, \cdots, x_{n_x}\}$ and a subset of R^n; $f_0 : X \rightarrow R$ is an objective function; $f_1 : X \rightarrow R^n$ are equality constraints and $f_2 : X \rightarrow R^n$ are inequality constraints are defined on X (Floudas 1995).

The modeling was done by a Sequential Modular (SM) approach (Biegler, Grossmann & Westerberg 1997) in the MATLAB Optimization Toolbox environment. In this methodology, each equipment class is not just a model but it has a built-in solution procedure. Hence, there is an order to solve each block of equipment or unit process, passing the output solution to the next block. Due to limited access to solvers and because of time expenses, a number of starting points (~30) were considered to find the optimal solutions. Table 2 shows the BF input and some of the output variables and their constraints, as well as sinter and coke mass production rate constraints of the plant.

Table 2 Some of the variables and constraints of the model.

Variable	Range	Variable	Range
BF production rate	130-160 t_{hm}/h	Bosh gas volume	150-220 km^3n/h
Recycled top gas	0-220 km^3n/h	Solid residence time	6.0-9.5 h
Blast oxygen content	21-99 vol-%	Slag rate	≥ 0 kg/t_{hm}
Specific fuel rate in BF	0-120 kg/t_{hm}	Top gas volume	≥ 0 km^3n/h
Blast temperature	250-1200 °C	Top gas CO content	≥ 0 vol-%
Specific pellet rate	0-600 kg/t_{hm}	Top gas CO_2 content	≥ 0 vol-%
Pyrolysis temp	150-500 °C	Top gas H_2 content	≥ 0 vol-%
Specific coke rate	≥ 0 kg/t_{hm}	Top gas N_2 content	≥ 0 vol-%
Flame temperature	1800-2300 °C	Top gas heating value	≥ 0 MJ/m^3n
Top gas temperature	115-250 °C	Sinter feed flow	0-160 t/h
Own coke feed flow	0-55 t/h		

Introducing superstructure (Figure 13) for carbon capturing utilization units for treatment of the off-gases in the system, the study of emerging technologies of blast furnace operation, effect of different reducing agents, fuels, and effect of investment costs lead to a Mixed Integer Non-Linear Programming (MINLP) problem. It can be expressed as

$$\begin{aligned} \min_{x,y} \quad & f_0(x,y) \\ S.t. \quad & f_1(x,y) = 0 \\ & f_2(x,y) \leq 0 \\ & x \in X \subseteq \mathcal{R}^n \\ & y \in Y \ integer \end{aligned} \tag{10}$$

where X is a vector of n continuous variables x, Y is a vector of integer variables y, $f_1(x,y)$ are n_h equality constraints, $f_2(x,y)$ are n_g inequality constraints, and $f_0(x,y)$ is the objective function.

A simultaneous modular or Equation Oriented (EO) approach (Biegler, Grossmann & Westerberg 1997) is selected to implement flowsheet optimization under different physical restrictions and external demands in the General Algebraic Modeling System (GAMS Development Corporation 2014). GAMS is a high-level modeling system for mathematical optimization. The system is tailored for complex, large-scale modeling applications and allows the user to build large maintainable models that can be adapted to new situations. It includes hybrid algorithms combining different local and global solvers.

The model has been formulated as Generalized Disjunctive Programming (GDP) problem

$$
\begin{aligned}
&Min && \sum_{k} C_k + f_0(x) \\
&S.t. && r(x) \leq 0 \\
& && \underset{l \in L_k}{\vee} \begin{bmatrix} Y_{lk} \\ g_{lk}(x) \leq 0 \\ C_k = \gamma_{lk} \end{bmatrix} \quad k \in K \\
& && \Omega(Y) = true \\
& && x \in \mathcal{R}^n, c_k \in \mathcal{R}^n \\
& && Y \in \{true, false\}
\end{aligned} \tag{11}
$$

where Y_{lk} are the Boolean variables that establish whether a given term in a disjunctive is true, while *Ω(Y)* are logical relations assumed to be in form of propositional logic involving only the Boolean variables, expressing relationships between the disjunctive sets. Y_{lk} are auxiliary variables that control the part of feasible space in which the continuous variables, x, lie, and the variable C_k represent fixed charges which are activated to a value γ_{lk} if the corresponding term of the disjunction is true. *r(x)* are common constraints and $g_{lk}(x)$ represent available constraints in disjunction. For modeling purpose, it is advantageous to start with the GDP model as it captures more directly both the qualitative (logical) and quantitative (equations) part of the problem. To explore the model with more solver options in GAMS, the GDP model was transformed to a MINLP problem. The most straightforward way is to replace the Boolean variables Y_{lk} by binary variables y_{lk}, and the disjunctions by "big-M" constraints:

$$
\begin{aligned}
&Min && \sum_{k \in K} \sum_{l \in L_k} \gamma_{lk} y_{lk} + f_0(x) \\
&S.t. && r(x) \leq 0 \\
& && g_{lk}(x) \leq M_{lk}(1 - y_{lk}) \\
& && \sum_{l \in L_k} y_{lk} = 1 \\
& && Ay \leq a \\
& && x \geq 0, \qquad 0 \leq y_{lk} \leq 1 \\
& && k \in K, l \in L_k, y_{lk} \in \{0,1\}
\end{aligned} \tag{12}
$$

where A and a are the coefficients for the set of inequalities obtained by translating Boolean variables into their linear mathematical form (Grossmann 2002).

Surrogate models for blast furnace is developed by partial least squares, Papers IV-VII (Eigenvector research incorporated 2011), and Kriging techniques (Lophaven, Nielsen & Sondergaard 2002) in Paper IV. A set of feasible data from observations was selected from a large set of possible input/output data of original BF model, considering the implementation of emerging BF technologies for different level of top gas recycling and oxygen enrichment. Because of high nonlinearity of the data, a piecewise linear regression approach discretizes the data that leads to more than 50 surrogate models to cover the effect of different reductants (heavy oil, natural gas, coke oven gas, pulverized coal, charcoal, torrefied biomass), the operation states ranging from conventional to full top gas recycling and the oxygen enrichment levels.

Table 3 shows three steps of oxygen enrichment including conventional blast furnace operation "(21-32 %)" , medium enrichment "(55-65%)" and oxygen blast furnace operation "(84-99 %)" in conjunction of no, medium and high level of top gas recycling. The feasibility of the data set is according to the practical constraints. Hence, a stepwise surrogate model based on oxygen enrichment and recycling degree was introduced.

Table 3 Regions of operation used to generate surrogate model.

Oxygen enrichment of the blast (%)	Top gas recycling rate (km^3n/h)		
	0	80-100	180-200
21-32	States 1, 2 and 3	States 1, 2	-
55-65	-	States 1, 3	States 1, 3
84-99	-	States 1, 2, and 3	States 1, 3

After pre- and post-processing, the coefficient of determinations (R^2) were calculated. Table 4 represents calculated R^2 based on multiple linear regression for multivariate Y where inputs are: production rate, reducing agent injection rate, oxygen enrichment, blast/top gas temperature, pellet rate and top gas recycling rate. These values are for blast furnace with natural gas as reducing agent injectant and high level of preheated top gas recycling and cold oxygen injection. Further information for the case study of conventional BF can be found in supplemental material of Paper IV.

Table 4 Coefficient of determination for blast furnace with high level of preheated top gas recycling, oxygen injection and natural gas as reducing agent injectant

Y	R^2	Y	R^2	Y	R^2
Blast volume	0.9941	TG Temperature	0.9290	Air volume	0.9861
Flame temperature	0.9853	CO composition in rTG	0.9642	CO volume in TG	0.9902
Residence time	0.9933	CO_2 composition in rTG	0.9637	CO_2 volume in TG	0.9915
Coke rate	0.9930	H_2 composition in rTG	0.9647	H_2 volume in TG	0.9950
Slag rate	0.9764	N_2 composition in rTG	0.9851	N_2 volume in TG	0.9782
TG volume	0.9898	rTG volume	0.9945	CO volume in rTG	0.9711
CO composition in TG	0.9711	Bosh gas volume	0.9929	CO_2 volume in rTG	0.9770
CO_2 composition in TG	0.9713	Sinter rate	0.9999	H_2 volume in rTG	0.9790
H_2 composition in TG	0.9896	Quartz flow rate	0.9775	N_2 volume in rTG	0.9865
N_2 composition in TG	0.9705	O_2 injection	0.9956		

The overall model for the proposed superstructure of a steel plant with a polygeneration system can be expressed as

$$
\begin{aligned}
&\max \quad f_0\\
&S.t.\quad \bigvee_{ji\tau}\begin{bmatrix} Y_{ji\tau ms}\\ h^{m}_{ji\tau ms}(f,x)\\ h^{e}_{ji\tau ms}(f,T)\end{bmatrix} \quad i\in\{materials\}, j\in\{BF,CHP\}, m\in\{fuels\}, s\in\{states\}\\
&\begin{bmatrix} Y_{PSA,i\tau}\\ h^{m}_{PSA,i\tau}(f,R)=0\\ h^{p}_{PSA,i\tau}(f,x,R,\beta)=0\\ h^{e}_{PSA,i\tau}(f,T)=0\\ h^{c}_{PSA,i\tau}(f)=0\end{bmatrix} \vee \begin{bmatrix} Y_{MEM,i\tau}\\ A^{MEM}f_{MEM,i\tau}=a^{MEM}\\ h^{p}_{MEM,i\tau}(f,x)=0\\ h^{e}_{MEM,i\tau}(f,T)=0\\ h^{c}_{MEM,i\tau}(f)=0\end{bmatrix}\\
&\bigvee_{j}\begin{bmatrix} Y_{ji\tau}\\ A^{j}f_{ji\tau}=a^{j}\\ h^{e}_{ij\tau}(f,T)=0\\ h^{c}_{ij\tau}(f)=0\end{bmatrix} \quad j\in\begin{Bmatrix} reactors: [SMR,CDR,POR][LPMEOH,GPMEOH]\\ seperators: [TSA,COPUR][CCA,VPSA/CCM]\end{Bmatrix}\\
&\bigvee_{j}\begin{bmatrix} Y_{ji\tau}\\ A^{j}f_{ji\tau}=a^{j}\\ h^{p}_{ji\tau}(f,T)=0\\ h^{e}_{ji\tau}(f,T)=0\\ h^{c}_{ji\tau}(f)=0\end{bmatrix} \quad j\in\{compressors\}\\
&\begin{bmatrix} Y_{ji\tau}\\ A^{j}f_{ji\tau}=a^{j}\\ h^{e}_{ij\tau}(f,T)=0\\ h^{c}_{ji\tau}(f)=0\end{bmatrix} \vee \begin{bmatrix} \neg Y_{ji\tau}\\ f_{ji\tau}=0\\ h^{e}_{ij\tau}=0\\ h^{c}_{ji\tau}=0\end{bmatrix} \quad j\in\{DME,PYRU,HS\}\\
&A^{j}f_{ji\tau}=b^{j} \quad j\in\{ASU,WSP,GSP,CP,SP,\mathrm{BOF},MEOH\}\\
&h^{c}_{ij\tau}(f)=0 \quad j\in\{ASU,WSP,GSP,MEOH\}\\
&Y_{ji\tau} \Rightarrow (P^{min}\le P\le P^{max},\ T^{min}\le T\le T^{max}) \quad j\in\{reactors; seperators\}\\
&\neg Y_{ji\tau} \Rightarrow Y_{comp,i\tau}\\
&Y_{GPMEOH,i\tau} \Rightarrow Y_{DME,i\tau}\\
&x^{L}\le x\le x^{U}\\
&f,x,T\ge 0
\end{aligned}
\tag{13}
$$

where f , x and T are molar flow rates, composition and temperature of the material i for each unit j in period τ; h^m and h^e express the mass and energy balance terms and h^c and h^p are the cost and pressure functions.

By selecting each of disjunctions, the next task implies the necessity of the compressors and the heat exchangers. If the process unit is chosen then the mass and energy balances are enforced and the corresponding cost term is considered. The integrated system was reformulated as a mixed integer nonlinear problem. Due to bi/tri-linear terms and polynomial terms in the energy balances, the model is nonlinear and non-convex; therefore, in the most of the case studies global optimum cannot be guaranteed, except in the use of BARON as a global solver.

Some of the non-convex terms were transformed using convex hull to related linear forms. Linear under-estimators of the cost function are generated with an existence and sizing value, which is represented by binary and continuous variables, respectively.

5.2.2 Economic Evaluation

Figure 15 shows the structure of a typical economic evaluation model. The first step in the evaluation procedure is to map design decisions into flow rates and process equipment specifications using process models. The flow rates can be converted into recurring cash streams (e.g. revenues and operating costs) by multiplying them by unit prices. Process equipment specifications can be translated into purchased equipment costs by cost correlations or equipment fabrication cost models.

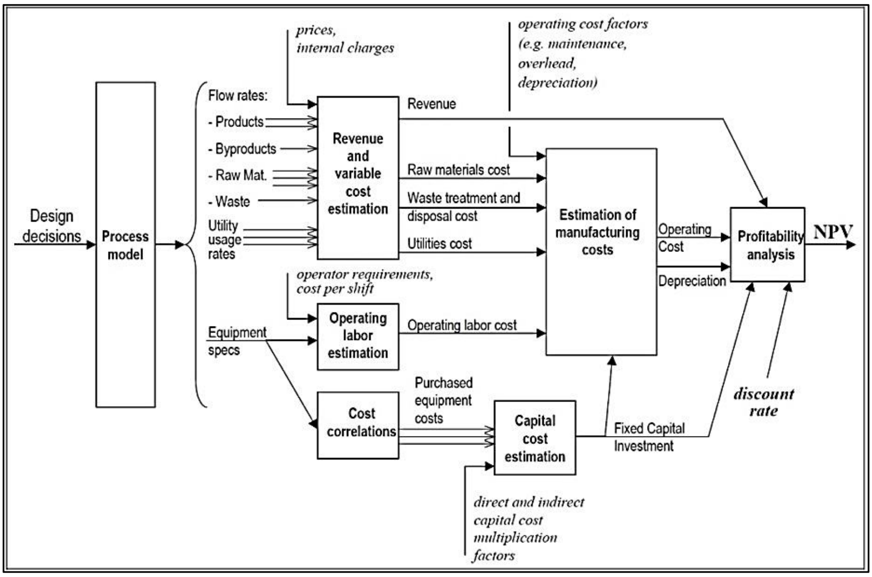

Figure 15 Element of an economic valuation model (Cano Ruiz 1999).

At the conceptual design stage, all other capital costs are estimated as a function of the purchased equipment cost. Additional recurring cash streams (e.g. operating labor and maintenance costs) are also a function of the equipment specifications. The last step of the analysis is the combination of capital costs and recurring cash streams into a single measure of economic performance. Recurring cash streams occurring in future periods can be discounted and added to the capital cost to obtain a net present value (NPV), or the capital costs can be annualized and added to the recurring cash streams to obtain a total annualized profit (Cano Ruiz 1999).

In Papers I-III, the objective function was considered to be manufacturing cost per ton of liquid steel as determined by

$$[f.mc]_{ls} = \sum\left([f.c]_p - [f.c]_F - [f.c]_{emis\&seq}\right) \quad (14)$$

where *mc* is the manufacturing cost of liquid steel. It should be stressed that the values of the costs are indicative only, as actual costs could not be used for reasons of confidentiality. However, the internal relations between the costs of, e.g., the fuels, are considered appropriate. Still, one should keep in mind that the selected cost setup, as well as the internal and external constraints imposed on the system and its units will naturally affect the optimal solutions found. Therefore, in interpreting the results the main emphasis should be put on the observed overall trends rather than on the absolute values reported.

In Papers IV-VII, since the primary steelmaking plant was taken to be existent, the cost estimation includes capital and operational expenditure (capex & opex) for extended chemical unit operations.

A linear under-estimator is used to approximate capital expenditure based on a power law function and scaling factor as

$$BMC = \sum_j \left\{ C_j^{\circ} \left(\frac{S_j^{max}}{S_j^{\circ}} \right)^{\alpha} \right\}, S_j^{max} \geq S_{j\tau} \tag{15}$$

where *BMC* is the bare module cost of equipment, S is capacity of the related parameter for sizing of equipment, S° and C° are the base capacity and cost and α is exponential scaling factor updated for the year 2010. The annual investment cost and net profit can be expressed as

$$TCI^{*} = TCI\left(\delta / \left[1 - (1+\delta)^{-\theta_{lp}}\right]\right) \tag{16}$$

$$NP = \sum\left([fc]_p - [fc]_F - [fc]_{emis\&seq}\right) \tag{17}$$

where *TCI* is the total capital investment given by fixed and working capital, *NP* is the net profit of the integrated system annually ($*$) which is the sum of profit from products (p) and cost of feed materials *(F)* including fuels, emission *(emis)* price and sequestration *(seq)* cost.

In addition, the operational expenditures are estimated as a percentage of capital expenditure including net profit, working capital and direct expenses. Net present value *(NPV)* is introduced as economic objective function as

$$NPV = \frac{1}{\delta} \cdot \left(1 - \frac{1}{(1+\delta)^{\theta_{lp}}}\right) NP - \left(1 - \frac{\lambda}{\theta_{dp}} \cdot \frac{1}{\delta} \cdot \left(1 - \frac{1}{(1+\delta)^{\theta_{dp}}}\right)\right) TCI \tag{18}$$

where λ =40% is the tax rate, θ_{lp}=30 , θ_{dp}=10 are the life and depreciation time (years) of the project, respectively, and δ =12% is the annual discount rate.

Fixed capital investments were assumed to be the sum of manufacturing and non-manufacturing cost and is estimated as 1.4 times by bare module cost with 25% contingency. Working capital cost and direct expenses were considered to be 19.4% and 4% of fixed capital investments, respectively. The economic parameters used in this study are presented in Table 5.

Table 5 Economic parameter considered in this study ([€/$]$_{index}$=1.3).

Parameter	Value	Parameter	Value	Parameter	Value
c_{ore}	104 $/t	c_{dme}	200 $/t	c_{O_2}	65 $/km³n
c_{pel}	156 $/t	c_{ls}	550 $/t	c_{scrap}	130 $/t
c_{coal}	143 $/t	c_{el}	65 $/MW	c_{meoh}	325 $/t
$c_{coke,ext}$	390 $/t	c_{dh}	13 $/MW	c_{dme}	200 $/t
c_{oil}	195 $/t	$c_{emi.}$	0 – 150 $/t	c_{pc}	230 $/t
$c_{limestone}$	39 $/t	$c_{seq.}$	0 – 150 $/t	c_{bm}	65 $/t
c_{quartz}	39 $/t	c_{ng}	260 $/t	c_{cbm}	340 $/t

5.2.3 Environmental Impact

The CO_2 emissions are calculated as environmental factor based on an overall carbon balance equation for the system, including all fossil carbon-bearing inputs (coal, oil, natural gas, external coke, limestone) and excluding the outflows of carbon with liquid steel, methanol, sold coke and stripped CO_2. Thus, the feed flow of biomass is excluded from the balance, as biomass was considered to be renewable. The emissions associated with the production of external raw materials (e.g., pellets, external coke) were not considered, as the units were outside the balance boundaries of the system

$$f_{CO_2}^{ave} * f_{ls} * \tau = \sum_{\substack{F_t=fuel,coal,lime,RAR \\ p_t=seq.,ls,coke_{ext},meoh}} \{(f\chi)_F - (f\chi)_p\}_\tau \qquad (19)$$

where χ is a variable for each material expressing the mass fraction of carbon which has a carbon dioxide emission contribution in period τ .

6 PREENGINEERING FEASIBILITY STUDY

This chapter presents some of the results on feasibility studies undertaken in this work reported in Papers I-VII of the thesis, focusing on technical, economic and environmental aspects. In the last two sections of the chapter, some results from multi-objective and multi-periodic optimization are presented.

6.1 Technical Evaluation

6.1.1 Optimal States of Operation

Table 6 shows the effect of integration of a steel plant with a methanol plant on some key process variables for the TBF and OBF concepts. The optimal TBF states are seen to apply high, but not maximum, oxygen levels in the blast, higher coke rates and clearly higher oil rates. Furthermore, the BF top gas temperature is at its lower limit. The OBF concepts, in turn, apply practically full top gas recycling and “pure” oxygen injection.

Table 6 Optimal process variables for a steel plant (with TBF or OBF operation of the blast furnace) integrated with methanol production steel production rate of 180 t/h, costs of emissions c_{CO_2}=50 €/t and capturing $c_{storage}$=10 €/t. Variable values at their bounds are written in bold face.

Variable	**TBF**	**TBF-INT**	**OBF**	**OBF-INT**
Blast volume (km^3n/h)	51.6	52.6	27.0	26.3
Oxygen enrichment (vol-%)	86.6	84.4	99.0	99.0
Blast furnace top gas volume (km^3n/h)	192	193	203	215
Blast furnace recycling gas volume (km^3n/h)	109	108	201	212
Sinter feed rate (t/h)	160	160	160	160
Coal feed rate (t/h)	79.1	79.1	79.1	79.1
Specific coke rate (kg/t_{hm})	312	311	280	297
Specific oil rate (kg/t_{hm})	**120**	**120**	26.0	10.5
Specific pellet rate (kg/t_{hm})	513	513	513	513
Flame temperature (ºC)	**1800**	**1800**	**1800**	**1800**
Blast temperature (ºC)	**1200**	**1200**	**1200**	**1200**
Bosh gas volume (km^3n/h)	197	197	197	204
Top gas temperature (ºC)	115	115	178	193
Burden residence time (h)	7.0	7.0	7.6	7.3
Slag rate (kg/t_{hm})	215	215	198	199
Coke oven gas volume (km^3n/h)	17.6	17.6	17.6	17.6
Basic oxygen furnace gas volume (km^3n/h)	6.5	6.5	6.5	6.5
Oil needed for other units than BF (t/h)	-	9.0	-	7.2
Bought coke (t/h)	1.49	1.23	-	-
Sold coke (t/h)	-	-	3.66	0.91
Sold methanol (t/h)	-	26.2	-	18.0
Sold electricity (MW)	35.0	-	-	-
Sold district heat (MW)	178	-	36.4	-
Specific emission (t_{CO2}/t_{ls})	1.17	1.13	0.54	0.48
Specific steel cost ($€/t_{ls}$)	288.1	274.7	251.6	232.7

For all optimal states, the blast temperature is at its upper and the flame temperature is at its lower bound. This is logical, as it is practically always beneficial to apply maximum gas preheating in the blast furnace to save coke, while the latter follows from a need to inject large volumes of gases, which part of it is cold. The plants with integrated methanol production are seen to export neither electricity nor district heat. Indeed, this may be a problem if external constraints are imposed, e.g., required district heat supply from the plant. The OBF plant without methanol production exports only little heat, but some coke, which is spared due to the efficient top gas recycling.

Table 7 shows comparisons among optimal states of operation of the nine conceptual cases for integrated steelmaking under different fuel systems. In all optimized states, the sinter plant operates at maximum production (160 t/h) and the remaining required iron ore is brought into the BF as pellets. For all states, the blast or recycled gas is heated to the maximum temperature (1200 °C). In the cases where biomass is used, it is always processed at the maximum temperature, i.e., to maximum carbonization. For the TBF (except operation with NG) and OBF concepts, the flame temperature is at its minimum due to the injection of cold gases. CBF and TBF apply (practically) maximum injection of auxiliary fuel, while the level for OBF is lower.

Table 7 Optimal process variables for the system with a steel production rate of 170 t_{ls}/h, costs of CO_2 emissions c_{CO_2}=40 €/t and storage $c_{storage}$=20 €/t. Boldface numbers indicate values at their constraints.

Variable	CBF-BM	CBF-NG	CBF-OIL	TBF-BM	TBF-NG	TBF-OIL	OBF-BM	OBF-NG	OBF-OIL
Blast volume (km^{3}n/h)	150.4	129.9	126.8	40.0	123.6	47.5	25.4	25.7	26.0
Blast oxygen (vol %)	22.0	30.1	28.0	98.4	31.9	88.1	**99.0**	**99.0**	**99.0**
BFG volume (km^{3}n/h)	221.5	217.2	203.0	178.4	216	179.0	183.8	187.0	179.3
BF TG rate (km^{3}n/h)	-	-	-	130.6	7.4	102.2	179.5	183.3	173.8
Sinter feed rate (t/h)	**160.0**	**160.0**	**160.0**	**160.0**	**160.0**	**160.0**	**160.0**	**160.0**	**160.0**
Coal feed rate (t/h)	79.1	79.1	79.1	79.1	79.1	79.1	79.1	79.1	79.1
Specific coke rate (kg/t_{hm})	326.7	330.8	320.7	299.5	330.4	308.6	220.4	289.4	256.0
Specific fuel rate (kg/t_{hm})	**120.0**	**120.0**	**120.0**	**120.0**	**120.0**	**120.0**	91.7	16.18	48.3
Specific pellet rate (kg/t_{hm})	457.6	457.6	457.6	457.6	457.6	457.6	457.6	457.6	457.6
Flame temperature (ºC)	2265	1881	2246	**1800**	1862	**1800**	**1800**	**1800**	**1800**
Blast temperature (ºC)	**1200**	**1200**	**1200**	**1200**	**1200**	**1200**	**1200**	**1200**	**1200**
Pyrolysis temperature(ºC)	**500.0**	-	-	**500.0**	-	-	**500.0**	-	-
Bosh gas volume (km^{3}n/h)	193.7	**220.0**	186.0	174.5	**220.0**	183.3	178.6	184.6	179.4
Top gas temperature (ºC)	194.6	221.9	143.0	**115.0**	221.0	**115.0**	184.1	155.2	156.5
Burden residence time (h)	7.2	7.1	7.3	7.7	7.2	7.5	**9.5**	7.9	8.6
Slag rate (kg/t_{hm})	210.7	211.0	216.4	209.4	211.0	214.7	205.3	208.9	203.9
COG volume (km^{3}n/h)	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6
BOFG volume (km^{3}n/h)	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Aux. fuel excluding BF	10.1	10.5	9.3	12.4	10.5	10.1	11.6	6.3	8.1
Bought/sold coke (t/h)	5.8	9.8	0.0	-3.1	9.4	-2.0	-14.7	-4.5	-9.5
Sold methanol (t/h)	21.8	40.1	28.6	20.1	39.9	25.6	18.2	18.2	18.4
Specific emission (t_{CO2}/t_{ls})	1.1	1.4	1.5	0.6	1.4	1.2	0.4	0.6	0.7
Specific steel cost (€/t_{ls})	234.9	246.2	257.4	219.7	246.2	252.5	198.0	224.5	225.0

However, for TBF with natural gas, the optimal top gas-recycling rate is very low and the operation resembles that of CBF. The OBF concepts with oxygen injection apply more than 95% recycling irrespective of the auxiliary fuel used. OBF-BM shows the lowest specific emission, due to a non-fossil carbon source combined with carbon capture and storage, but also the lowest steel production cost of the nine cases studies.

6.1.2 Conceptual Design and Operation

Optimization techniques are used to find the optimal operation and design for the proposed superstructure for a CCU plant by maximizing NPV and minimizing the CO_2 emission from the system for one period of operation without any external energy demand (Paper IV, VI and Proceeding VII). Figure 16 depicts the optimal superstructure and gas distribution in the system considering top gas recycling with preheating for nitrogen-free blast furnace (OBF) under different reducing agents as blast furnace injectants and fuels in power plant, such as coke oven gas, oil, natural gas, pulverized coal and biomass, and CO_2 sequestration.

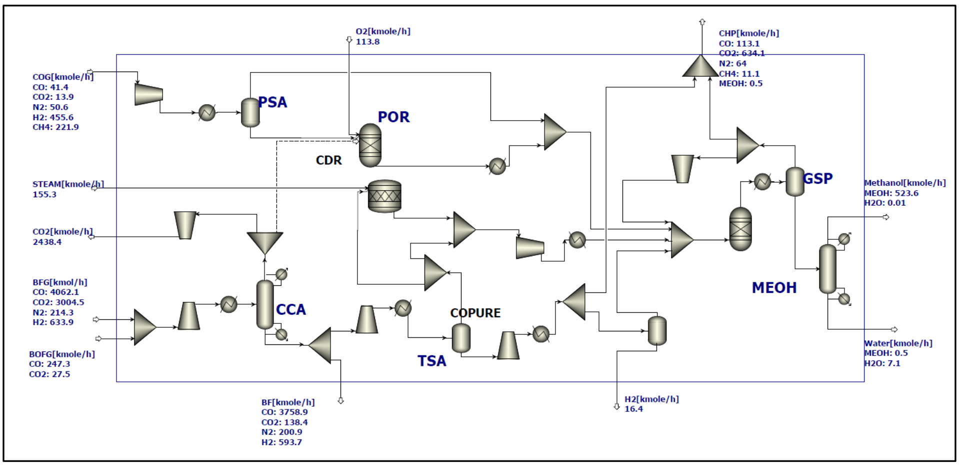

Figure 16 Optimal design and main flow for gasification, CCS and methanol plant by minimizing emission; and for maximizing NPV that CDR reactor replacing POR with stream CO_2 (dottedline).

Process synthesis shows in trade-off between economic and environmental impacts different topologies may achieve. Swing adsorption processes are the main gas separation units. For carbon dioxide capturing, depend on utility requirements and availability, VPSA and CCA processes can be more competitive than membrane technology. Due to availability of in-house oxygen, selection of POR technology seems to be preferable among other methane reforming. Methanol technology depends on fuel, BF operation and top gas composition may vary.
Figure 17 displays the suggested integrated steel plant (ISP) configuration and Table 8 shows the optimal values of some key variables in the integrated system as result of superstructure periodic optimization for the modified model covering all scenarios of

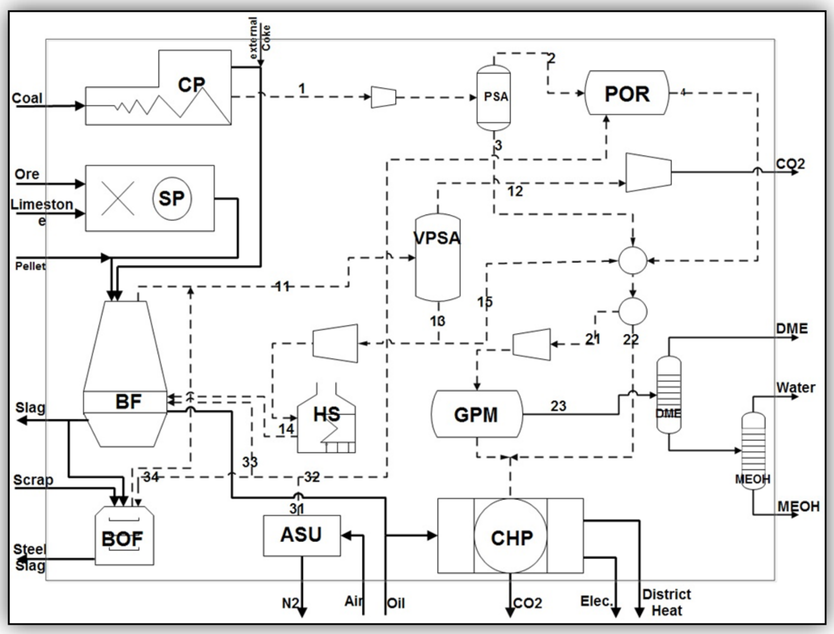

Figure 17 Suggested integrated plant (ISP-323) and the main streams.

Table 8 Main streams (in kmol/h) and BF variables in the ISP-323 system.

	CO	**CO_2**	**H_2**	**O_2**	**N_2**	**CH_4**	**H_2O**	**MEOH**	**DME**
1	41.4	13.9	456	1.1	50.7	222			
2	41.4	13.9	89.5	1.1	50.7	222			
3			366						
4	252	13.9	511		50.7	11.1			
11	3910	2787	731		997				
12		2647							
13	3910	139	731		997				
14	3618	135	703		989				
15	292	3.4	27.4		7.3				
21	439	13.9	877		50.7				
22	105	3.4	27.4		7.3	11.1			
23	21.9	0.7	4.3		50.7		13.2	438	8.7
31				1484					
32				105					
33				1076					
34				302					

Oxygen volume [km^3n/h]	33.2	Blast volume [km^3n/h]	23.9
Specific coke rate [kg/t_{hm}]	261	Flame temperature [ºC]	1800
Specific oil rate [kg/t_{hm}]	42.1	Recycled top gas temp. [ºC]	1200
Specific pellet rate [kg/t_{hm}]	458	Recycled top gas volume [km^3n/h]	180
Coal flow rate [t/h]	81.6	Bosh gas volume [km^3n/h]	183
Ore flow rate [t/h]	154	Top gas temperature [ºC]	193
Limestone rate [t/h]	21.3	Burden residence time [h]	8.8
Scrap rate [t/h]	37.1	Slag rate [kg/t_{hm}]	260
Sinter flow rate [t/h]	160	COG volume [km^3n/h]	17.6
External (sold) Coke flow rate [t/h]	9	BOFG volume [km^3n/h]	6.2
Average extra oil needed [t/h]	30	Carbon dioxide send out [t/h]	116

TGR and oxygen enrichment with oil as auxiliary reducing agent under seasonal external energy demand. Coke oven gas (stream-1) goes to the gasification plant. First, mainly hydrogen is separated from it in a pressure swing adsorption (PSA) unit, which operates at 10 atm, and is sent to the polygeneration system (stream-3). The rest of the gas, which has high methane content, is sent to the gasification reactor. The partial oxidation (POR) process was selected, which operates at low pressure and at its optimal temperature (1143 K).

A mixture of blast furnace and basic oxygen furnace gases (stream-11), taken to be mostly CO (46%), CO_2 (34%), H_2 (9%) and N_2 (11%) after scrubbing, goes to a vacuum pressure swing adsorption and after separation unit for CO_2 which, in turn, is pressurized to 110 atm and sent out of the system for sequestration.

The residual gases is rich in carbon monoxide are assumed to be divided between the polygeneration system and the blast furnace, before which it is preheated (stream-14). The solution has omitted the TSA unit based on the composition of the gases in this state (~88% CO). The residual gases from capturing and gasification are pressurized and sent to the polygeneration system to produce methanol, electricity and district heat according to the local demand, considering the economics.

6.1.3 Performance of Polygeneration System

Figure 18 depicts the performance of PG under different level of top gas recycling and external energy (electricity) demand. Electricity and district heat production are on their lower bounds external energy demands in all scenarios in Case 2 (and therefore not shown), but the production of methanol may vary up to 35 t/h from case to case (e.g., in scenario 101).

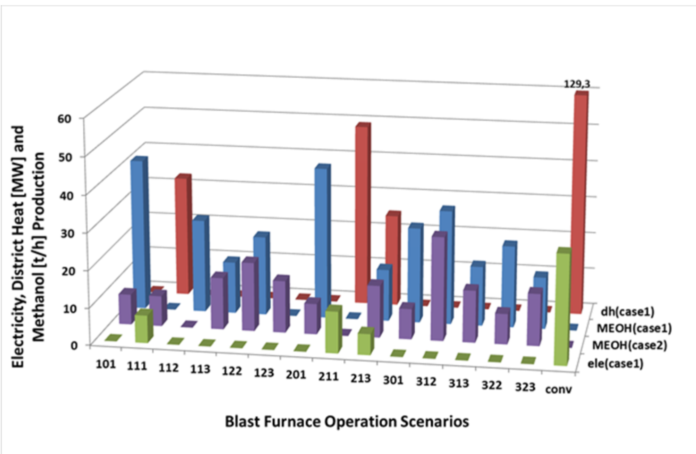

Figure 18 Electricity, district heat and methanol production of integrated plant without fixed external demand of electricity (Case 1) and, methanol production for the case with fixed external energy demand (Case 2), considering different scenarios of blast furnace operation. The scenario number codes are defined in the caption of Figure 20. The constraint considered as lower bound (external energy demand) is active for all scenarios in Case 2.

The conventional scenario is seen to have a high production of electricity and heat in Case 1, while the values are clearly lower for the other scenarios, except scenarios 211 and 111 (where oxygen enrichment is low). Overall, the production of methanol is lower in Case 2 compared to Case 1. The promising scenario 323 has a moderate methanol production of about 10 t/h.

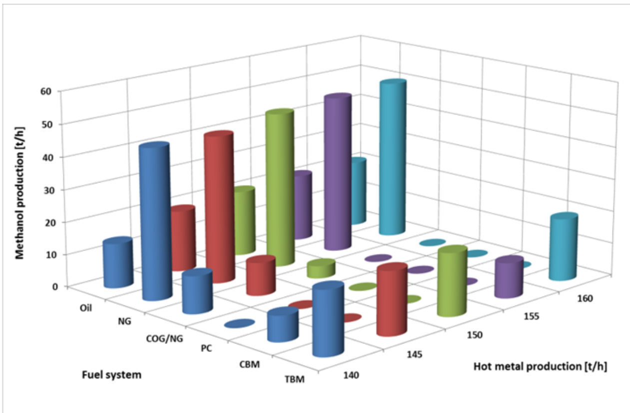

Figure 19 Methanol production for different hot metal production rate and fuels.

Figure 19 illustrates methanol production rate for the systems studied with different fuels and hot metal production rates by maximizing NPV for case 1. Methanol production may vary as a result of the flexible operation of the polygeneration system, which adapts itself to satisfy the demands of steam, electricity, district heat and methanol. The integrated system with torrefaction is seen to show a stable behavior in terms of methanol production despite varying steel production, by contrast to the case for other fuels studied. This is due to lower direct price of biomass as feed material and top gas composition. It is noticeable that maximum NPV does not happen in oxyBF operation for all fuel systems.

6.2 Economic Evaluation

6.2.1 Emerging BF Technologies

The system under TGR and oxygen enrichment is investigated for two different cases: Case 1 refers to operation without any external obligation: The integrated plant can be completely flexible to distribute by-products according to the price to reach the maximum net present value. In Case 2 an external demand for electricity (40 MW) was imposed on the system.

Figure 20 show the NPV and estimated steelmaking costs for both cases applying different blast furnace technologies, compared to conventional blast furnace operation. On the horizontal axis the first number refers to blast furnace states (1-3, cf. Figure 14), the second to the top gas recycling rate (0 = no, 1= intermediate and 2= high level of recycling) and the last to the oxygen enrichment (1=normal, 2= intermediate level of enrichment and 3=oxyBF). Thus, e.g., 213 means BF state 2 with intermediate top gas recycling rate and cold oxygen injection.

It can be seen that scenario 323 has the highest NPV for Case 1, while the external electricity demand has a strongly reducing effect on the estimated value, also in comparison with the optimized conventional BF operation. In addition, scenario 313 (with intermediate top gas recycling rate) turns out to be promising in Case 1. It is also perceived how the combination of recycling and enrichment affects the final cost of steel production. These results illustrate the economics of integration of conventional BF (conv) with CCU (scenarios 101,201,301) and further with TGR technology.

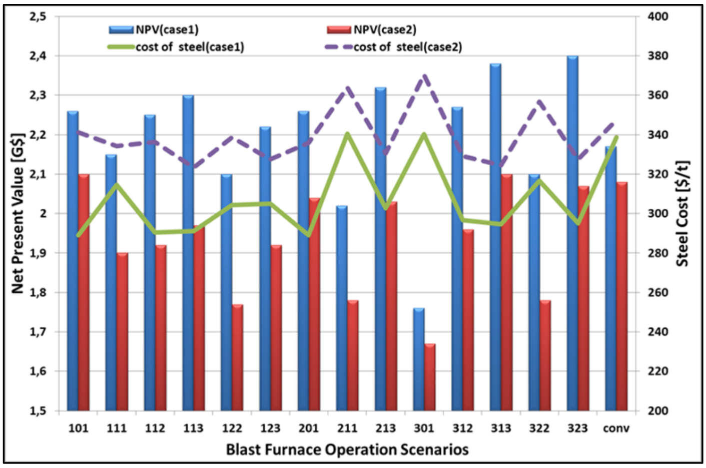

Figure 20 NPV and steel production cost of the integrated plant without (Case 1, left blue bars) and with (Case 2, red right bars) external energy demand considering different scenarios of blast furnace operation. The number codes on the abscissa express the BF operation scenario, extent of top gas recycling and oxygen enrichment. Conv represents conventional steelmaking without integration with CCU and MEOH plants. Number code: First number expresses BF states (1-3, cf. Figure 14), second the top gas recycling rate (0 = no, 1 = intermediate and 2 = high recycling) and the third the oxygen enrichment (1= normal, 2=intermediate enrichment and 3 = cold oxygen injection, i.e. oxyBF).

6.2.2 Effect of Steel Plant Production Rate and Fuels

The effect on the production rate of hot metal is investigated by varying it in the range of 140-160 t_{hm}/h and maximizing the net present value. Figure 21 shows the NPV of the integrated plant for different hot metal production rates and fuel systems. It is seen that by increasing the production rate the net present value increases. The capacity of the plant has stronger effect for the system using biofuels. The lowest value is calculated for lowest production rate with PC system and the highest value is estimated for full capacity steel plant integrated with a biomass torrefaction unit.

The specific emissions only change marginally with the production rate particularly for the system with PC, COG and NG. System with COG injection has lowest specific emission from the plant among fossil fuels. For system with biofuels, by increasing production rate, the specific CO_2 emission decreases.

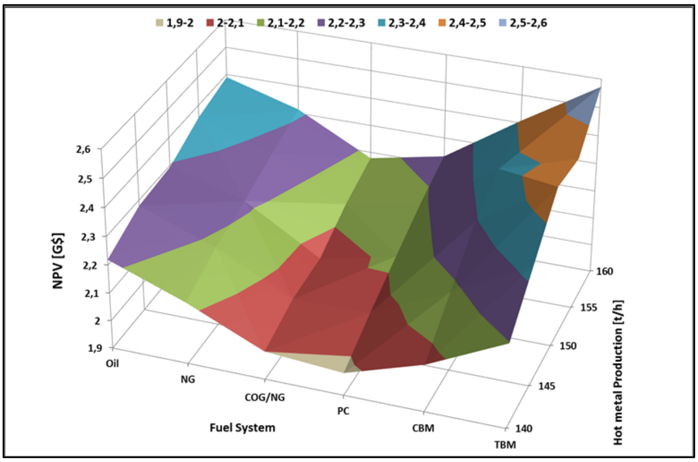

Figure 21 Net present value for different hot metal production rate and fuel systems.

6.2.3 Sensitivity Analysis

In order to analyze the sensitivity of the suggested system with oil (ISP-323), Figure 22 shows the changes in the net present value of the optimized system as perturbations of ±50% in the price of the feed material and byproducts were introduced. Quite naturally, the price of ore has the highest influence (up to 25%), followed by emissions, pellets and coal. Electricity has the lowest effect on the net present value due to the small power production in the initial state.

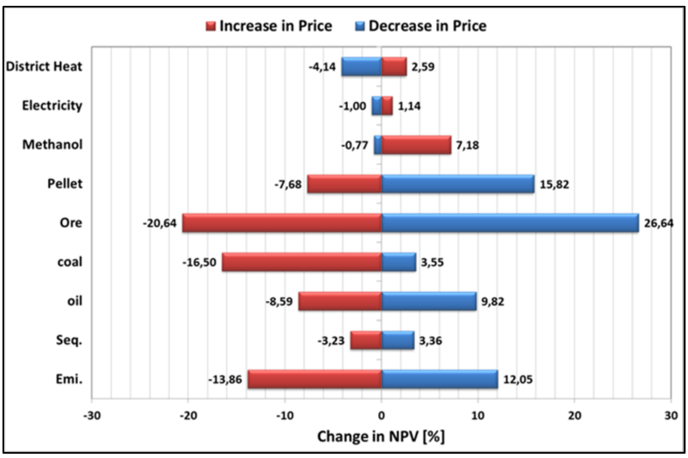

Figure 22 Sensitivity analysis of ± 50 % change in price of key feed materials and byproducts on net present value for integrated steelmaking (ISP-323).

As environmental restrictions increase, it becomes more challenging to deliver low price electricity from the steelmaking sector. On the other hand, social acceptance of electricity produced from nuclear reactors has decreased. This could be an initiative toward the concept of integration in steel plants to suppress emission from the system by replacing carbon carriers in the blast furnace, such as coke, also converting the residual off gases to fuels, which may replace fossil fuels and therefore increase the life cycle of carbon.

Figure 23 shows the sensitivity of the NPV and specific emission based on changes in the cost of CO_2 emission from the system. The results were obtained after maximizing the net present value for the superstructure with defined costs for feed materials and sequestration and price of products.

For all cases, the system has proportionally higher NPV and specific emission for a decrease in the costs of emissions (from the reference value of 56$). This effect is shown less for the system with biofuel due to minimize use of necessary fossil carbon.

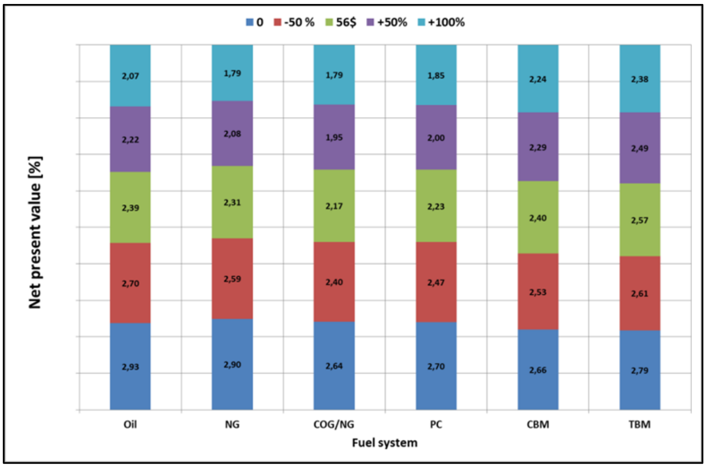

Figure 23 Sensitivity of net present value of carbon dioxide emission cost for different fuel systems.

For the system with COG/NG, CBM and PC, oxyBF operation has shown economic benefit while decreasing the specific emission due to higher cost of fuel and external coke price.

For the system with CBM and PC, extra coke is available to sell from the integrated plant. Other fuels, the first step on specific emission is for moving toward top gas recycling and oxygen enrichment and the second shift is for changing in optimal state of operation in plant particularly in PG and MEOH production. This can be seen for the system with TBM gradually effect on decrease on emission level. Among fossil fuels, the system with oil is more sensitive to change in emission costs. In higher emission costs, all fossil fuels have shown a lower boundary (~0.5 t_{CO2}/t_{ls}) for suppressing of CO_2 from the system.

6.2.4 Investment Cost Distributions

Figure 24 shows the bare module cost of unit operations selected in integrated system with different fuel supply systems by maximizing NPV over one period of operation. Results are shown for the maximum production rate of the steel plant, considering investment costs for the new processes.

The integrated system with torrefaction shows the highest NPV, it also has the second highest investment cost among the alternative fuels studied for the system. Swing adsorptions, partial oxidation of methane and gas phase methanol production are selected as the main unit processes.

CBM, PC and COG/NG are selected to operate as oxyBF with no external energy production, therefore main investment cost is for CO_2 capturing and sequestration units. Vacuum pressure swing adsorption is the main CO_2 capturing unit process. Conventional BF operation has highest NPV for the system with NG. The system has highest investment cost due to treatment of off-gases for high production of MEOH.

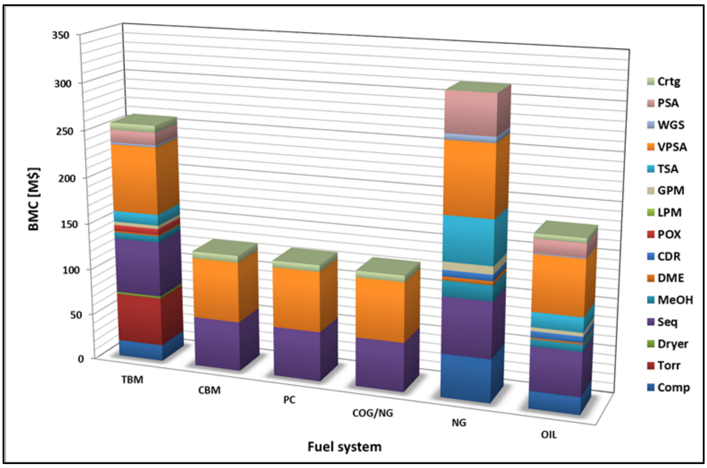

Figure 24 Percentage of bare module cost (BMC) of unit operations in different fuel systems for optimum operational state.

By comparing each scenario for NPV and emissions, there is a tradeoff between process economics, environmental impacts and energy demands. For instance, for the system with NG, OxyBF and conventional operation are competitive in the amount of emission from the system. This is balanced by the amount of carbon, which leaves from the system as methanol varying between 30-50 t/h.

This results to higher NPV for conventional operation with higher amount of methanol production for approximately 40% increase in investment costs.

6.3 Environmental Evaluation

6.3.1 Effect of Production Rate and Fuels

The effect of production rate and fuel systems on carbon dioxide emissions is investigated by maximizing the net present value. Figure 25 presents the specific emission for the integrated system for different fuels and hot metal production. The optimization results show that for biofuels, by increasing the capacity of the plant the specific emission may decrease slightly while for other fuel system a marginal increase in emission is expected. The results express that usage of coke oven gas can reduce emissions from the sector although it has lower net present value compared to the oil and natural gas systems. The integrated system with pulverized coal shows a medium behavior in terms of economic and environmental impacts: It has lower NPV and specific emission compared to the other fossil fuel-based systems.

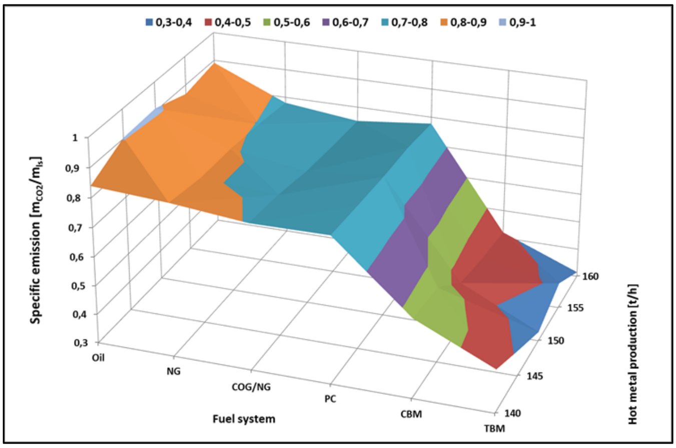

Figure 25 Specific carbon dioxide emission for different hot metal production rate and fuel systems.

6.3.2 Carbon Flow in the System

Figure 26 shows the percentage of carbon flow based on fossil resources in the integrated system and different fuel supplies after maximizing the NPV. In all cases, coal is the main source of carbon in the blast furnace steelmaking, varying between 30% and 47%.

The results show that the production of methanol can affect the carbon flow in the system while it gives a wide flexibility to distribute energy depending on demand and price toward a more sustainable operation. In case of fossil fuels, there is a trade-off between carbon dioxide sequestration and emission. This depends on the economics and development of blast furnace technology in the future.

In the case of CBM and PC use, the system produces more coke than it needs, which leaves the system while in the other cases an external supply for coke is needed.

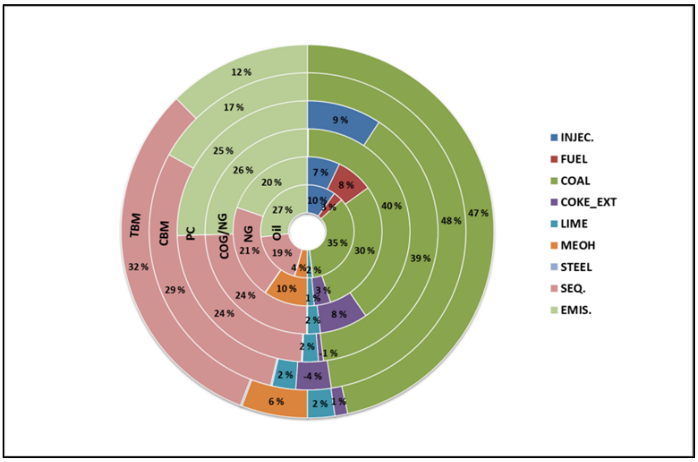

Figure **26** Percentage of carbon flow in different fuel systems for optimum operational state.

For the system with CBM, PC and COG/NG, No methanol production is expected. The optimal operation state is for oxyBF with utilization of off-gases to minimize extra fuel requirements for the system. This could be as result of higher price for these fuels. For the system with NG, conventional BF operation is chosen in combined with high MEOH production which decrease share of coal in the system down to 30% due to export of fossil based carbon as MEOH (10%) from the system.

This effect has seen by forcing the system with oxyBF operation, which exchanges 7% of carbon flow in the system between coal and MEOH. The results show, top gas recycling will change the injection rate from its upper bound (120 kg/t_{hm}) in conventional BF operation to a lower level depends on price of fuel and cost of emission and sequestration. This will affect the energy balance between preheating in hot stoves, oxygen enrichment, degree of top gas recycling and utilization of off-gases in polygeneration system considering external demands. For the system with biofuel, injection rate has observed at its upper boundary and for the system with COG/NG is 60% of available COG that it is included as carbon in coal flow.

6.4 Multi-Objective Optimization

In order to investigate the economic and environmental impact on process synthesis, a set of single objective optimization problems, applying the ε-constraint method (Bhaskar, Gupta & Ray 2000, Liu 2009), were solved using a MINLP solver in GAMS. In this case study, a set of NPV were found at different specific emission levels for given costs of specific emissions and sequestration of CO_2 (52 \$/t and 26 \$/t_{CO2}, respectively) under conventional BF operations. An advantage of a multi-objective approach is that it provides solutions from which one may select a suitable compromise based on both economic and environmental aspects. Since the objectives are non-dominated they can be represented as a Pareto frontier in a diagram, as depicted in Figure 27. The results show that for lower emission states CDR and LPMEOH and for higher net present values POR and GPMEOH are dominant unit processes.

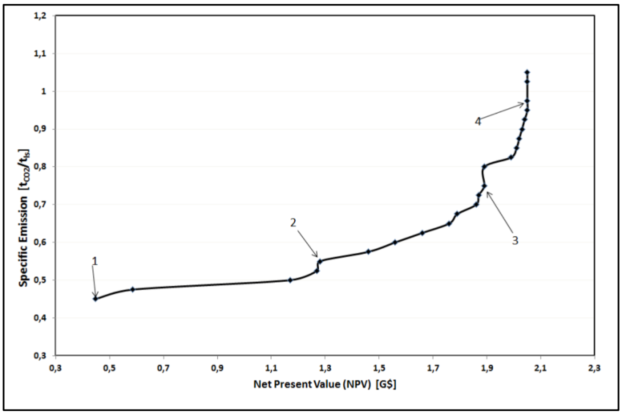

Figure 27 Pareto frontiers for maximization of net present value and minimization of specific emission rate for a conventional steel plant integrated with a polygeneration system, at a hot metal production rate of 150 t_{hm}/h and constant costs of emission and sequestration of (52 and 26 $/ t_{CO2}). Points 1-4 indicated by arrows refer to the optimal states reported in Table 9.

Table 9 Results from the model for four-selected point in the frontier diagram (Figure 27). The solutions were obtained by using MINLP solver in GAMS and maximum NPV is reported.

	1	2	3	4
NPV (G$)	0.49	1.28	1.89	2.05
Specific emission (t_{CO2}/t_{ls})	0.45	0.55	0.75	0.975
Coal flow rate (t/h)	0.0	0.0	80.1	80.16
Ore flow rate (t/h)	133.1	133.1	153.6	153.6
External Coke Rate (t/h)	56.14	52.6	0.0	0.0
Limestone Rate (t/h)	25.13	24.8	23.5	23.5
Quartzite Rate (t/h)	0.012	0.07	0.03	0.03
Pellet Rate (t/h)	90.0	90.0	70.2	70.2
Air Volume Rate (knm^3/h)	106.5	113.0	113.0	113.0
Oxygen flow Rate (knm^3/h)	21.96	17.3	17.8	18.7
Slag Rate (kg/t_{hm})	220	218.4	216.2	216.2
Scrap Rate (t/h)	37.5	37.5	37.5	37.5
Nitrogen flow rate (t/h)	47.2	56.0	56.0	56.0
DME flow rate (t/h)	0.0	0.0	0.0	0.6
Oil flow rate (t/h)	21.64	21.9	18.0	18.0
CO_2 Sequestrated (t/h)	148.7	118.8	116.1	81.6
Methanol production (t/h)	23.38	20.86	21.15	19.34
Steel Cost ($/tls)	358.4	355.1	300.3	311.0

In all states, TSA is selected for carbon monoxide recovery, PSA for hydrogen recovery, and amine-based chemical absorption for carbon dioxide capturing. Table 9 shows some of the properties (main inputs and outputs from the system) for the solutions at the four points (1-4) indicated in Figure 27. Due to relaxed constraint on external district heat and electricity in the power plant and the price of these “products”, no external district heat and electricity are produced in the states. In the low emission scenario (cf. point 1) a supply of external coke, though is more expensive, is needed to achieve lower emissions resulting in an increase in the production costs of steel. To reach a minimum emission from the suggested integrated steelmaking plant, an increase of more than 50 $\$/t_{ls}$ would be expected in the costs of steel production.

6.5 Multi-Periodic Optimization

To investigate the effect of external energy demands on the operation of the integrated system, a time period of four seasons with 0, 15, 30 and 40 MW external electricity demands was assumed. Thus, these values were activated as lower bounds during the four periods and the multi-period task was optimized. In many cases, the results of the optimization show similar states of blast furnace operation for all periods. Conventional steelmaking (conv.), integrated conventional steelmaking (ISP-201) and integrated steel plant with novel blast furnace operation (ISP-323) are three cases represented here for the sake of comparison. Figure 28 shows net present value, specific emissions, methanol production, fuel required in polygeneration, amount of CO_2 sent out of the system, BF coke rate and cost of steel production.

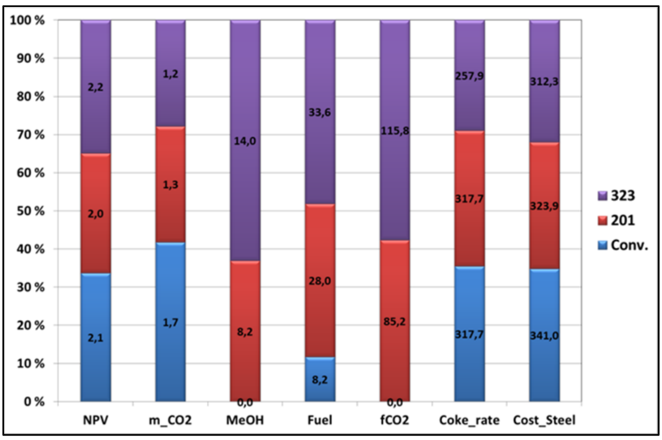

Figure 28 Comparison of net present value (NPV), specific CO_2 emissions, methanol production, external fuel (oil), carbon dioxide flow for sequestration, coke rate in the blast furnace and estimated cost of steel for conventional steelmaking, ISP-201 and ISP-323. The numbers on the bars show the value of each term for the system under periodic external energy demand.

The net present value decreases by the first step of the integration (ISP-201), but by applying blast furnace top gas recycling and oxygen enrichment, the net present value of the system may increase. Considering the result of the case studies in the paper VI, seasonal operation can be concluded to increase total net present value of the system.

The specific emissions decrease by each step of integration from 1.7 to 1.2 t_{CO2}/t_{ls}, which is lower than for the single-period operation with oil as fuel in the system.

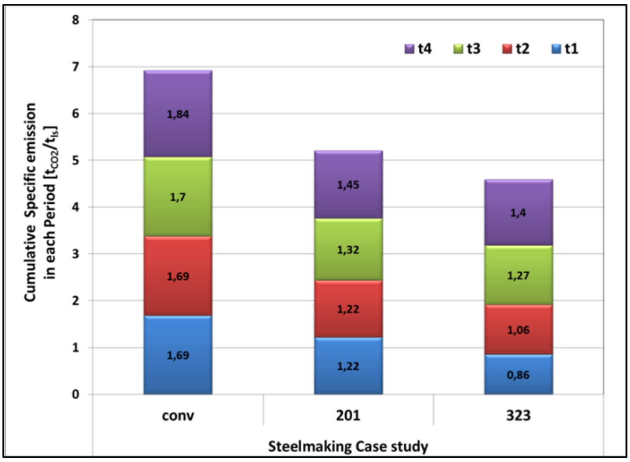

Figure 29 Cumulative specific emissions in all periods for conventional steelmaking (conv), ISP-201 and ISP-323.

Methanol, fuel and captured carbon dioxide flows increase compared to conventional steelmaking. There is a trade-off between fuel consumption and integration, which indicates the importance of the selection of auxiliary fuel, and, naturally, of fuel costs. The specific coke rate decreases by about 60 kg/t_{hm} by injecting top gases as reducing agent. From net profit analysis the cost of liquid steel production was estimated for each case, showing a potential decrease of more than 25 $/$t_{ls}$ for the integrated system.

Figure 29 illustrates the specific emissions for three cases in each of the periods. The specific emissions from the system increase along with the external electricity demand. Conventional steelmaking is seen to operate with specific emissions close to 1.7 t_{CO2}/t_{ls} up to period 3. The cumulative emissions illustrate the lower emissions of the top gas recycling concepts, despite the increase along with the increasing external demand of electricity.

Finally, Figure 30 shows the estimated steelmaking cost for the optimized cases in each period. The maximum difference in the steel cost occurs in Period 1 (without specific external demand) which indicates the flexibility of the integrated system to reach lower costs by flexible production. The largest difference in the cost of steel production is between the conventional system and the system with top gas recycling and cold oxygen injection in the BF (ISP-323). The flexibility of the integration is also seen for the period with maximum external power demand (Period 4), where the steelmaking cost of ISP-323 are still lower than in conventional steelmaking without external constraints on the power production.

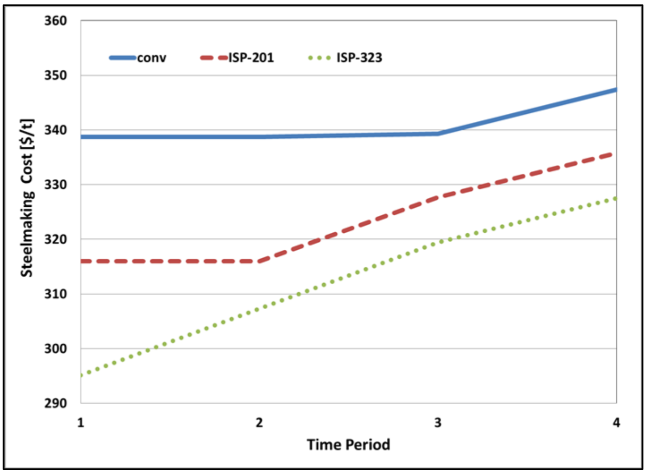

Figure 30 Comparison between steel costs for conventional steelmaking, ISP-201 with sequestration and ISP-323 for different periods.

7 CONCLUSION AND FUTURE PROSPECTS

In this study, process integration techniques have been applied to numerically investigate future steelmaking concepts and their possibilities for enhanced sustainability. Several options have been studied, where difficult decision-making situations arise. Limitations in terms of mathematical formulations, hardware and computational time however impose restrictions on the level of details in the studies.

Primary steelmaking is characterized by regional constraints as each blast furnace has a unique behavior and its operation depends on availability of feed materials, and also the other conditions in the steel plants vary. Economy and environmental aspects as well as social impacts are other important factors to be considered.

As Nordic blast furnaces are already highly optimized, it is important to investigate the effect of new technologies and developments on the economy of the steelmaking operation. Paper I investigates the effect of methanol as carbon and energy carrier, produced as byproducts of a future steel plant with a blast furnace operated under top gas recycling and blast oxygen enrichment, using different costs of CO_2 emission and sequestration. The results indicate that the oxygen blast furnace could be a promising approach due to a suitable composition of the top gases and the eco-environmental effects of CCS. It is important to stress that for low emission costs the optimized system operates without top gas recycling and for the oxygen blast furnace; the degree of recycling is not on its highest level at the economic optimum.

Paper II studies steel production rate and different fuels in the integrated system. Pyrolysis of the biomass was considered to examine effects of integration by minimizing the manufacturing costs of steel. The effect of partial replacement of coke with biomass can be more effective when the cost of emission is high and its effect will decrease by minimizing amount of coke requirement in the BF.

Paper III focuses on the effect of reducing agents injection in the oxygen blast furnace as a main potential to minimize the emission levels. In all cases studied, injecting auxiliary reductants to the blast furnace lowers the steel production cost, but this positive effect decreases at increasing specific emission costs. At the highest emission cost, there is no economic benefit of oil or natural gas injection. In all scenarios, injecting auxiliary reductants increases the specific emission rate mainly due to lower optimal top gas recycling rate. This effect becomes less prominent at increasing emission costs.

In the further analysis, a different optimization method known as the equation-oriented approach replaced the sequential modular one used in the earlier papers of the thesis to tackle broader problems. Paper IV proposes a superstructure for carbon capturing and utilization considering different available technologies for gas treatment integrated with primary conventional steelmaking. Process synthesis and analysis suggest an optimal operation and design for the system.

Paper V modifies the model to implement top gas recycling and oxygen enrichment concepts together with a polygeneration system, using with different auxiliary reductants/fuels under different seasonal energy demands. The result shows the effect of external energy demands on single periodic operation of the system on the level of design and operation as an integrated energy system. This concept further developed in Paper VI, combined with three different gas (recycled top gas and/or blast) preheating concepts considering a VPSA unit process for CO_2 capturing. In the analysis, a large number of scenarios of design and operation are investigated, and the complex entity is studied under multi-periodic optimization method with respect to economic objectives. The results demonstrate that there is a trade-off between economic profit and emissions from the system. Applying top gas recycling and cold oxygen injection in the blast furnace decreases the emissions from the system and an integration of the steel plant with a polygeneration system increases the economic profitability.

Finally, in Paper VII the system is studied with different auxiliary reducing agents, including the integration with a torrefaction unit for biomass processing under different steel production rates. The model can explore different scenarios and states for future sustainable development of the traditional blast furnace-based steelmaking route. Top gas recycling combined with oxygen enrichment of the blast can reduce emission from steel industry and cold oxygen operation may have economic advantages. The results show that the incorporation of a torrefaction process can be an option to suppress emissions in the path towards sustainable development of this industrial sector.

As for future prospects work, replacing the pricewise linear model used in the present work for the blast furnace with an explicit model that can be integrated in the optimization scheme would reduce the number of binary variables, which decreases the computational effort. Furthermore, the laborious re-linearization and model validation needed when new operational states (e.g., new raw materials or reductants) are to be considered. Some of the unit process models, as well as for CO_2 transportation and sequestration should be updated to become more detailed to consider the entity better and to achieve results on more realistic cases.

An extension of the integration to consider secondary steelmaking processes, such as rolling, and the use of new raw materials and alternative reduction processes, e.g., for direct reduced iron (DRI), or integration with other industrial units (e.g., a bio-refinery and ammonia production) are also expected to provide useful information for future developments.

Furthermore, Stochastic and enterprise-wide optimization approaches could be applied to consider raw material uncertainty and addressing integrated planning, scheduling, real-time optimization and inventory control of the supply chains of the process.

ABBREVIATIONS

(V)PSA	(Vacuum) Pressure Swing Adsorption
3R	Reduce, Reuse, Recycle
6R	Reduce, Reuse, Recover, Redesign, Remanufacture, Recycle
ASU	Air Separation Unit
BATs	Best Available Technologies
BB	Branch and Bound
BF	Blast Furnace
BFG	Blast Furnace Gas
BL	Blast
BMC	Bare Module Cost
BOF	Basic Oxygen Furnace
BOFG	Basic Oxygen Furnace Gas
CBF	Conventional Blast Furnace
CBM	Charcoal BioMass
CCA	CO_2 Chemical Absorption
CCM	CO_2 Capturing Membrane
CCP	Carbon Capturing Plant
CCU	Carbon Capturing and Utilization
CDR	Carbon Dioxide Reforming
CFD	Computational Fluid dynamics
CHP	Combined Heat and Power plant
COG/cog	Coke Oven Gas
COPURE	Chemical absorption unit
COURSE50	CO_2 Ultimate Reduction in Steelmaking Process by Innovation Technology for Cool Earth 50
CP	Coke Plant
DEM	Discrete Element Method
DME	Dimethyl Ether purification
DR	Direct Reduction
DRI	Direct Reduction Iron
EAF	Electric Arc Furnace
EBFC	European Blast Furnace Committee
ECP	Extended Cutting Plane
EO	Equation Oriented
EWO	Enterprise Wide Optimization
GBD	General Bender Decomposition
GDP	General Disjunctive Programming
GHG	Green House Gases
GPMEOH	Gas Phase methanol rector
GS	Gas Separation units
GSP	Gas Separation unit
HYL	Hylsa steel company
INT	Integrated
IT	Information Technology
ITmk3	Ironmaking Technology mark three
LP	Linear Programming
LPMEOH	Liquid Phase methanol reactor

M	Big-M
MATLAB	MATrix LABoratory
MEM	Membrane separation
MEOH	Methanol purification
MIDREX	Midland Ross Experimental
Min	Minimizing
MINLP	Mixed Integer Nonlinear Programming
MOO	Multi-Objective Optimisation
MP	Methanol Plant
NLP	Non-Linear Programming
NP	Net Profit
OA	Outer Approximation
OBF	Oxygen Blast Furnace
PGS	PolyGeneration System
PI	Process Integration
POR	Partial Oxidation Reforming
PS	Process Synthesis
PSE	Process System Engineering
PYRU	PYRolysis Unit
s.t.	Subject to
rTG	recycled Top Gas
SCM	Supply Chain Management
Seq.	Sequestration
SL/RN	Stelco,-Lurgi,/Republic steel- National lead
SM	Sequential Modular
SMR	Steam Methane Reforming
SP	Sinter Plant
SR	Smelting Reduction
TBF	Top gas recycling Blast Furnace
TBM	Torrefied BioMass
TCI	Total Capital Investment
TG	Top Gas
TSA	Temperature Swing Adsorption
ULCOS	Ultra Low CO_2 Steelmaking
WCED	World Commission on Environment and Development
WGS	Water Gas Shift reactor
WSP	Water Separation unit

Roman and Greek symbols

θ	Time period
C°	Base Cost
S°	Base Capacity
A, a	(In)equalities coefficients
c	Cost Factor
F	Flow Rate, Feedstock
f_0	Objective Function
f_1	Equality constraints
f_2	Inequality constraints

G	Constraint in disjunctions
h^c	Cost Equations
h^e	Energy Equations
h^m	Mass Equations
h^{p}	Pressure Equations
P	Pressure
r	Common constraints
R	Product Recovery
S	Capacity
T	Temperature
t	tone
X	Vector of components
Y	Vector of integers/Boolean variables, integers
Y	integer
Ω	Propositional logic
C	Fixed Charges
α	Exponential Scaling
β	Adsorbent Selectivity
γ	Corresponding term for Fixed Charges in disjunction
δ	Annual Discount Rate
λ	Tax Rate
τ	Period
χ	Mass Fraction of Carbon in Materials

Subscripts and superscripts

c	cost
dp	Depreciation period
e	Energy
emis.	Emission
ext.	External
hm	Hot metal
i	Materials
inj	Injectant to BF
injr	Injection rate to BF
j	Unit Processes
k	disjunction
K	Set of disjunctions
L, l	Set or number of terms
lp	Life period
ls	Liquid Steel
m	Mass
m	Fuels
mc	Manufacturing Cost
n	Number of components
P	Pressure
p	Product
s	States of BF operations

REFERENCES

Ambrosio, C. & Lodi, A. 2013, "Mixed integer nonlinear programming tools: an updated practical overview", *Annals of Operations Research,* vol. 204, no. 1, pp. 301-320.

Arvola, J., Harkonen, J., Mottonen, M., Haapasalo, H. & Tervonen, P. 2011, "Combining Steel and Chemical Production to Reduce CO2 Emissions.", *Low Carbon Economy,* vol. 2, no. 3, pp. 115-122.

Babich, A., Gudenau, H., Mavrommatis, K., Froehling, C., Formoso, A., Cores, A. & Garcia, L. 2002, "Choice of technological regimes of a blast furnace operation with injection of hot reducing gases", *Revista de metalurgia,* vol. 38, no. 4, pp. 288-305.

Batidzirai, B., Mignot, A.P.R., Schakel, W.B., Junginger, H.M. & Faaij, A.P.C. 2013, "Biomass torrefaction technology: Techno-economic status and future prospects", *Energy,* vol. 62, pp. 196-214.

Belotti, P., Lee, J., Liberti, L., Margot, F. & Wächter, A. 2009, "Branching and bounds tighteningtechniques for non-convex MINLP", *Optimization Methods & Software,* vol. 24, no. 4, pp. 597-634.

Bermúdez, J.M., Arenillas, A., Luque, R. & Menéndez, J.A. 2013, "An overview of novel technologies to valorise coke oven gas surplus", *Fuel Processing Technology,* vol. 110, pp. 150-159.

Bhaskar, V., Gupta, S. & Ray, A. 2000, "Applications of multiobjective optimization in chemical engineering", *Reviews in Chemical Engineering,* vol. 16, no. 1, pp. 1-54.

Biegler, L.T., Grossmann, I.E. & Westerberg, A.W. (eds) 1997, *Systematic Methods of Chemical Process Design*, 1st. edn, Prentice Hall PTR, NJ, USA.

Birat, J.P. 2009, "Steel and CO2 -the ULCOS program, CCS and Mineral carbonation using Steelmaking Slag", 1st International Slag Valorisation Symposium, Leuven, Belgium., 6-7 Apr.

Bisio, G. & Rubatto, G. 2000, "Energy saving and some environment improvements in coke-oven plants", *Energy,* vol. 25, no. 3, pp. 247-265.

Bisio, G., Bosio, A. & Rubatto, G. 2002, "Thermodynamics applied to oxygen enrichment of combustion air", *Energy Conversion and Management,* vol. 43, no. 18, pp. 2589-2600.

Biswas, A.K. 1981, *Principales of Blast Furnace Ironmaking,* 1st Ed. edn, Cootha Publishing House, Brisbane, Australia.

Brundtland, G.H. 1987, *World Commission on Environment and Development (WCED):Our Common Future*, UN Documents, Gathering a Body of Global Agreements, Oslo, Norway.

Burer, S. & Letchford, A.N. 2012, "Non-convex mixed-integer nonlinear programming: A survey", *Surveys in Operations Research and Management Science,* vol. 17, no. 2, pp. 97-106.

Cano Ruiz, J.A. 1999, *Decision support tools for environmentally conscious chemical process design*, Massachusetts Institute of Technology, MA, USA.

Castle, W. 2002, "Air separation and liquefaction: recent developments and prospects for the beginning of the new millennium", *International Journal of Refrigeration-Revue Internationale Du Froid,* vol. 25, no. 1, pp. 158-172.

Chen, Y. 2012, *Optimal design and operation of energy polygeneration systems*, Massachusetts Institute of Technology, MA, USA.

Cheng, W. & Kung, H.H. 1994, *Methanol production and use,* 1st edn, CRC Press, NY, USA.

Chu, Y. & Gao, C. 2014, "Data-based multiscale modeling for blast furnace system", *AIChE Journal,* vol. 60, no. 6, pp. 2197-2210.

Costello, R. 2011, *COPureSM Process*, Personal communication.

Danloy, G., Berthelemot, A., Grant, M., Borlée, J., Sert, D., Van der Stel, J., Jak, H., Dimastromatteo, V., Hallin, M., Eklund, N., Edbery, N., Sundqvist, L., Sköld, B.-., Lin, R., Feiterna, A., Korthas, B., Müller, F., Feilmayr, C. & Habermann, A. 2009, "ULCOS-Pilot testing of the low-CO2 Blast Furnace process at the experimental BF in Luleå", *Revue de Métallurgie, An International Journal of Metallurgy,* vol. 108, no. 106, pp. 1.

Eberle, A., Bohrn, W., Milionis, K., Tessmer, G. & Reidetschlager, J. 1999, "Smelting reduction and direct reduction of iron ores VAI technologies for scrap substitutes (COREX (R), FINMET (R), FINEX (R))", *Australian Institute of Mining and Metallurgy Publication Series,*International Conference on Alternative Routes of Iron and Steelmaking, , 15-17 Sep, pp. 211.

Eigenvector research incorporated 2011, *"PLS_Toolbox v.6.5.2" Advanced Chemometrics software for use with Matlab*, http://www.eigenvector.com/.

Eklund, N., Lindblom, B., Winstrom, J. & Bjorkman, B. 2009, "Operation at High Pellet Ratio and Without External Slag Formers - Trials in an Experimental Blast Furnace", *Steel Research International,* vol. 80, no. 6, pp. 379-384.

El-Halwagi, M. 2012, *Sustainable Design through Process Integration - Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement,* 1st edn, Elsevier, MA, USA.

EPA 2012, *Available and Emerging Technologies for Reducing Greenhouse Gas Emissions from the Iron and Steel Industry*, Sector Policies and Program Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

Erwee, M.W. & Pistorius, P.C. 2012, "Nitrogen in SL/RN direct reduced iron: origin and effect on nitrogen control in EAF steelmaking", *Ironmaking & Steelmaking,* vol. 39, no. 5, pp. 336-341.

Faleiro, R.M.R., Velloso, C.M., de Castro, L.F.A. & Sampaio, R.S. 2013, "Statistical modeling of charcoal consumption of blast furnaces based on historical data", *Journal of Materials Research and Technology,* vol. 2, no. 4, pp. 303-307.

Fick, G., Mirgaux, O., Neau, P. & Patisson, F. 2014, "Using Biomass for Pig Iron Production: A Technical, Environmental and Economical Assessment", *Waste and Biomass Valorization,* vol. 5, no. 1, pp. 43-55.

Floudas, C.A. 1995, *Nonlinear and mixed-integer optimization: fundamentals and applications,* 1st edn, Oxford University Press, New York, USA.

Fu, J., Tang, G., Zhao, R. & Hwang, W. 2014, "Carbon Reduction Programs and Key Technologies in Global Steel Industry", *Journal of Iron and Steel Research, International,* vol. 21, no. 3, pp. 275-281.

GAMS Development Corporation 2014, *GAMS (General Algebraic Modeling System) Software v23.7.3*, http://www.gams.com/.

Ghosh, A. & Chatterjee, A. 2008, *Ironmaking and Steelmaking: Theory and Practice,* 1st edn, Prentice-Hall of India Private Limited, New Delhi, India.

Ghosh, A. & Majumdar, S.,K. 2011, "Modeling blast furnace productivity using support vector machines", *The International Journal of Advanced Manufacturing Technology,* vol. 52, no. 9-12, pp. 989-1003.

Grossmann, I. 2005, "Enterprise-wide optimization: A new frontier in process systems engineering", *AIChE Journal,* vol. 51, no. 7, pp. 1846-1857.

Grossmann, I.E. & Guillén-Gosálbez, G. 2010, "Scope for the application of mathematical programming techniques in the synthesis and planning of sustainable processes", *Computers & Chemical Engineering,* vol. 34, no. 9, pp. 1365-1376.

Grossmann, I. 2002, "Review of Nonlinear Mixed-Integer and Disjunctive Programming Techniques", *Optimization and Engineering,* vol. 3, no. 3, pp. 227-252.

Guo, T., Chu, M., Liu, Z., Tang, J. & Yagi, J. 2013a, "Mathematical Modeling and Exergy Analysis of Blast Furnace Operation With Natural Gas Injection", *steel research international,* vol. 84, no. 4, pp. 333-343.

Guo, W., Wang, J., Gao, W. & Wang, H. 2013b, "Study on the Preparation of Higher Alcohols Using Blast Furnace Gas and Coke Oven Gas", *Advances in Chemical, Material and Metallurgical Engineering,* vol. 634-638, pp. 842-845.

Gupta, P.K., Rao, A.S., Sekhar, V.R., Ranjan, M. & Naha, T.K. 2010, "Burden distribution control and its optimisation under high pellet operation", *Ironmaking & Steelmaking,* vol. 37, no. 3, pp. 235-239.

Harvey, J. & Gheribi, A.E. 2014, "Process Simulation and Control Optimization of a Blast Furnace Using Classical Thermodynamics Combined to a Direct Search Algorithm", *Metallurgical and Materials Transactions B,* vol. 45, no. 1, pp. 307-327.

Hasanbeigi, A., Arens, M. & Price, L. 2014, "Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review", *Renewable and Sustainable Energy Reviews,* vol. 33, pp. 645-658.

Hasanbeigi, A., Price, L. & Arens, M. 2013, *Emerging Energy-efficiency and Carbon Dioxide Emissions-reduction Technologies for the Iron and Steel Industry*, Ernest Orlando Lawrence, Berkeley National Laboratory, CA, USA.

Hayashi, M. & Mimura, T. 2013, "Steel Industries in Japan Achieve Most Efficient Energy Cut - off Chemical Absorption Process for Carbon Dioxide Capture from Blast Furnace Gas", *Energy Procedia,* vol. 37, pp. 7134-7138.

Hein, M. & Kaiswe, M. 2012, *Environmental Control and Emission Reduction for Coking Plants, Air Pollution - A Comprehensive Perspectiven,* InTech, Rijeka, Croatia.

Helle, H. 2014, *Towards sustainable Iron-and steelmaking with economic optimization*, Åbo Akademi University, Åbo, Finland.

Helle, M., Pettersson, F., Chakraborti, N. & Saxén, H. 2006, "Modelling noisy blast furnace data using genetic algorithms and neural networks", *Steel research international,* vol. 77, no. 2, pp. 75-81.

Helle, H., Helle, M. & Saxén, H. 2011, "Nonlinear optimization of steel production using traditional and novel blast furnace operation strategies", *Chemical Engineering Science,* vol. 66, no. 24, pp. 6470-6481.

Henis J.M.S. & Tripodi, M.K. 1980, *Multicomponent Membrane for Gas Separations*, US4230463 edn, USA.

Hooey, P.L., Bodén, A., Wang, C., Grip, C. & Jansson, B. 2010, "Design and application of a spreadsheet-based model of the blast furnace factory", *ISIJ International,* vol. 50, no. 7, pp. 924-930.

Hooey, L., Tobiesen, A., Johns, J. & Santos, S. 2013, "Techno-economic Study of an Integrated Steelworks Equipped with Oxygen Blast Furnace and CO2 Capture", *Energy Procedia,* vol. 37, pp. 7139-7151.

Huitu, K., Kekkonen, M. & Holappa, L. 2009, *Novel Steelmaking Process-Liturature Study and Critical Review*, Helsinki University of Technology Publications, Finland.

Husain, R., Sneyd, S. & Weber, P. 1997, "Circored((R)) and Circofer((R)) two new fine ore reduction processes", *Australian Institue of Mining and Metallurgy Publication Series*International Conference on Alternative Routes of Iron and Steelmaking, Victoria, WA, AUS, pp. 129.

Jahanshahi, S., Deev, A., Haque, N., Lu, L., Mathieson, J., Norgate, T., Pan, Y., Ridgeway, P., Rogers, H. & Somerville, M. 2014, "Current Status and Future Direction of Low-Emission Integrated Steelmaking Process", *Celebrating the Megascale: Proceedings of the Extraction and Processing Division Symposium on Pyrometallurgy in Honor of David GC Robertson*John Wiley & Sons, Inc., , pp. 303.

Jak, E. & Hayes, P. 2012, "The Use of Thermodynamic Modeling to Examine Alkali Recirculation in the Iron Blast Furnace", *High Temp. Mater. Process,* vol. 31, pp. 657-665.

Jayal, A.D., Badurdeen, F., Dillon Jr., O.W. & Jawahir, I.S. 2010, "Sustainable manufacturing: Modeling and optimization challenges at the product, process and system levels", *CIRP Journal of Manufacturing Science and Technology,* vol. 2, no. 3, pp. 144-152.

Johansson, M.T. & Söderström, M. 2011, "Options for the Swedish steel industry – Energy efficiency measures and fuel conversion", *Energy,* vol. 36, no. 1, pp. 191-198.

Joyner, K. 2000, "Fastmet (R)/Fastmelt (R): the final steps in waste recovery", *Revue De Metallurgie-Cahiers D Informations Techniques,* vol. 97, no. 4, pp. 461-469.

Klawonn, R. & Siuka, D. 2006, "Current status and future of the Midrex direct reduction technology", *Stahl Und Eisen,* vol. 126, no. 3, pp. 23-29.

Klemes, J.J. (ed) 2013, *Handbook of Process Integration (PI)*, Woodhead Publishing, Cambridge, United Kingdom.

Klemes, J.J., Varbanov, P.S. & Kravanja, Z. 2013, "Recent developments in Process Integration", *Chemical Engineering Research and Design,* vol. 91, no. 10, pp. 2037-2053.

Kulinich, V. 2007, "Thermodynamic modeling of the blast-furnace smelting of hot metal", *Steel in Translation,* vol. 37, no. 4, pp. 356-361.

Kuramochi, T., Ramírez, A., Turkenburg, W. & Faaij, A. 2012, "Comparative assessment of CO2 capture technologies for carbon-intensive industrial processes", *Progress in Energy and Combustion Science,* vol. 38, no. 1, pp. 87-112.

Kuramochi, T., Ramírez, A., Turkenburg, W. & Faaij, A. 2011, "Techno-economic assessment and comparison of CO2 capture technologies for industrial processes: Preliminary results for the iron and steel sector", *Energy Procedia,* vol. 4, pp. 1981-1988.

Lam, H.L., Klemes, J.J., Kravanja, Z. & Varbanov, P.S. 2011, "Software tools overview: process integration, modelling and optimisation for energy saving and pollution reduction", *Asia-Pacific Journal of Chemical Engineering,* vol. 6, no. 5, pp. 696-712.

Lampreia, J., De Araujo, Maria Silvia Muylaert, De Campos, C.P., Freitas, M.A.V., Rosa, L.P., Solari, R., Gesteira, C., Ribas, R. & Silva, N.F. 2011, "Analyses and perspectives for Brazilian low carbon technological development in the energy sector", *Renewable and Sustainable Energy Reviews,* vol. 15, no. 7, pp. 3432-3444.

Lee, S. & Grossmann, I.E. 2001, "A global optimization algorithm for nonconvex generalized disjunctive programming and applications to process systems", *Computers & Chemical Engineering,* vol. 25, no. 11–12, pp. 1675-1697.

Li, B., Duan, Y., Luebke, D. & Morreale, B. 2013, "Advances in CO2 capture technology: A patent review", *Applied Energy,* vol. 102, pp. 1439-1447.

Lie, J.A., Vassbotn, T., Hägg, M., Grainger, D., Kim, T. & Mejdell, T. 2007, "Optimization of a membrane process for CO2 capture in the steelmaking industry", *International Journal of Greenhouse Gas Control,* vol. 1, no. 3, pp. 309-317.

Linnhoff, B., Townsend, D.W., Boland, D., Hewitt, G.F., Thomas, B.E.A., Guy, A.R. & Marsland, R.H. 1994, *A User Guide on Process Integration for the Efficient Use of Energy,* revised edition edn, Institution of Chemical Engineers, Rugby, U.K.

Linnhoff, B. & Hindmarsh, E. 1983, "The pinch design method for heat exchanger networks", *Chemical Engineering Science,* vol. 38, no. 5, pp. 745-763.

Liu, P. 2009, *Modelling and Optimisation of Polygeneration Energy Systems*, Imperial College London, London, UK.

Lophaven, S.N., Nielsen, H.B. & Sondergaard, J. 2002, *Aspects of the Matlab toolbox DACE*, Informatics and mathematical Modeling, DTU, Denmark.

Luengen, H., Peters, M. & Schmöle, P. 2012, "Ironmaking in Western Europe", *Iron and Steel Technology,* vol. 9, no. 3, pp. 63.

Lungen, H.B. & Schmöle, P. 2004, "Blast furnace operation without coke and carbon?", *Stahl Eisen,* vol. 124, pp. 63.

Mitra, T. 2011, *Modelling of blast furnace focusing on transition to 100% pellet operation*, Åbo Akademi Univesity, Åbo, Finland.

Modesto, M. & Nebra, S.A. 2009, "Exergoeconomic analysis of the power generation system using blast furnace and coke oven gas in a Brazilian steel mill", *Applied Thermal Engineering,* vol. 29, no. 11–12, pp. 2127-2136.

Moon, J., Kim, S. & Sasaki, Y. 2014, "Effect of Preheated Top Gas and Air on Blast Furnace Top Gas Combustion", *ISIJ International,* vol. 54, no. 1, pp. 63-71.

Moya, J.A. & Pardo, N. 2013, "The potential for improvements in energy efficiency and CO2 emissions in the EU27 iron and steel industry under different payback periods", *Journal of Cleaner Production,* vol. 52, pp. 71-83.

Nogami, H., Chu, M. & Yagi, J. 2005, "Multi-dimensional transient mathematical simulator of blast furnace process based on multi-fluid and kinetic theories", *Computers & Chemical Engineering,* vol. 29, no. 11, pp. 2438-2448.

Nogami, H., Kashiwaya, Y. & Yamada, D. 2014, "Simulation of Blast Furnace Operation with Hydrogen Injection", *Tetsu to Hagane-Journal of the Iron and Steel Institute of Japan,* vol. 100, no. 2, pp. 251-255.

Norgate, T. & Langberg, D. 2009, "Environmental and economic aspects of charcoal use in steelmaking", *ISIJ International,* vol. 49, no. 4, pp. 587-595.

Oda, J., Akimoto, K., Sano, F. & Homma, T. 2009, "Diffusion of CCS and energy efficient technologies in power and iron & steel sectors", *Energy Procedia,* vol. 1, no. 1, pp. 155-161.

Pettersson, F., Chakraborti, N. & Saxén, H. 2007, "A genetic algorithms based multi-objective neural net applied to noisy blast furnace data", *Applied Soft Computing,* vol. 7, no. 1, pp. 387-397.

Pettersson, F., Saxén, H. & Deb, K. 2009, "Genetic algorithm-based multicriteria optimization of ironmaking in the blast furnace", *Materials and Manufacturing Processes,* vol. 24, no. 3, pp. 343-349.

Phanphanich, M. & Mani, S. 2011, "Impact of torrefaction on the grindability and fuel characteristics of forest biomass", *Bioresource technology,* vol. 102, no. 2, pp. 1246-1253.

Porter, M.C. 1990, *Handbook of Industrial Membrane Technology: The Separation of Gases by Membrane,* 1st edn, Noyes Publications, NJ, USA.

Quintella, C.M., Hatimondi, S.A., Musse, A.P.S., Miyazaki, S.F., Cerqueira, G.S. & Moreira, A.d.A. 2011, "CO2 capture technologies: An overview with technology assessment based on patents and articles", *Energy Procedia,* vol. 4, pp. 2050-2057.

Rabo, J.A., Francis, J.N. & Angell, C.L. 1977, *Selective Adsoption of Carbon Monoxide from Gas Streams*, US4019879 edn, USA.

Remus, R., Monsonet, M.A.A., Roudier, S. & Sancho, L.D. 2013, *Best Available Techniques (BAT) Reference Document for Iron and Steel Production*, Industrial Emissions Directive, JRC Reference Report, 2010/75/EU.

Richlen, S. 2000, *Using coke oven gas in a blast furnace saves over 6$ million anually at a steel mill*, Office of Industrial Technologies Energy Efficiency and Renewable Energy, EE-20 U.S. Department of Energy, PA, USA.

Rist, A. & Meysson, N. 1967, "A dual graphic representation of the blast furnace mass and heat balances", *J METALS,* vol. 19, no. 4, pp. 50-59.

Roark, S.E. & White, J.H. 2004, *Selective Removal of Carbon Monoxide*, US6787118 edn, USA.

Rocha, E.P.d., Guilherme, V.S., Castro, J.A.d., Sazaki, Y. & Yagi, J. 2013, "Analysis of synthetic natural gas injection into charcoal blast furnace", *Journal of Materials Research and Technology,* vol. 2, no. 3, pp. 255-262.

Ruthven, D.M., Farooq, S. & Knaebel, K.S. 1994, *Pressure Swing Adsorption,* 1st edn, VCH wiley, USA.

Saari, J., Zakri, B., Sermyagina, E. & Vakkilainen, E. 2013, "Integration of Torrefaction Reactor with Steam Power Plant", *The 8th International Black Liquor Colloquium – Black liquor and Biomass to Bioenergy and Biofuels,*Federal University of Minas Gerais (UFMG), Brazil, May 19-23.

Sahinidis, N. 1996, "BARON: A general purpose global optimization software package", *Journal of Global Optimization,* vol. 8, no. 2, pp. 201-205.

Sandberg, J., Wang, C. & Larsson, M. 2013, "Analysis of Oxygen Enrichment and its Potential Influences on the Energy System in an Integrated Steel Plant Using a New Solution Space Based Optimization Approach", *International Journal of Energy Engineering,* vol. 3, pp. 28.

Saxén, H., Bramming, M., Wikstrom, J. & Wiklund, P. 2001, "Theoretical limits on operation under high oxygen enrichment in the blast furnace", *60th Ironmaking Conference*Iron and Steel Society Ironmaking Division, Ironmaking Conference, MD, USA, March 25-28, pp. 721.

Slaby, S., Andahazy, D., Winter, F., Feilmayr, C. & Bürgler, T. 2006, "Reducing ability of CO and H2 of gases formed in the lower part of the blast furnace by gas and oil injection", *ISIJ International,* vol. 46, no. 7, pp. 1006-1013.

Steel Stewardship Forum 2014, *, Bluescope Steel, Basic Oxygen Steel Making Process*. Available: http://steelstewardship.com/.

Suopajärvi, H. & Fabritius, T. 2013, "Towards more sustainable ironmaking—an analysis of energy wood availability in finland and the economics of charcoal production", *Sustainability,* vol. 5, no. 3, pp. 1188-1207.

Suopajärvi, H., Pongrácz, E. & Fabritius, T. 2014, "Bioreducer use in Finnish blast furnace ironmaking–Analysis of CO2 emission reduction potential and mitigation cost", *Applied Energy,* vol. 124, pp. 82-93.

Suopajärvi, H., Pongrácz, E. & Fabritius, T. 2013, "The potential of using biomass-based reducing agents in the blast furnace: A review of thermochemical conversion technologies and assessments related to sustainability", *Renewable and Sustainable Energy Reviews,* vol. 25, pp. 511-528.

Tobiesen, F.A., Svendsen, H.F. & Mejdell, T. 2007, "Modeling of blast furnace CO2 capture using amine absorbents", *Industrial & Engineering Chemistry Research,* vol. 46, no. 23, pp. 7811-7819.

Tonomura, S. 2013, "Outline of Course 50", *Energy Procedia,* vol. 37, pp. 7160-7167.

Torp, T.A. 2005, "Drastik reduksjon av drivhusgasser fra stalproduksjon med CO2 Fangst & Lagring (CCS)–ULCOS prosjektet", *Technical Committee, ULCOS Steering Committee Meeting*ULCOS Consortium, Rome, Italy, 27 June.

Tseitlin, M.A., Lazutkin, S.E. & Styopin, G.M. 1994, "A Flow-Chart for Iron Making on the Basis of 100-Percent Usage of Process Oxygen and Hot Reducing Gases Injection", *ISIJ International,* vol. 34, no. 7, pp. 570-573.

Tsuge, O., Kikuchi, S., Tokuda, K., Ito, S., Kobayashi, I. & Uragami, A. 2002, "Successful iron nuggets production at ITmk3 pilot plant", *61st Ironmaking Conference Proceedings,* vol. 61, pp. 511-519.

Ueda, S., Natsui, S., Nogami, H., Yagi, J. & Ariyama, T. 2010, "Recent progress and future perspective on mathematical modeling of blast furnace", *ISIJ International,* vol. 50, no. 7, pp. 914-923.

Van Dijk, C.P., Solbakken, A. & Rovner, J.M. 1983, *Methanol from coal and Natural Gas*, US4407973 edn, USA.

Vaswani, S. 2000, *Development of Models for Calculating the Life Cycle Inventory of Methanol by Liquid Phase and conventional Production Process*, Department of Civil Engineering, Raleigh, NC, USA.

Vecchietti, A. & Grossmann, I.E. 1997, "LOGMIP: a disjunctive 0–1 nonlinear optimizer for process systems models", *Computers & Chemical Engineering,* vol. 21, Supplement, pp. S427-S432.

Viswanathan, J. & Grossmann, I.E. 1990, "A combined penalty function and outer-approximation method for MINLP optimization", *Computers & Chemical Engineering,* vol. 14, no. 7, pp. 769-782.

Wang, C., Cameron, A., Bodén, A., Karlsson, J. & Hooey, L. 2011a, "Hot stove oxygen-enriched combustion in an iron-making plant", *Swedish-Finnish Flame Days, "Challenges in Combustion Technology today"* The National Committees of Sweden and Finland of the International Flame Research Foundation (IFRF) and the Scandinavian-Nordic Section of the Combustion Institute, Piteå, Sweden, Jan 26-27.

Wang, C., Karlsson, J., Hooey, L. & Bodén, A. 2011b, "Application of oxygen enrichment in hot stoves and its potential influence on the energy system in an integrated steel plant", *International conference of World Renewable Energy Congress*Linköpning universitet, Linköping, sweden, May 8-13.

Wang, C., Larsson, M., Ryman, C., Grip, C.-., Wikström, J.-., Johnsson, A. & Engdahl, J. 2008, "A model on CO2 emission reduction in integrated steelmaking by optimization methods", *International Journal of Energy Research,* vol. 32, no. 12, pp. 1092-1106.

Wang, S., Lu, G. & Millar, G. 1996, "Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art RID C-5507-2008 RID A-2859-2008", *Energy & Fuels,* vol. 10, no. 4, pp. 896-904.

Watakabe, S., Miyagawa, K., Matsuzaki, S., Inada, T., Tomita, Y., Saito, K., Osame, M., Sikström, P., Ökvist, L.S. & Wikstrom, J. 2013, "Operation Trial of Hydrogenous Gas Injection of COURSE50 Project at an Experimental Blast Furnace", *ISIJ International,* vol. 53, no. 12, pp. 2065-2071.

Wieder, K., Boehm, C., Schmidt, U. & Grill, W. 2009, "COREX (R) Prepared for Present and Future Iron Making Challenges", *Journal of Iron and Steel Research International,* vol. 16, pp. 1238-1244.

World Steel Association 2013a, *Steel Statistical Yearbook 2013*, worldsteel Committee on Economic Studies, Brussels, Belgium.

World Steel Association 2013b, *Steel's Contribution to a Low Carbon Future*, World Steel Association, http://www.worldsteel.org/.

Xu, C. & Cang, D. 2010, "A Brief Overview of Low CO2 Emission Technologies for Iron and Steel Making", *Journal of Iron and Steel Research, International,* vol. 17, no. 3, pp. 1-7.

Zevenhoven, R., Fagerlund, J. & Songok, J.K. 2011, "CO2 mineral sequestration: developments toward large scale application", *Greenhouse Gases: Science and Technology,* vol. 1, no. 1, pp. 48-57.

Zhu, J., Zhang, D. & King, K. 2001, "Reforming of CH4 by partial oxidation: thermodynamic and kinetic analyses", *Fuel,* vol. 80, no. 7, pp. 899-905.

Zuo, G. & Hirsch, A. 2009, "The Trial of the Top Gas Recycling Blast Furnace at LKAB's EBF and Scale-up", *Revue De Metallurgie-Cahiers D Informations Techniques,* vol. 106, no. 9, pp. 387-392.

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