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Chemical and process integration for environmental assessment

Development and evaluation of a chemical recycling concept for plastic waste

Thesis for the degree of philosophiae doctor

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Abstract

The thesis focuses on systems oriented methods in conceptual design and analysis of chemical processes, both with respect to environmental performance. The areas of process synthesis and process systems engineering offer a considerable number of methodologies and tools for designing integrated production systems, ranging from individual processes to total sites. In this thesis the well established tools, life cycle assessment (LCA) and process integration (PI), have been applied in evaluation and design of sustainable production systems. LCA considers the environmental performance of a process or product (more common) from “cradle to grave”, whereas process integration focus on optimization of energy consumption in a system. In addition, chemical integration and substance flow analysis (SFA) that also aim at sustainability through more efficient use of raw materials and chemicals have been adapted and applied to processes. In the case of chemical integration, a new definition has been proposed that makes it closely related to process integration.

An important concept used in process synthesis, design and optimization of production systems is the so-called superstructure representation. The idea is to include alternative raw materials, alternative processing steps and to some extent alternative products and by-products in a common representation of multiple flowsheets, where the selection of a single flowsheet with corresponding feed and product streams is made (through optimization) by setting binary variables to either zero or one. In this work, the superstructure concept is not used for optimization purposes, but rather to illustrate how a mix of raw materials, a mix of products, by-products and intermediates, as well as a mix of processing steps can be used to obtain maximum utilization of chemicals and energy. In other words, a multi chain chemical complex may result rather than a single production chain focusing on one main product.

The thesis also demonstrates, the benefits of combining process integration and LCA, in particular when the focus is on CO_2 emissions and mitigating the global warming problem. LCA sets the scene for process integration by indicating where the largest emissions are generated, while process integration improves the quality of the LCA by delivering better and more consistent data to the LCA study. An algorithm (LCA-PI) for combined use of LCA and process integration has been developed with accompanying models in Excel and HYSYS. Division of the emissions into process and utility waste has proven helpful in tracking of the origin of all emissions. While LCA has been used for a long time to assess the environmental performance of a product that serves a specific function, there are so far few studies where LCA has been used to analyse processes and production systems.

The plastic waste to plastic concept (PtP) has been used as a case study throughout the thesis. The PtP concept is a new concept for chemical recycling of plastic waste back to new plastic materials. In the core PtP concept, plastic waste is chemically converted to synthesis gas in an oxygen operated gasifier. After adjusting the H_2/CO ratio in a water gas shift reactor (WGS), the synthesis gas is converted into methanol before olefins are produced by the Hydro/UOP patented methanol to olefins (MTO) process. Olefins are

then the building block for several different types of plastic. The concept is flexible both with regard to input (other carbonaceous material) and output (methanol, hydrogen, energy), and intermediate products can be added in order to adjust for scale. By inclusion of other inputs, outputs or intermediates the term “extended PtP concept” is used.

The core PtP concept has been developed and evaluated by use of both traditional systems oriented methods, like process integration and life cycle assessment, and application of the methodologies and the algorithm proposed by the thesis. Further, the same methodologies have been used in development and evaluation of the extended PtP concept, which are able to decrease the greenhouse gas emissions from the plastic waste to plastic concept.

Preface

First of all I will give my thanks to my teaching supervisor Truls Gundersen at Department of energy and process engineering. Lots of thanks also to Jon Hovland, Steinar Kvisle, Unni Ingvild Musdalslien and Per Sandberg at Norsk Hydro for valuable discussions and providing data for the calculations.

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Thanks also to my friends who have encouraged me to fulfil the task, and of course to my colleagues that have challenged my ideas and helped me with valuable discussions. I must also express my gratitude to the students that have been involved in my project during their Master thesis, the work you have been doing have been most helpful to me.

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Kristin Herder Kaggerud

Table of contents

1 Introduction

The topic of this thesis is use of systems oriented methods in conceptual design and analysis of chemical processes, with respect to environmental performance. The scope is limited to the early design phase and a concept for recycling of plastic waste is used as the main case study throughout the thesis. The unit operations have been modeled with a limited level of details, for example with respect to the number of chemical components and the complexity of the reactor models. For most chemical reactors a Gibbs model has been used. The reason for not doing a more rigorous process modeling is the scope of the study. The focus is on system analysis at a superior level, looking at the theoretical optimum. If the theoretical optimum shows promising results, more detailed modeling and assessment should be undertaken; this is, however, not the scope of this thesis. Rather than spending large resources on complex models in the early design phase, the potential of the system is screened by use of simplified models.

Process design has been categorized as an iterative three step procedure by Hendry et al. (1973), where conceptual design (process synthesis) and process analysis are the first two steps, whereas process optimization is the final step. The thesis focuses on the first two steps. A short introduction to how evaluation/optimization can be applied to the system is, however, given in Chapter 8. The aim is to show how Life Cycle Assessment (LCA) and other systems oriented methods can be applied in minimization of greenhouse gas emissions (CO_2-equivalents) in the early design phase of a system. As greenhouse gas emissions represent an important aspect in treatment of carbonaceous materials, special attention has been given to this impact category. The methods used and developed in this thesis can, however, easily be expanded to include other impact categories.

A new plastic recycling concept has been chosen as the case study throughout the thesis. Plastic waste available for recycling is increasing steadily due to increased use of plastics. The increased environmental awareness has also led to more stringent directives and legislation for the treatment of plastic waste. One example is the ban on landfilling of carbonaceous waste in Germany and Sweden. There are several waste treatment options available, but most of them either require a small and uncontaminated waste stream, or produce products of lower value. The idea behind the recycling concept presented and evaluated here is to be able to treat large, mixed waste streams and convert them into high quality products by use of chemical recycling.

Increased environmental awareness has led to more environmentally friendly products and processes. Over the last decades a new aspect has been increasingly important; the life cycle perspective. The life cycle perspective means that all activities related to a product should be included, from cradle to grave, in order to decrease the overall environmental impact with respect to the given product and to provide a fair comparison between alternative configurations and products that serve a given function. The best solution is to avoid waste from being generated, both within the production processes and the rest of the lifetime of a product. In a production process, waste minimization brings the dual benefit of lower effluent treatment costs and lower raw material cost. In the remaining lifetime of the product, minimization of transport, waste generated during use and of course final disposal that is subject to waste minimization. This thesis deals with all these perspectives.

Detailed economic evaluation of the system is not part of this thesis. Economic considerations will, however, be included in some of the system evaluations. In Pinch analysis, the choice of a smallest allowed temperature difference in heat exchangers (ΔT_{min}) is based on economic assessments. Furthermore, the discussion about additional units in the system is both an economic and environmental question as they can improve the performance of the system, while additional investment costs and emissions from construction and operation need to be accounted for. Finally, in Chapter 8 a qualitative discussion is provided on how to perform a multiobjective optimization based on both economic and environmental criteria.

1.1 Outline of the thesis

Chapter 2 introduces the reader to the field of systems oriented methodologies. The chapter provides an overview of the methodologies used throughout the thesis within process synthesis and environmental assessment. The aim is not to present a thorough literature review of the field, but rather to present some of the early contributions (to familiarize with the terms) as well as important (and more recent) review articles. In particular, the chapter provides the basis for Chapter 3 and subsequent systems oriented discussions.

Chapter 3 shows how the superstructure approach can be applied at a block diagram level in order to utilize both energy and chemicals (atoms). The idea of integrating energy and chemicals is applied to case studies where power is produced from natural gas. The systems discussed have the underlying constraint that any power production must be subject to CO_2 capture. The chapter is based on two published papers; Kaggerud et al. (2004a) and Kaggerud et al. (2006).

Chapter 4 gives an overview of the use of plastic materials in Europe as well as the availability of plastic waste. Various recycling options are described briefly, and the future prospective of plastic waste handling is discussed.

Chapter 5 presents the chemical recycling concept "Plastic waste to plastic" (PtP), followed by a description of the unit operations in the PtP and the extended PtP scheme. The PtP concept is used as the main case study throughout the rest of the thesis. Part of the chapter is based on Kaggerud et al. (2004b).

Chapter 6 presents results from the various system evaluations of the PtP concept, in order to show the potential and limitations of the concept. The results indicate the need for combination of various methods in order to do a thorough environmental assessment. The chapter ends with a comparison of the PtP concept with virgin production of plastic, other recycling alternatives for plastic waste as well as a comparison with the use of biomass instead of plastic waste in the same process train as the PtP scheme. The chapter is based on Kaggerud et al. (2005a), Kaggerud et al. (2005b), Kaggerud and Gundersen (2006a), Nouri and Kaggerud (2006) and Nouri, Kaggerud and Tillman (2007).

Chapter 7 shows how process integration and life cycle assessment can be combined to improve the quality of both. The combination of life cycle assessment and process integration has been implemented in the form of an algorithm. It is shown how life cycle assessment and process integration can be used in process design, and the extended PtP concept is used as a case study to quantify the findings in the improved assessment. The early results are published in Kaggerud and Gundersen (2006b).

Chapter 8 gives an introduction to how process optimization, which is the last stage in the process design, can be envisaged in the content of the topics of this thesis.

Chapter 9 sums up the work and highlights its contributions before giving suggestions and directions for further research.

1.2 Main contributions

The main contributions in this work are divided into two categories; 1) methodology development, and 2) development and evaluation of a chemical recycling concept for plastic waste. The main contributions in each category are listed below:

1. Methodology development
    - Use of a superstructure representation to illustrate combined chemical and process integration (best combination of raw materials, process steps, intermediates and final products, both materials and energy).
    - A new definition of chemical integration is proposed that makes it strongly related to process integration.
    - Chemical integration and the superstructure approach have been used to evaluate how the atom utilization within a system can be maximized.
    - Process integration and LCA applied to processes rather than products.
    - Algorithm for combined use of process integration and LCA.
    - Division of the emissions into process and utility waste has been applied for tracking of the origin of all emissions.

2. Chemical recycling concept
    - Application of the above mentioned methodologies to a chemical recycling concept.
    - Development and evaluation of the core plastic waste to plastic concept.
    - Decreased greenhouse gas emissions from the plastic waste to plastic concept by development and evaluation of the extended plastic waste to plastic concept.

2 Systems oriented methodologies

Purpose of the chapter:

1. *Introduce the reader to the field of systems oriented methodologies*
2. *Overview of the methodologies used throughout the thesis*
3. *Some details about tools*
4. *Literature review of early contributions as well as important review articles*

2.1 Why systems approach?

A system as the term is used here is defined as (Walker, 1999):

"A portion of matter, or a group or set of things that forms a complex or connected whole."

Systems consist of components or sub-systems which interact with each other to perform some larger function (Rudd and Watson, 1968). Within the field of chemical engineering, examples of components are heaters, reactors, tanks and dryers, whereas a sub-system might be the methane steam reformer section of a methanol plant. The components and sub-systems interact with each other in such a way that the performance of each component is strongly dependent of the other components. In order to understand the system, one needs to know both the operation of each component and the links between them (Rudd and Watson, 1968).

General systems theory was introduced in the late 1940s by Bertalanffy (1950). It is an interdisciplinary field that studies the properties of systems. When systems theory is applied to engineering tasks it is called systems engineering. Systems engineering integrates all of the engineering disciplines while considering the complete problem throughout the entire lifecycle of a product or process. Cybernetics is a related field (François, 1999). One branch of systems engineering is process systems engineering (PSE), where systems engineering is applied to process systems. Process synthesis, process integration and life cycle assessment are examples of various approaches within process systems engineering.

Systems oriented methodologies take into account both the components and how they are interacting, which means that the approach is good at analysis of large complex systems. Further, a systems approach helps in making decisions about the total process or plant, rather than only the unit operations. It is important to take the total system into account when making decisions with respect to economy, energy, operability, environmental performance and so on.

2.2 Process synthesis

Process synthesis was pioneered by Rudd and co-workers in the late 1960s (Rudd and Watson, 1968; Masso and Rudd, 1969) based on treatments of the synthesis of heat-exchange networks and synthesis of multicomponent distillation sequences. Arthur D. Little developed the concept of unit operations in 1915 which gave birth to the field of chemical engineering (King, 2000). With the chemical engineering concept, case studies and trial and error were used, putting various unit operations into flowsheets for development of new concepts. With process synthesis or "conceptual design" the development of new concepts and processes moved to a more systems oriented approach. The more or less ad hoc analysis of flowsheets was replaced by systematic numerical solution techniques. Process synthesis is a systematic approach to the selection between potentially profitable alternatives to produce desired products from available raw materials and is part of the larger field, process systems engineering (PSE). PSE is a class of systems oriented approaches to the engineering of processes, including control, simulation, integration, optimization, etc. The first textbook in process synthesis was published by Rudd et al. (1973).

Several review articles have been published, showing a steady increase in the number of available papers. The first review on process synthesis dates back to 1973 and was undertaken by Hendry, Rudd and Seader (1973). Later, Hlavacek (1978), covering the years from 1973-1978, followed by Westerberg (1980), Nishida, Stephanopoulos, and Westerberg (1981) and Umeda (1983) provided additional reviews. A thorough review of the field has not been undertaken the last 20 years, but according to Westerberg (2004), the number of papers is increasing rapidly. Li and Kraslawski (2004) have given a review of the trends in conceptual process synthesis. They have adopted the three scales of process synthesis development suggested by the Committee on chemical engineering frontiers (1988); micro, meso and macro scale. This is shown in Figure 2.1.

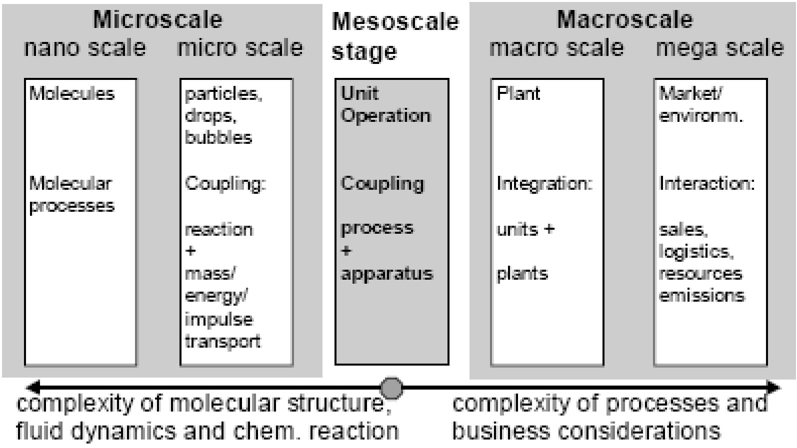

Figure 2.1: Three scales of development in process synthesis (Li and Kraslawski, 2004)

Li and Kraslawski (2004) claim that process synthesis started at the meso scale, then by 1990 the macro scale was adopted due to the increasing environmental awareness, and finally the micro scale was introduced in 1995 with development of new unit operations and molecular design. Examples of methods and applications used in the meso scale are optimization-based approaches and heuristic approaches like synthesis of heat exchanger networks, reaction systems and separation. The macro scale typically requires the simultaneous optimization of environmental and economic objectives, and the entire system and life cycle is described rather than the individual elements. Finally, the micro scale deals with process intensification and design of specialty chemicals. The micro scale is outside the scope of this thesis. Methods and applications are described in more detail in Sections 2.2.1 and 2.2.2.

Process systems are characterized by the nature of the process components and their interconnections, as well as the capacities and the operating conditions of the process components (Hendry et al., 1973). Consequently, process design is an iterative process due to the interrelationships between the stages. In synthesis, the goal is to conceive a system that will, upon analysis, meet the requirements and specifications. An analysis starts with a postulated system structure, which is evaluated with respect to a given set of design specifications and system operating processes. Synthesis is the first stage in a proper design procedure (Hendry et al., 1973):

1) **Synthesis**: Combining the process elements into a coherent whole.
2) **Analysis**: Decomposition of the whole into its constituent elements for individual study of performance.
3) **Evaluation/Optimization**: Select and improve the best solution of the candidates identified by the iterative process of synthesis and analysis.

There are two different situations that can be encountered in process synthesis; grassroot and retrofit design (Smith, 2005). Grassroot design is the design of new plants, whereas retrofit is modification of existing plants. The most straightforward design is the grassroot design, as it has the freedom to choose the design options and the size of the equipment. Retrofit on the other hand, makes changes or additions to an existing plant in order to achieve expanded and/or more economical operation, meaning that the plant with its equipment is given, and the design needs to take that into account. This thesis deals only with grassroots design.

Examples of process synthesis methods and applications are given in the following sections. The intention is not to give a thorough review of the field, but rather to list some of the early contributions.

2.2.1 Process synthesis methods

Process synthesis methods are divided into the categories as given by Hendry et al. (1973): Process design decomposition, heuristics, direct optimization and evolutionary systems. In addition, thermodynamic methods are introduced as a separate category. The various approaches are presented and the major, early contributions are listed.

1. Process design decomposition

Design of new systems is extremely complex, including a large number of potential unit operations and interconnections. Rudd (1968) proposed to overcome the problem by braking down the system to manageable subsystems. Large systems where no previous technology exists are consequently decomposed into a sequence of sub-design problems where the technology exists. Later, Linnhoff et al. (1982) presented the onion diagram which has been used to conceptually decompose the design procedure into distinct steps, starting with selection of the reactor path, followed by separators, compressors and expanders and finally the heat exchanger network. Douglas (1985) developed a hierarchical decomposition approach, which is now widely accepted: 1) choosing between continuous and batch operation, 2) selecting the raw materials and products, 3) selecting the reactor system based on the reaction selectivities, 4) designing the vapor and liquid separation systems, and 5) designing the heat recovery system.

2. Heuristic synthesis techniques

The use of heuristics and rules of thumb are common in chemical engineering, and process synthesis is not an exception. Without heuristics, the problems faced in design of industrial processes would be too difficult to converge and too large to search (Westerberg, 2004). Masso and Rudd (1969) suggested a modification of the process design decomposition by including heuristics in design of heat exchanger networks. However, optimality of the resulting solution can, of course, not be guaranteed by use of heuristics.

3. Synthesis by direct optimization

In this case, all possible process flowsheets are embedded into one combined flowsheet (often referred to as a superstructure) by defining all the unit operations and interactions that might exist between them. Techniques of optimization and mathematical programming are then applied to choose among the options in the combined flowsheet. This technique was introduced by Ichikawa et al. (1972), following the proposal by Sargent (1967) that design and operation of chemical processes could be looked at as mathematical programming problems. Design tasks are formulated as optimization problems with mathematical models consisting of an objective function and a set of equality and inequality constraints. Without simplifications and approximations, the vast majority of process synthesis problems will be mixed integer non-linear programming (MINLP) models. MINLP models are the most complicated models to solve, with only a few solution methods, none of them being general. For all classes of mathematical programming models, there are two major challenges when it is applied to process design (Gundersen, 1991): 1) Non-convex models (which create local optima) and 2) Combinatorial explosion (which makes it impossible to solve large industrial problems). Papoulias and Grossmann (1983a,b,c) published a series of three articles which describe how a structural optimization approach in process synthesis can be applied to utility systems, heat recovery networks and total processing systems.

4. Evolutionary synthesis

Evolutionary synthesis is the synthesis of new processes by modification of existing ones. The objective is to find the subtask which after modification gives rise to an improvement of the system. McGalliard and Westerberg (1972) published a procedure to determine whether a feasible modification to a given feasible structure would improve the system, whereas King, Gantz and Barnes (1972) applied evolutionary synthesis to an ethylene plant.

5. Thermodynamic methods
Thermodynamic methods have been used to identify the performance targets before the more detailed design of the system or process is undertaken. The knowledge about the target values are used in the design phase by providing guidelines for the design. Examples of thermodynamic methods are pinch technology and exergy analysis. Pinch analysis is, for example, used in order to identify the minimum amount of utilities needed within a system. Pinch analysis used in targeting is described by Linnhoff et al. (1982). Exergy analysis provides information of available energy within the system, or the ability to do work. Kotas (1995) gives an introduction to the exergy method and how exergy can be applied to analyze unit operations and entire plants.

2.2.2 Applications of process synthesis techniques

Synthesis of heat exchanger networks and synthesis of entire chemical processes are used in this thesis, whereas reactor networks, separation sequences and retrofit are outside the scope of this thesis.

The applications are presented in the sequence proposed by Douglas (1985), and divided into design of homogeneous and heterogeneous systems. Homogeneous approaches are those who concentrate on one type of unit operation only, such as heat exchangers or distillation columns. Heterogeneous approaches are those who combine various types, like distillation and absorption. It is important to distinguish these terms as homogeneous systems often can be made complete, meaning that all possible alternatives can be embedded in the superstructure. This is not the case with heterogeneous approaches, and the engineer will usually have to make several heuristic based decisions in the superstructure.

1. Synthesis of reaction paths (Homogenous)
The problem is to find the sequence of reactions which can be used to reach the desired product from available raw materials. Umeda (1983) and Westerberg (2004) provide an overview of the research in reaction path synthesis. The direct evaluation of chemical reactions is a difficult task, where most approaches are based on thermodynamic calculations like heat of reaction and Gibbs free energy (Umeda, 1983). Thermodynamics alone is, however, not enough as the kinetics of the system needs to be estimated to assess the commerciality.

2. Reactor networks (Homogeneous)
When the desired reaction path is chosen, the next step is to choose the reactor network and type of reactors. Reactor networks can be advantageous compared to using single reactors. Aris (1964) developed a dynamic programming model that determines the optimum number of reactor stages in a CSTR. Chitra and Govind (1985 a,b) proposed

to optimize a superstructure where both stirred tanks and continues plug flow reactors were present. Later Glasser et al. (1987) proposed to use the attainable region to map all possible compositions from fixed feed and a given set of reactions with corresponding rate equations. They further combined this with the choice of reactors. Feinberg (2002) has given a review of the attainable regions used for reactors.

3. Multicomponent distillation sequences (Homogeneous)
The multicomponent distillation problem is concerned with the optimal selection and sequencing of distillation columns to meet the product requirements. Due to the combinatorial difficulties which result in a rapid increase in number of possible column sequences, the system can be formidable to solve beyond just a few components. To overcome the combinatorial problem, Lockhart (1947) developed heuristics to reduce the number of combinations. The first quantitative approach to the optimum distillation sequence was taken by Rod and Marek (1959). Other fields of interest are the best heat integrated sequences introduced by Andrecovich and Westerberg (1985) and separation of azeotropic mixtures by Poellmann and Blass (1994) and Petlyuk (1998). The latest approach within multicomponent distillation is separation systems with reactions in the columns, introduced by Balashov and Serafimov (1980).

4. Selection and sequencing of separation processes (Heterogeneous)
The more general multicomponent separation problem where several alternative separation techniques are being considered was first approached by Siirola and Rudd (1971) and Powers (1972). El-Halwagi and Manousiouthakis (1989) developed the synthesis of mass exchange networks, which can be applied to separation processes that use a mass-separating agent. The method is close to pinch analysis, based on thermodynamics and identification of pinch points.

5. Heat exchanger networks (Homogeneous)
A homogenous sub-problem of process synthesis is the synthesis of networks with heat-exchangers, heaters, coolers, condensers and vaporizers to supply the heating and cooling required by the system. Synthesis of heat exchanger networks was one of the pioneer approaches to process synthesis. Early investigators dealt with fixed equipment arrangements (Broeck, 1944). Later Westbrook (1961) presented a more general optimization approach based on dynamic programming. The pinch design method was introduced in 1983 (Linnhoff and Hindmarsh, 1983), and is based on thermodynamic methods. Important review articles on heat exchanger network systems are provided by Gundersen and Naess (1988), Ježowski (1994a,b), and a more recent “annotated bibliography” by Furman and Sahinidis (2002).

6. Energy transfer networks (Heterogeneous)
In addition to synthesis of heat exchanger networks as described above, this approach does also include expansion, compression and the use of refrigerants for cooling within a system. King et al. (1972) were the first to apply heterogeneous energy transfer networks in their study. Later Andrecovich and Westerberg (1985) showed how distillation columns could be included in the evaluation of energy transfer networks.

Biegler et al. (1997) showed how side strippers, enrichers, intercoolers and heaters could be included in the same evaluation.

7. Entire chemical processes (Heterogeneous)
The goal for all process synthesis activities is to discover the best complete flowsheet to accomplish a chemical manufacturing goal. The problem of synthesizing the entire chemical process is a formidable task, and an initial step towards the difficult problem was taken by Siirola (1970) and Powers (1971). Siirola et al. (1971), Siirola and Rudd (1971) and Powers (1972) have used a combination of the method of heuristics, direct search and evolutionary search in their approach to synthesis of entire chemical processes. The hierarchical approach by Douglas (1985) and the onion diagram by Linnhoff et al. (1982), both discussed in Section 2.2.1, are later examples of how process synthesis have been applied to entire chemical processes. Friedler et al. (1992a,b, 1993 and 1995) introduced the concept of process-graphs (P-graphs) which represent the structures of a process system mathematically.

8. Retrofit
Systematic process synthesis reached the stage of being routinely used in industrial *grassroot* design projects during the 1980s. Retrofit problems, however, were not systematically approached until the late 1980s. Most design tasks are retrofit tasks, rather than grassroots design (Barnicki and Siirola, 2004). Grossmann et al. (1987) argued that retrofit projects are more complicated than grassroots design, as the design space include doing a grassroots design as an alternative. A review of retrofit process design was undertaken by Gundersen (1990).

It is evident that process synthesis is complex and covers a large number of applications and approaches. In addition to the applications mentioned above, process synthesis has been used within operational issues, like operability, flexibility and control, however, these topics are not included in this thesis.

Process integration, as stated above, was one of the early applications of process synthesis. Chemical integration is less known, dealing with atom utilization and waste reduction through integration of processes. Process integration and chemical integration are presented in Section 2.3 and 2.4. Before going into the details of integration, some important aspects of the superstructure approach is given in Section 2.2.3.

2.2.3 Superstructure

A superstructure can be constructed at different levels of detail, starting with a superior description on block diagram level, through a more detailed choice between for instance absorption and distillation as the separation process, down to the most detailed level of for instance heat exchanger networks. Smith (2005) and Biegler et al. (1997) give examples of the last two superstructures. The various levels are summarized below:

1) Block diagram level: choice between e.g. methanol production or ammonia production from syngas

2) Complete flowsheets: choice between e.g. absorption or distillation as the separation process
3) Detailed subflowsheets: choice between e.g. various heat exchanger networks, distillation sequences or reactor schemes

The block diagram level is the one used in chemical integration, described in Section 2.4, whereas process integration will typically be part of a detailed subflowsheet. The superstructure approach on block diagram level is adopted in Chapter 3, showing how it can be used on a natural gas based process system, and in Chapter 5 where it is applied to a waste handling system for plastic waste. A special issue in the waste handling system is that rather than knowing the desired products, as is typical in process synthesis, the raw material is known, whereas the products can be chosen based on economic, technical and environmental criteria.

The first time a formal mathematical definition of a superstructure was given, was by use of the P-graph. Process graphs (P-graphs) have been proposed to alleviate difficulties encountered by approaches based on conventional graphs, e.g. digraph and signal-flow graph. The P-graph was introduced as a process synthesis approach by Friedler et al. (1992a,b, 1993 and 1995). The P-graph is bipartite, containing information of both the syntactic and semantic content in order to represent the structures of a process system. This is necessary to be able to describe process synthesis superstructures. The aim of the P-graph is to give a unique characterization of the superstructure, where materials and unit operations are given as the vertices, and the arcs of the graph give direction of the material flows in the system.

Mathematical programming was introduced in Section 2.2.1, in this section it is discussed in relation with P-graphs. A mathematical programming method consists of two steps, the generation of the mathematical model (process synthesis) and solving the mathematical model (process analysis). According to Friedler et al. (1993), the majority of the mathematical programming methods deal only with the second step, and further the mathematical description of a superstructure, despite its importance, has not been subject to in-depth mathematical properties. The description of the superstructure by use of P-graphs is one way to describe the model mathematically. Friedler et al. (1993) have developed an algorithm which can be used to generate maximal structures from P-graphs and a set of axioms. The maximal structure is the union of all combinatorial feasible process structures and is also the combinatorial minimized superstructure of a synthesis problem.

The P-graphs have been widely used in process synthesis, among other integrated process and heat exchanger networks (Nagy et al., 2001), modeling of systems for renewable resources (Halasz et al., 2005) and synthesis of mass exchange networks (Lee and Park, 1996).

2.3 Process integration

The definition of process integration (PI) varies. However, a general definition has been given by the International Energy Agency (IEA, 1993):

"Systematic and general methods for designing integrated production systems, ranging from individual processes to total sites, with special emphasis on the efficient use of energy and reducing environmental effects."

The IEA definition has later been broadened to include aspects of operation and maintenance for both new and retrofit applications:

"Process Integration is the common term used for the application of methodologies developed for System-oriented and integrated approaches to industrial process plant design for both new and retrofit applications.

Such methodologies can be mathematical, thermodynamic and economic models, methods and techniques. Examples of these methods include: Artificial Intelligence (AI), Hierarchical Analysis, Pinch Analysis and Mathematical Programming.

Process Integration refers to Optimal Design; examples of aspects are: capital investment, energy efficiency, emissions, operability, flexibility, controllability, safety and yields. Process Integration may also refer to some aspects of operation and maintenance".

A closer look at one of the process integration methodologies, pinch technology is taken below. Pinch technology is applied in Chapter 6 and 7 in the thesis.

2.3.1 Pinch technology

Pinch technology is a widely used methodology within process integration. Hohman (1971) and Linnhoff and Flower (1978a,b) provided the remarkable observation that one could compute the minimum utility requirement for a given heat recovery problem without inventing the network. Pinch technology first identifies sources of heat (termed hot streams) and sinks (termed cold streams) from the material and energy balances of the system. The enthalpy of all hot and cold streams is added, respectively, in order to produce the composite curves. When the composite curves for the hot and cold streams are plotted in a temperature-enthalpy diagram, the energy target for the process can be identified. An illustration of composite curves is given in Figure 2.2. The composite curves accumulate heating and cooling demand in all temperature intervals.

The pinch point is found where the temperature difference between the two curves is at the minimum. The process is divided at pinch; below pinch there is heat surplus (heat source) and above pinch there is heat deficit (heat sink). Heat is recovered in the overlapping region between the composite curves, and the remaining parts of the composite curves give the targets for hot and cold utilities above and below pinch, respectively. The correct relative location of the composite curves is given by an economic trade-off between capital and energy, represented by a specific value of ΔT_{min}.

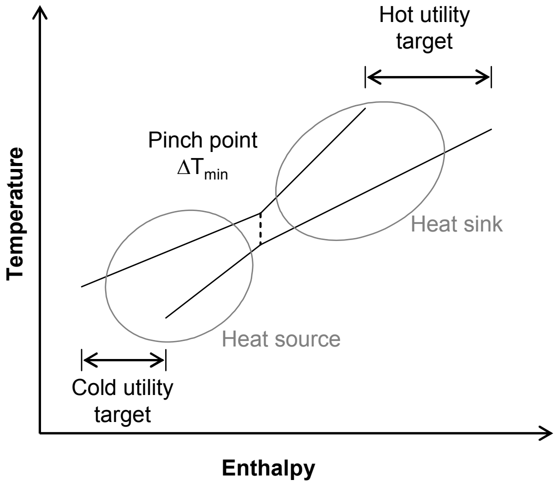

Figure 2.2: Temperature-enthalpy diagram with composite curves for the process (Linnhoff et al., 1982)

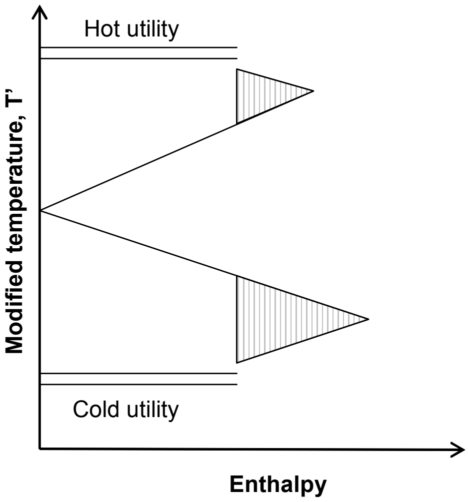

Figure 2.3: Temperature-enthalpy diagram with grand composite curve (Linnhoff et al., 1982)

Another pinch technology tool, the grand composite curve (GCC), is shown in Figure 2.3. The grand composite curve was developed independently by Umeda, Harada and Shiroko (1979) and Linnhoff and coworkers (Linnhoff et al., 1982; Townsend and Linnhoff, 1983). This curve directly indicates the hottest temperatures where heat can be removed, and the coldest temperature where utilities can be supplied. One can see where best to extract work from heat in combined cycles, and visualize where to place heat pumps for heat recovery. This tool helps the designer to choose the best utility mix for the process. The grand composite curve presents the profile of the horizontal (enthalpy) separation between the composite curves with a built-in allowance of ΔT_{min}, given as the modified temperature T'. Figure 2.3 shows where the process can satisfy its own heat demand (pocket/shaded area), and where heat has to be transferred between the process and the utilities. In addition, the grand composite curve gives information about the required quality (temperature) of the utilities.

Graphical representation of the heat transfer, as given by the composite curves and the grand composite curve, is very informative. However, changing ΔT_{min} requires the composite curves to be redrawn. The problem table method was developed by Linnhoff and Flower (1978a,b) in order to avoid drawing the composite curves. It is a numerical method for determining the pinch temperatures and minimum utility requirements. For maximum heat recovery and minimum use of utilities, three rules have been identified:

1) Do not transfer heat across the pinch (process - process)
2) Do not use hot utilities below the pinch
3) Do not use cold utilities above the pinch

A systematic design procedure based on pinch decomposition and subsequent network optimization by evolution exists and is commonly referred to as the pinch design method (Linnhoff and Hindmarsh, 1983). Targets also exist for fewest number of heat transfer units (Hohmann, 1971 and Linnhoff et al., 1979) and minimum total heat transfer area (Townsend and Linnhoff, 1984).

The success of pinch technology has been proven by a large number of successful industrial applications, and is now an established field taught in universities. The latest textbook within the field was published by Smith (2005).

Pinch technology was introduced as a tool dealing with heat integration (Linnhoff and Hindmarsh, 1983), but has later been extended to management of other single resources as well as combined approaches. Examples of the first include water pinch (Wang and Smith (1994), based on the more general mass exchange network synthesis problem introduced by El-Halwagi and Manousiouthakis (1989)) and hydrogen pinch (Alves and Towler, 2002). Zhelev (2007) have listed combined approaches, including heat and power combined with flue gas.

Within the heat integration category, pinch technology has been extended to include other process operations such as separation columns, evaporators, reactors, compressors/expanders, boilers and heat pumps. As mentioned earlier, King et al. (1972) were the first to apply heterogeneous energy transfer networks in their study. Later Biegler et al. (1997) showed how side strippers, enrichers, intercoolers and heaters can be included in the same evaluation.

Andrecovich and Westerberg (1985) presented a method which enable easy evaluation of the potential for integration of distillation columns with the background process. The key to this method is making the assumption that the product of the condenser or reboiler duty and the temperature difference between the reboiler and condenser, is constant for a single distillation task over a wide range of pressures. The distillation column is then drawn as a box in the GCC, at the appropriate temperature level. Distillation columns can be integrated with the background process if condensers are above pinch or reboilers are below pinch. In order to secure controllability of the distillation column, it is recommended to integrate either the reboiler or the condenser, only.

Pinch technology has also been applied to total sites, where multiple processes are linked by a common central utility system. This approach was introduced by Dhole and Linnhoff (1993). In the total site methodology, sink and source profiles are constructed for the entire site, based on composite curves for each unit. From the sink and source profiles the total site pinch is identified as well as targets for utility heating and cooling. Later Klemeš et al. (1997) proposed to use the total site methodology for reduction of fuel, power and CO_2 on total sites. Axelsson et al. (1999 and 2003) have extended the approach to include cost assessment. Later Ådahl et al. (2004) presented a systematic greenhouse gas emission calculation method for retrofit situations including improved heat exchange, integration of combined heat and power units, and a combination of both. The combination of LCA and process integration proposed in Chapter 7 is a related approach.

2.4 Chemical integration

Chemical integration was introduced by Westerterp et al. (1977) and defined as:

"Starting from a raw material, all products - final products and intermediates as well – are exploited to achieve the optimal utilization of know-how, investments and raw material."

The term has not been widely used in the literature, probably because of its close relationship with the more established terms process integration and process synthesis. Where many of the process integration methods focus heavily on energy utilization, chemical integration is more focused on chemical and atom utilization.

Chemical integration, as it is used in this thesis, focuses on utilization of raw materials, with the following definition:

"Systematic methods for designing integrated production systems with special emphasis on high atom utilization."

With this definition, chemical integration is strongly related to process integration, and could even be part of a broader definition. By looking at atom utilization within the system, the benefits of for example co-production and additional raw materials can be identified. The superstructure approach (Section 2.2.3) at block diagram level and substance flow analysis (Section 2.6) applied to processes are examples of methods that can be used in chemical integration.

In addition to the relationship with process integration, there is a link between chemical integration and the concept of green chemistry. Green chemistry was introduced in the late 1990s (Anastas and Williamson, 1998) with focus on atom utilization and minimization of hazardous substances. The definition of green chemistry as given in Anastas and Williamson (1998) is as follows:

"Green chemistry is carrying out chemical activities – including chemical design, manufacture, use and disposal – such that hazardous substances will not be used and generated."

Green chemistry is in particular focused on the minimization of hazardous substances, however, general waste minimization and atom utilization are also important elements. Atom utilization and waste minimization are core strategies in chemical integration. In order to achieve high atom utilization, combination reactions are the preferred reaction route. Other reaction types, like displacement reactions and decomposition reactions, both give by-products in addition to the desired products (Matlack, 2001).

Combination reactions are chemical reactions where two or more molecules combine to form a larger one. Combination reactions are limited to chemical compounds that have multiple-bonded atoms (double or triple bonds). The alternative term "addition reactions" are often used for organic reactions. By use of a combination reaction, no by-products are formed and all raw-materials end up in the final product, giving high atom utilization. An example of a combination reaction is the production of ammonia from nitrogen and hydrogen, Equation (2-1).

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{2-1}$$

Displacement reactions on the other hand, are reactions where a functional group in a chemical compound is replaced by another group. This means that a by-product is always formed in a displacement reaction. For organic reactions, the term "substitution reaction" is normally used. An example of a displacement reaction is production of NaCl and hydrogen from pure sodium and hydrochloric acid, Equation (2-2).

$$2Na + 2HCl \rightarrow 2NaCl + H_2 \tag{2-2}$$

Like the displacement reaction, *decomposition reaction* always yields by-products. In a decomposition reaction, a molecule is divided into two or more molecules. The term "elimination reaction" is often used in organic chemistry. An example of a decomposition reaction is the decomposition of carbonic acid into water and carbon dioxide, Equation (2-3).

$$H_2CO_3 \rightarrow H_2O + CO_2 \tag{2-3}$$

From the reaction types presented, it is evident that the production of by-products is dependent on the reaction type. Combination reactions do not generate by-products at all, whereas both displacement and decomposition reactions produce by-products. When considering high atom utilization, like in chemical integration, there are two important aspects with regard to reaction type; 1) avoid the production of by-products or 2) utilize the by-products. By avoiding the production of by-products through use of the combination reactions, the atom-utilization into desired products will of course be high as all atoms will end up in the final product. It is, however, not possible to avoid the use of the other reaction types as they all represent important synthesis routes to requested products, thus by-products will be formed. In the second case, utilization of by-products can be ensured by co-production of various products and combination of process operations that can utilize the by-products and give high *total* atom utilization. Both aspects are examples of chemical integration.

As a concluding remark it is worth noting that high atom utilization is not sufficient when looking at the overall environmental impact of a process. Within green chemistry, use of solvents, separation efficiency, toxicity of compounds used and overall waste generated in the system is among the aspects included in the assessment. In this thesis, the overall environmental aspects of the system are quantified by use of life cycle assessment, which is described next. The environmental concerns have extended the system boundary of process design and moved it into the macro scale, where the environmental impact of the entire life cycle is assessed.

2.5 Life cycle assessment (LCA)

Life Cycle Assessment (LCA), Input/output analysis (I/O-analysis) and other similar tools for environmental analysis of systems have been developed from material and energy balances used in chemical engineering (Wrisberg et al., 2002). LCA was introduced in the early 1970s, by simple calculations of energy usage during the entire life span of the product (Bousted, 1972; Hannon, 1972; Sundstrom, 1973). Later studies included waste and emissions (Hunt, 1974; Barber, 1977; Ayres, 1978; Lundholm, 1985; Bousted, 1989), but the studies were limited to quantification of energy and materials use. The general framework of the LCA has changed over the years, and LCA is now mainly an environmental performance tool used to compare the environmental merits of various alternatives (Azapagic, 1999).

The development of the LCA framework is presented in a review article by Azapagic (1999). The development of an LCA framework was initiated by the Society for Environmental Toxicology and Chemistry (SETAC) in 1990, and soon afterwards the International Organisation for Standardisation (ISO) started similar work. The first approaches by SETAC and ISO are given in Fava et al. (1991) and ISO 14040 (1997), respectively. The two approaches were similar on the methodological framework, involving four main stages; goal and scope definition – inventory analysis – impact assessment – interpretation/improvement assessment as an iterative process (Azapagic, 1999). The principles and framework for LCA have now been collected in a set of ISO-standards, ISO 14040 (1997), ISO 14041 (1998), ISO 14042 (2000) and ISO 14043 (2000). The framework is still under development, however, the four phases included in an LCA are agreed on (ISO 14040, 1997) and are shown in Figure 2.4.

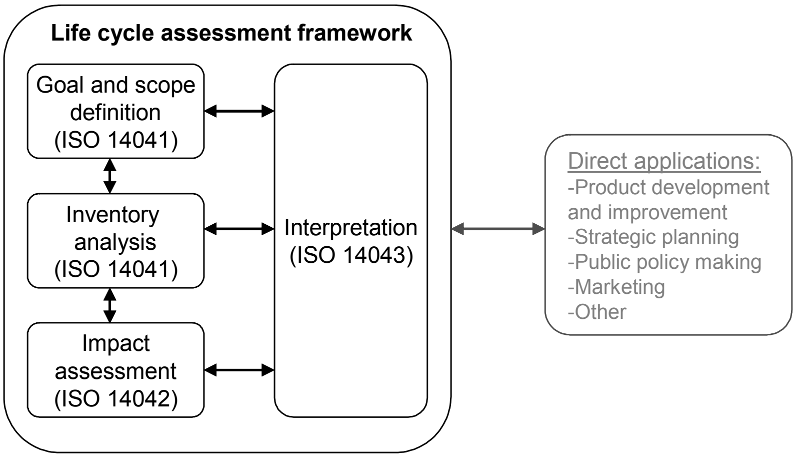

Figure 2.4: Life cycle assessment framework given by ISO 14040 (1997)

The LCA is said to have a "cradle to grave" approach, which means that all activities needed for the entire lifespan of a product or process have to be included. The activities required in the life span include extraction and processing; manufacture; transport and distribution; use; reuse and maintenance; recycling; and final disposal (Heijungs, 1996). A schematic presentation of the system in focus is given in Figure 2.5, with activities within the systems, and inputs/outputs over the system boundaries. LCA is based on thermodynamics and system analysis which are central elements in process engineering (Azapagic and Clift, 1994).

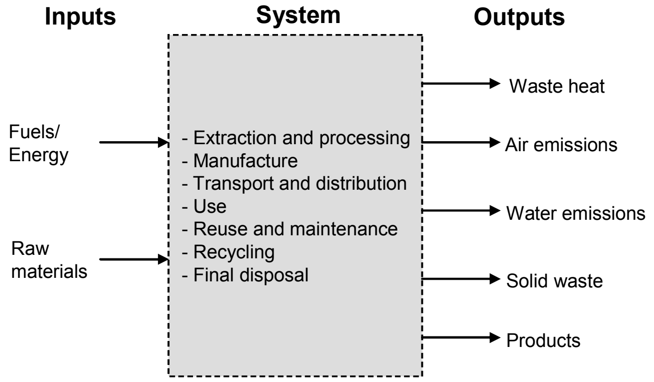

Figure 2.5: Schematic representation of a system

The remaining of Section 2.5 gives more details on the main steps in the LCA framework, major applications, some of the most frequent difficulties experienced during application and some initial guidelines on how LCA can be applied to processes.

2.5.1 Goal and scope definition

The goal and scope of the study should be defined in consistency with the intended applications of the study (Heijungs, 1996). In addition, a functional unit and the system boundaries must be chosen. The functional unit is the function that the product is to fulfil. An example of a functional unit is "drinking one cup of coffee" when comparing a paper cup with a china cup. By setting the system boundaries, one decides which unit operations to include in the study, hence the system boundaries are closely related to the goal definition. It is important to include all the essential elements of the production processes and exclude everything else. It is often useful to distinguish between "foreground" and "background system" (Clift et al., 1998), where foreground systems are the set of processes that is directly affected by the study of delivering the functional unit. The background system is the processes that supplies energy and materials to the foreground system.

2.5.2 Inventory analysis

In the inventory analysis, mass and energy balances required to produce the functional unit are established and the environmental burdens are quantified (Azapagic, 1999). The burdens are defined by resource consumption and emissions to air, water and solid waste, shown in Figure 2.5. Environmental impacts for each unit operation are identified, and finally the environmental impacts from all streams within the system are summarized.

The establishment of all mass and energy balances for the system determines the quality of the assessment. It is necessary to assure high quality of the data for this step in order to secure the relevance of the study. The inventory analysis is the stage in the LCA framework where process integration can be included to improve the study. This is discussed in Section 6.5 and implemented in Chapter 7.

2.5.3 Impact assessment

The impact assessment includes three steps, where the last is used only when meaningful (Heijungs, 1996):

1) Classification
2) Characterization
3) Weighting

A number of methods for impact assessment have been suggested, however the problem oriented method developed by Heijungs et al. (1992) is the most widely used. In the problem oriented method, the burdens are aggregated in impact categories relative to their environmental potential. The most widely used impact categories are given in Table 2.1.

Table 2.1: Impact categories in LCA (Heijungs et al. 1992)

Impact category	Sample category indicator
Climate change	Global warming potential (GWP)
Ozone depletion	Ozone depletion potential
Summer smog	Photochemical oxidant generation potential
Eutrophication	Eutrophication potential
Acidification	Acidification potential
Human toxicity	Human toxicity potential
Ecosystem toxicity	Ecosystem toxicity potential
Land use	Area
Abiotic resource use	Abiotic resource depletion potential
Biotic resource use	Biotic resource depletion potential

In the classification step, all environmental burdens that are quantified in the inventory analysis are classified according to the impact categories. The classification is a purely qualitative step (Heijungs, 1996). Classification includes the creation of complex stressor/impact chains, because a single pollutant can have multiple impacts (Khan et al., 2002). In the characterization, contributions to each of the impact categories are quantified. The models used in the characterization provide equivalency and characterization factors. An example is the contribution to the global warming potential, where CO_2 is the reference substance, and substances like CH_4 are multiplied with a factor yielding the impact in CO_2 equivalents (Heijungs, 1996). Models for characterization exist, but they are constantly under development, as the knowledge about various impacts increases. In the weighting step, the various impact categories are compared. The categories are assigned a weighting factor, making e.g. the acidification and global warming potential categories comparable (Heijungs, 1996). The weighting factors are subjective, and the use of weighting is under debate.

There are several well established methods for impact assessment (Baumann and Tillman, 2004), where Ecoindicator'99 is one of the most widely used (NOH, 1996, Goedkoop et al., 1998). The method is based on Ecoindicator'95 and Ecoindicator'98, and includes a model for assessing average numbers for Europe. Another well known method is the EDIP method, developed by Wenzel et al. (1997). In this thesis, the focus is on global warming potential, and consequently the method IPCC 2001 GWP (with 100 years and 20 years) is used. The IPCC methods do only take the global warming impact category into account.

2.5.4 Interpretation

In the interpretation phase, the need and opportunities to reduce the impact of the system on the environment are systematically evaluated (Heijungs, 1996). The results from the inventory analysis and the impact assessment are used to reach conclusions and recommendations for improvements of the system. The findings should be relevant to the goal and scope of the system.

2.5.5 Application of LCA

Azapagic (1999) and Heijungs (1996) have evaluated the use of LCA and found that the most common applications are strategic planning or environmental strategy development, product and process optimization, design, and innovation and identification of environmental improvement opportunities. They further report that the use of LCA in the industry is increasing, whereas this trend has not been followed by the governments.

So far, LCA has been applied mainly to products, whereas the processes included in the assessment have not been the focus of the studies. The LCA does, however, include the processes involved in the production of the given product and clearly the data valid for the product is also valid for the process steps involved in the manufacture of products. A small number of LCA studies applied to processes have been performed; an overview is given in Burgess and Brennan (2001) and Baumann and Tillman (2004).

2.5.6 Difficulties experienced in LCA

LCA is often criticized because it is difficult to compare different studies as LCA has not yet matured into a well defined tool (Burgess and Brennan, 2001). However, Guinee et al. (1993) have pointed out that methodological proposals are never going to suit all cases, and the different methodologies should be looked upon as a possibility in order to find the best methodology for a given case. LCA studies take into account the whole life cycle of the product or process. Various problems have been reported when LCA has been applied. First, problems arise when the system boundary is to be set. The challenge is to set the system boundary so that no major environmental impacts are left out, at the same time the amount of data needed as input must be kept at a reasonable level (Hertwich, 2001).

Another challenge in LCA, related to setting the system boundary, is the data availability and quality. In order to do a complete LCA, large amounts of data are needed. It is not easy to obtain detailed data from processes, due to confidentiality. Databases with average data for various processes are under development, but do not cover all possible activities. As a result, parts of the data sets are comprehensive and solid, whereas other parts are characterized by assumptions and average numbers. Peters and Hertwich (2004) have studied different production factors and pollution embodied in trade. Their approach was an input/output analysis, which also requires large amounts of data. They argue that it would be ideal if all the data needed would come from the same source, this would avoid the use of different aggregation, methodology and country coverage. Data can alternatively be collected from operating processes, like production and transport. Access to such data sources is of course limited, but when available these sources can provide high quality data. When production processes are assessed, data can be collected from the control and operation system for the process. Additionally, trading and production statistics can give valuable input to data collection.

When system boundaries have been chosen and the data collected, another difficulty is faced; allocation of the various environmental impacts to the products. If only one product is produced, all the emissions are allocated to this product. However, when various products are produced, like cogeneration of heat and electricity, the question on how to allocate the emissions to the different products has to be answered. The environmental impacts can be allocated according to product volume, mass, monetary value or spread equally on all the products. Alternatively, all impacts can be assigned to the main product. Allocation can be avoided by extension of the system boundaries to include alternative process routes to produce the same products (Ekvall and Tillman, 1997). Which of the allocation rules to follow, depends on the products and scope of the study. Most of the LCA studies performed have used allocation by volume, mass or value (Burgess and Brennan, 2001).

The last and voluntary step in the impact assessment is also associated with uncertainty. The idea of weighting is to compare the different impact categories by adding them to a single value, which is easy to communicate. This means that by weighting, one decides which of the environmental burdens that is of greatest concern. In other words, you compare e.g. global warming potential and acidification. The weighting will always be based on preferences and social values. When it is included in a model, it is difficult to show the weighting factors used. However, if the weighting step is left out of the impact assessment, you will still have to do a weighting when comparing the data of the model. The latter is done by the expert/users when they evaluate the outcome of the characterization step. As a consequence of these difficulties, LCA is only to be used as an aid in decision-making processes relating to environmental policy (Troge, 2000).

2.5.7 LCA applied to processes

The main application of LCA has been the evaluation of products. LCA applied to processes has, however, been introduced and a limited number of studies has been performed. In this section, a general introduction to LCA used on processes is given, starting with the distinction between the LCA approach and process analysis.

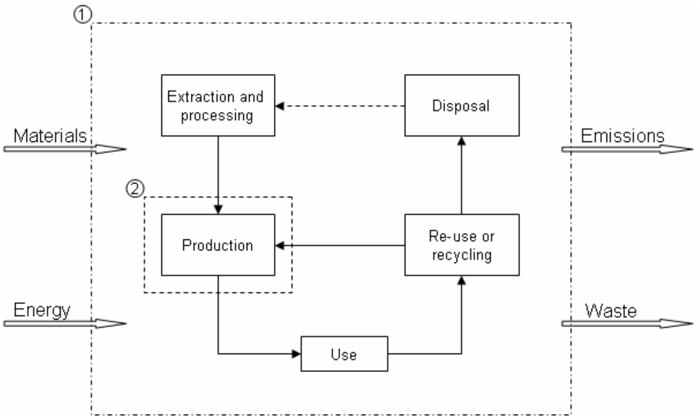

Figure 2.6: LCA approach (1) compared with the process analysis approach (2) (Azapagic and Clift, 1999a)

In Figure 2.6, the difference between life cycle assessment and process analysis is illustrated. While the chemical and process engineering approach to evaluate a process only takes the process itself into consideration (box 2 in the figure), the life cycle assessment includes every activity that enters the system boundary (box 1 in the figure). The system boundary includes the complete economic system for the process, both upstream and downstream the process. Materials and energy are entering the system, whereas emissions and waste are outputs of the system. Everything that crosses the system boundary will affect the surrounding environment to some extent. The flows between the various processes included in the system give rise to the input and output from the system.

LCA is said to have a “cradle to grave” approach, which means that all activities needed for the entire lifespan of a product, process or activity have to be included. An example taken from LCA applied to products is the production of cars. If only the production of the car is taken into account in an environmental study, the material of choice in the car would be steel rather than aluminium due to the lower environmental burdens of steel production compared to aluminium production. The steel is, however, heavier than aluminium for the same material properties, which means that during the use phase of the car, more fuel is needed for the heavier steel car. As is typical for products using energy in the use phase, the major environmental burden is associated with the use phase. When the production phase and the use phase are combined in an LCA of the car, the aluminium car is the one at choice. Correspondingly for processes, the optimum operation for one unit might not be the same as when this unit is one unit in a long process train. Examples within process systems include the required quality of an intermediate product, compared to a final product, and process integration opportunities between processes. The macro scale of process synthesis introduced in Section 2.2 is an example of how process synthesis focuses on the entire system, as given by box 1 in Figure 2.6.

The fundamental difference between LCA applied to processes and products is that rather than evaluation of various products that can fulfil a defined function, various process configurations that can produce a defined product are evaluated. When LCA is applied to processes, functional units can still be defined as the product from the system. Further, inventory analysis and impact assessment are carried out for the system evaluated. The only major difference when LCA is applied to processes rather than products, is the goal and scope definition with corresponding interpretation. The focus is shifted from the impact of various ways to fulfil the function, to process optimization based on the entire system with utilities, construction, transport and other activities in the life span of the product.

2.5.8 Tools used in LCA

Baumann and Tillman (2004) report on more than 24 different software packages that are available for LCA. Software tools are developed to handle both general and special problems. Almost all software packages comply with the ISO 14040 standard. The software usually includes a user interface where the user adds the operations and mass flows included in the assessment, a large database with average numbers for a large amount of processes, one or several weighting methods and presentation of the results as figures and tables. In this thesis the LCA tools Simapro and LCA-iT are used.

2.6 Substance flow analysis (SFA)

Substance flow analysis (SFA) is one approach within material flow accounting (MFA) (Wrisberg et al., 2002). MFA aims at specifying the pathways of materials in, out and through the economy of a nation, region, a community, business sector, company or household over a given period of time. *Bulk* material flow analysis (*b*-MFA) looks at total flows of bulk materials like steel, wood, water or total mass. Substance flow analysis, on the other hand, looks at one single component, usually associated with specific environmental effects. Components taken into account typically include chlorine, lead, CO_2, bromine or sulfur. While the results from *b*-MFA can be used to set priorities for policy measures towards increased resource efficiency, sustainable supply and waste management systems, SFA allows for an effective cause-effect modelling within the system analysed.

The traditional application of SFA is in the support of governments in evaluation and development of policies (Wrisberg et al., 2002). Here it is suggested that the SFA approach can be used in the early design phase of processes which exists of two or more unit operations. By looking at the flow of carbon and hydrogen atoms within a system, carbon and hydrogen efficiencies can be calculated for each step in the system. The efficiencies can then be used to identify the bottlenecks in the system, with respect to atom utilization, by taking advantage of the cause-effect modelling that SFA provides.

2.7 Process design

The process design tools used in the thesis are categorized in Figure 2.7. The division into synthesis, analysis and evaluation is in agreement with the design procedure given by Hendry et al. (1973) in Section 2.2. The well established links between tools and phases are given by solid drawn arrows, whereas the new links proposed through this thesis are given by dotted arrows. When process integration (PI) and life cycle assessment (LCA) are applied in evaluation of existing processes, they both act as analysis tools only. However, both PI and LCA can act as synthesis tools when the possibility of iteration between the tools is included, as they aid in developing alternative configurations. LCA and PI normally act as both synthesis and analysis tools in design of new processes.

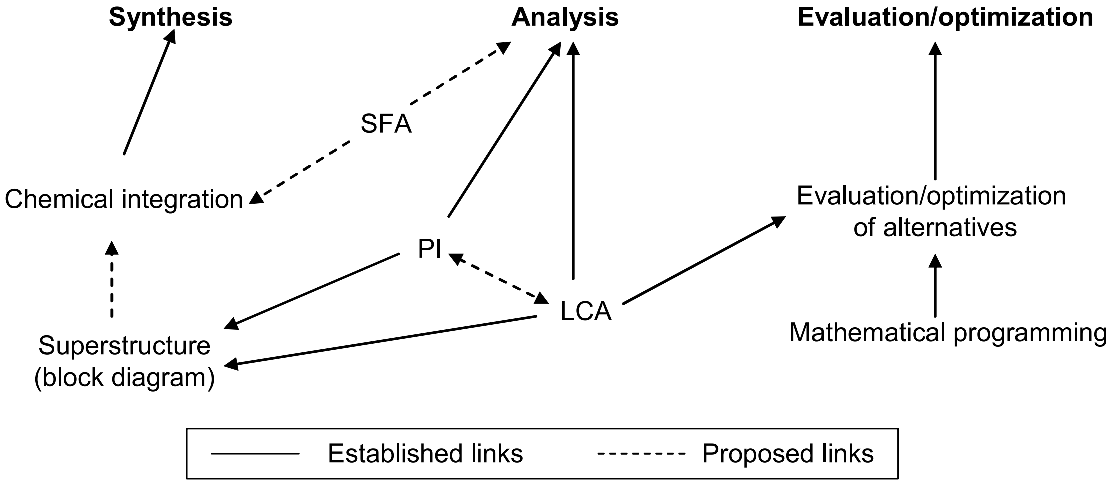

Figure 2.7: Process design tools used in the thesis.

The use of chemical integration in generation of superstructures is discussed in Chapter 3, 5 and 6. Process integration and life cycle assessment are used independently in Chapter 6, whereas the two methods are combined in Chapter 7. Substance flow analysis is used in Chapter 6 in order to analyze the various process configurations. Evaluation/optimization of processes is not the focus of this thesis, however, in Chapter 8 some initial thoughts are given on the use of LCA in optimization together with mathematical programming.

3 Co-production of energy and chemicals with CO_2 capture

Purpose of the chapter:

1. *Show the superstructure concept applied to natural gas*
2. *The idea of integrating energy and chemicals*
3. *Membranes used for separation of gases in power production and co-production of various chemicals*

Power production without emission of CO_2 is a main issue in the context of sustainable development. The main part of current power production is based on fossil fuels. Besides developing new power production technology entirely from renewable sources, it is necessary to develop methods which include CO_2 management in fossil fuel based power production. Many possible ways have been suggested, and these can mainly be divided in post-combustion capture, oxy-fuel combustion and pre-combustion capture. The efficiency reduction for the various power production technologies with CO_2 capture, compared with a standard high efficiency gas turbine combined cycle without CO_2 capture, is in the range of 9-13%-points. It is assumed that 90% of the generated CO_2 is to be captured and compressed to 100 bars, giving the following numbers: The standard high efficiency gas turbine combined cycle without CO_2 capture (58%), post-combustion (49.6%), oxy-fuel (47%) and pre-combustion (45.3%) (Bolland and Undrum, 2003). The loss in efficiency increases the demand for fuel, thereby giving reduced resource efficiency.

In order to increase the efficiency, co-production of power and chemicals is proposed. By use of large scale process units one can expect economy of scale savings and higher overall efficiency. This is achieved by both process and chemical integration. Previous work on co-production of power and hydrogen from natural gas has shown some synergies from the integrated production. However, the synergies obtained were smaller than expected, mainly due to the large amounts of thermal energy released in both the reformer and the combustion chamber (heat sources) of the combined cycle power plant (Løvholm, 2003). By including processes that require thermal energy (heat sinks) in the production scheme, the synergies are expected to be significant.

3.1 Co-production of energy and chemicals from natural gas

In Section 2.2, various process synthesis techniques are described. Synthesis by direct use of a superstructure approach is applied at a block diagram level in this section. More details are given in Kaggerud et al. (2006). The superstructure given in Figure 3.1 suggests possible process trains for co-production of chemicals and energy from natural gas. In addition to natural gas, the superstructure is fed with air, steam/water and possibly other, preferable renewable, energy sources. In the superstructure, high purity H_2, methanol, urea, electricity and fertilizer are all possible products. In addition, N_2,

CO_2 and different steam qualities are produced which can be used as inputs in other stages of the process.

The superstructure in Figure 3.1 is not a complete opportunity set, as it can clearly be expanded with other products, its purpose it simply to show how the superstructure can be used in chemical integration at a block diagram level.

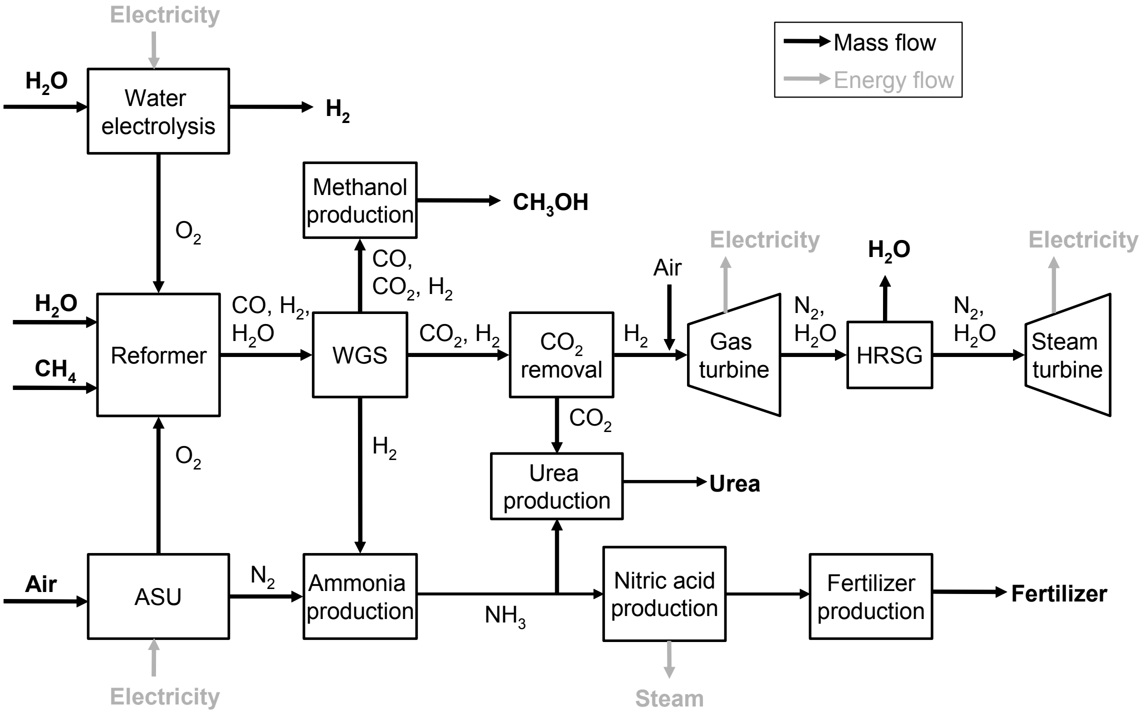

Figure 3.1: Superstructure block diagram of some possible process trains for co-production of chemicals and energy. Black arrows represent mass flow and grey arrows represent energy flows.

The superstructure is based on the pre-combustion principle for capturing CO_2 from power plants, which is evident by following the base line from methane to electricity through the gas and steam turbine. The possible add-ons of both input and output material given in the superstructure are introduced in order to increase the overall efficiency. The economy of the reformer can be improved by optimum design and integration of the air separation system (ASU), the water electrolysis and all the down-stream units. In addition, the steam needed for the reformer and the water gas shift reactor (WGS) can be taken from the heat recovery steam generator (HRSG) (Higginbotham et al., 2004).

Oxygen can be produced in an Air Separation Unit (ASU), but at high energy and capital cost. Unfortunately, nitrogen is produced simultaneously often without taking credit for this. Nitrogen is, for example, a very important constituent in ammonia, nitric acid and eventually mineral fertilizers, and the nitrogen from the ASU could be utilized in such products. Likewise, hydrogen can be produced from water electrolysis at very high cost and low energy efficiency. While the value of nitrogen is not always recognized in ASU units, the value of pure oxygen is not appreciated in water electrolysis for producing hydrogen. No doubt, making use of both products from air separation units and water electrolysis will significantly reduce the cost and efficiency penalties of such units.

Following the base line, the pre-combustion principle, CO_2 is separated from the hydrogen stream prior to the down-stream combined cycle power plant. The gas entering the combustion chamber in the combined cycle is hence carbon-free, and air is used as the oxygen source in the combustion. The existing gas turbines do not tolerate combustion of pure hydrogen in air due to the high temperature; hence a diluting agent needs to be added to the combustion chamber prior to the gas turbine. If an ASU is used to generate oxygen, a nitrogen stream is available and can be used. Alternatively, steam or CO_2 can be used as the diluting agent. Simulations done in PRO/II have shown little difference on the overall efficiency whether steam or nitrogen is used as the diluting agent (Løvholm, 2003). However, in today's gas turbines steam as the diluting agent can cause mechanical problems.

In the superstructure, both producers and consumers of thermal energy are given. Starting with the reformer; the output stream (CO, H_2 and H_2O) has a higher temperature than needed in the WGS reactor. The cooling of the synthesis gas can generate steam. In the production of nitric acid large amounts of steam is generated and can likewise be used elsewhere in the structure. The production of both methanol and urea is exothermic; hence both product streams have large amounts of thermal energy. The CO_2 removal unit consumes energy in the separation process. Additional purification of the various products and intermediates requires thermal energy, e.g. as steam. In the gas turbine and the steam turbine, thermal energy is converted to electricity, hence high temperatures are desired. Both the ASU and the water electrolysis consume electricity, produced in the gas and steam turbines. Steam is taken from the HRSG to be fed to the reformer. This will decrease the power output in the steam turbine, but an additional steam generation unit is avoided.

Rosen and Scott (1998) have evaluated production of hydrogen from various processes. The processes they evaluated were steam methane reforming, coal gasification, water electrolysis and combinations thereof. Steam methane reforming has the highest energy efficiency of the evaluated processes. Steam methane reforming produces hydrogen from both the non-renewable resource methane and renewable resource water. When hydrogen is produced from water electrolysis, the hydrogen is produced from renewable resources, provided the energy used in the electrolysis is generated from renewable resources. A combination of steam methane reforming and water electrolysis gives the highest energy efficiency among the integrated processes. Integrated processes increase their efficiency compared with the corresponding non-integrated processes and have the following additional advantages: reduced use of methane, increased overall efficiency and N_2 is avoided in the stack gases (Rosen and Scott, 1998).

3.2 High temperature membranes in power production

The main reason for the drop in efficiency when CO_2 is captured, is the energy loss in the CO_2 separation process. Normally amines are used to separate CO_2 from the other gases, and this is a very energy demanding unit operation. The introduction of high temperature membranes that can separate CO_2 from the other species present in a pre-combustion decarbonisation can decrease the energy used in capturing the CO_2. A comparison between cycles with H_2-selective and CO_2-selective water gas shift (WGS) membrane reactors have been made using a Matlab membrane reactor model combined with Hysys simulations. The study is based on previous work published by Bredesen et al. (2004). More details and results are given in Kaggerud et al. (2004a).

Schematic layouts of the two power processes considered are shown in Figure 3.2. Natural gas is converted to synthesis gas in an autothermal reactor (ATR), given as the ITM-O_2 with methane reforming in Figure 3.2. The oxygen needed in the reformer is provided by separation of air over a high temperature oxygen membrane (ITM-O_2), whereas the steam is taken from the heat recovery steam generator, HRSG. The main difference between the two processes is the type of membrane employed in the water gas shift reactor, WGS reactor, which leads to different treatment of the streams out of the reactor. In the case with a CO_2 separating membrane reactor (WGS-CO_2) in Figure 3.2a, the retentate consists largely of H_2 and H_2O, which is fed to the gas turbine combustor. The permeate stream (mainly CO_2, but also H_2O which is used as sweep gas and small amounts of H_2 that permeate through the membrane) can be fed to a fuel cell or an additional gas turbine for further power generation, and finally storing of the CO_2.

In the case with a H_2 separating membrane reactor (WGS-H_2) in Figure 3.2b, the permeate stream is the hydrogen rich stream that is fed to the gas turbine combustor. The CO_2 rich retentate also contains H_2, CO and CH_4 which again can be taken to a fuel cell or an additional gas turbine before it is processed for CO_2 storage.

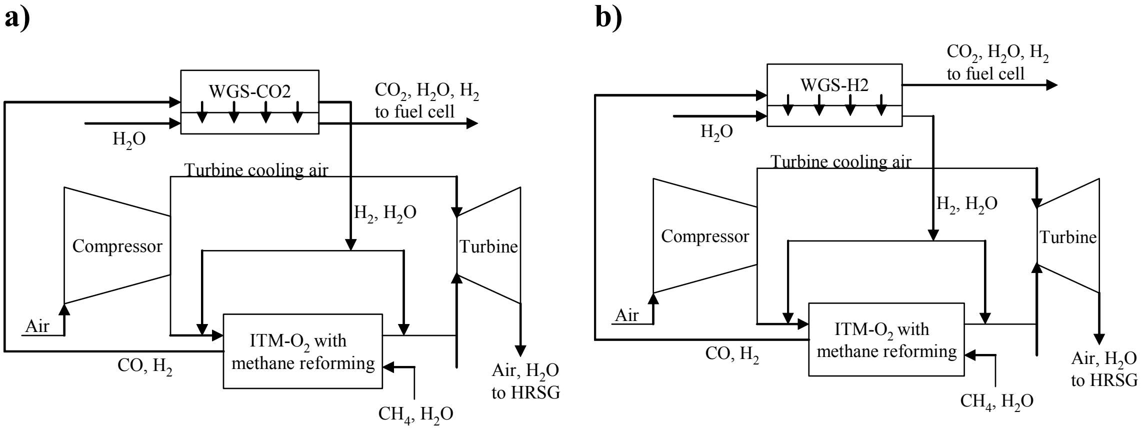

Figure 3.2: Gas turbine power process with integrated water gas shift membrane reactor for CO_2 capture a) with CO_2 membrane and b) with H_2 membrane.

There are two types of membrane reactor models used in this study. Firstly, in order to look at the overall potential, the membrane reactor is modelled as ideal, i.e. operating at chemical equilibrium, and with infinite selectivity and permeability. No fuel cell or additional gas turbine is included. Secondly, the membrane reactor is modelled rigorously as a tubular reactor, with a membrane at the wall, and with sweep gas on the other side of the membrane in countercurrent flow. The reactor side is modelled in two dimentions such that composition and temperature profiles are calculated in both radial and axial directions. The reaction kinetics as well as thermodynamics, heat and mass transport parameters are calculated as functions of temperature, gas velocity and physical properties. In both cases, the assumed required gas turbine fuel pressure (approximately 10-15% above compressor outlet pressure for H_2, in contrast to 25% for natural gas) must be allowed to govern the WGS reactor pressure – if the H_2 rich stream has a too low pressure out of the membrane reactor, it must be further compressed, which in the case of hydrogen is extremely energy consuming and detrimental to cycle efficiency. Hence, in the case of a WGS-CO_2 reactor, the total pressure of the *retentate stream* should be approximately 10-15% above compressor outlet pressure, whereas in the WGS-H_2 case, the *permeate stream* total pressure must be around 10-15% above the compressor outlet pressure. Natural gas has been modelled as 85.7% methane, 1.7% CO_2, 1.1% N_2 and the remaining higher hydrocarbons, mainly ethane. The target for CO_2 capturing is 90% based on carbon in the fuel.

3.2.1 Ideal membrane reactors

The overall efficiency for the base case scenarios show little difference between the two configurations, with a small advantage for the CO_2-membrane; 48.9% in the WGS-CO_2 case, and 48.1% in the WGS-H_2 case. The main reason for the advantage to the CO_2-membrane is that it is more energy demanding to compress equal amounts of H_2 than CO_2; hence the pressure loss over the membrane is more energy intensive to compensate for hydrogen than for carbon dioxide. The assumptions used in the basis scenario are a steam/carbon-ratio of 1.5, a permeate pressure of 2 bar and 20 volume% steam in the hydrogen stream.

The basis configurations for the ideal membranes are not optimized, but the various process conditions have been varied to show the effect on the efficiency. Both the H_2-membrane and the CO_2-membrane show the same trends.

Changes positive for the efficiency are:

1) increased pressure in the ATR
2) decreased temperature in the ATR
3) increased permeate pressure
4) decreased amount of sweep gas (steam)

3.2.2 Real membrane reactor data

The introduction of membrane data for both the H_2-membrane and the CO_2-membrane, and optimizing the process conditions, has shown that H_2-membranes have the highest potential for increasing the efficiency. Increasing the pressure and decreasing the temperature in the ATR has a good effect on the efficiency. This will lead to more unconverted methane in the ATR. With a H_2-membrane all unconverted methane will be kept in the CO_2 stream and can be combusted in the additional gas turbine used for the CO_2 stream. To obtain a high overall efficiency, a relatively high amount of the fuel should be utilized in the additional gas turbine due to the reduced exergy loss in the synthesis gas cooling at reduced temperature in the ATR. Both membranes benefit from such a high pressure in the ATR that the hydrogen after the membrane does not need further compression before the gas turbine. For the H_2-membrane a pressure in the ATR of 100 bars are required, while a pressure of 21 bars in the ATR is sufficient for the CO_2-membrane. Increasing the pressure further will give only a small increase in efficiency, and for the CO_2-membrane higher pressures will not meet the 90% target for CO_2 capture.

Table 3.1: Overall efficiency of the power cycle with increased pressure in the ATR

Membrane	ATR pressure [bar]	Selectivity	Permeability [mol/m^2sPa]	Efficiency, η [%]
CO_2-membrane	21	50	$1.0x10^{-7}$	48.4
H_2-membrane	100	Infinite	$1.0x10^{-5}$	52.9[1)]

[1)] Additional gas turbine in the CO_2 stream

At a steam/carbon-ratio of 2.5, the high pressure will increase the overall efficiency to 52.9% for the WGS-H_2 configuration. Increasing the pressure to 21 bars in the WGS-CO_2 configuration gives an efficiency of 48.4%. The results are given in Table 3.1.

Unconverted methane

Unconverted methane from the ATR will be contained in the synthesis gas entering the water gas shift reactor. When a CO_2-membrane is used, the unconverted methane will be kept in the hydrogen stream and burned in the combustion chamber of the gas turbine. This will give a reduced CO_2 capture due to the carbon dioxide formed in the combustion chamber of the gas turbine. When a H_2-membrane is used, the unconverted methane will follow the CO_2 and will not be utilized as fuel in the gas turbine. To avoid a decrease in efficiency due to loss of methane, a gas turbine or a fuel cell can be added on the CO_2 stream. The combustible gases, mainly CO, CH_4 and H_2, that are not contained in the hydrogen stream are oxidized in a combustion chamber and expanded in an additional gas turbine on the CO_2 stream. In order to optimize the efficiency of the process, the combustible gases in the CO_2 stream should *not* be minimized.

3.2.3 Discussion and conclusion

It is shown that CO_2-membranes are better in terms of cycle efficiency than H_2-membranes in the basis scenario due to the difference in compression work for CO_2(g) and H_2(g). The H_2-membrane, however, has a higher potential for improving the efficiency through process optimization, especially by increasing the pressure and decreasing the temperature in the ATR. Efficiencies up to 52.9% have been obtained by increasing the ATR pressure to 100 bars for the WGS-H_2 configuration.

The CO_2 emissions from the power plant are higher when a CO_2-membrane is used than when the membrane is hydrogen selective. The reason is the lower selectivity of the CO_2-membrane and the unconverted methane in the hydrogen stream. The difference in the emissions is influenced by the size of the CO_2-membrane. One of many other possibilities of high temperature membranes is to put a hydrogen selective membrane in the ATR. This will of course make the ATR more complex but the need for a WGS no longer exists. Some initial simulations on this configuration have been done, but detailed modeling still has to be implemented to give reliable results.

The hydrogen produced in the reformer and shift reactors can of course be recovered and used both as fuel for the combined cycle power plant and as a chemical product, either as an energy carrier in fuel cells or other applications for pure H_2. Likewise, the synthesis gas produced in the reformer can be utilized as feedstock in chemical production. Co-production of power and chemicals gives higher raw material utilization, through the utilization of byproducts and increased energy efficiency.

3.3 Co-production from other raw materials

Sections 3.1 and 3.2 have shown how natural gas can be utilized in both chemical and energy production. Plastic waste is an interesting substitute for natural gas feed due to the high calorific value of the waste and the increasing amounts generated. In addition, natural gas and other fossil fuels are not renewable, and will at some point become scarce. A superstructure similar to the one given in Section 3.1 has been set up for plastic waste (Kaggerud et al., 2004b). Of particular interest is the possibility of utilizing plastic waste in production of new plastics. This can be done by chemical breakdown of the plastic waste to synthesis gas, and then rebuild it to new plastic by taking the components through a process train with methanol production, methanol to olefins (MTO), and finally polymer production from olefins. The details of the plastic waste recycling concept are given in Chapter 5.

4 Plastic recycling

Purpose of the chapter:

1. *Use and recycling of plastic waste; overview and perspective (waste availability)*
2. *Existing recycling options*
3. *Set the scene for the succeeding chapters (challenges and opportunities)*

In this chapter the availability of plastic waste is identified based on known numbers for consumption and corresponding waste generation. This thesis is not meant to be a study of availability and collectability of plastic waste, hence general numbers for plastic waste availability are used. It is, however, important to note the difficulties experienced in collection of the waste if plastic waste is to be used in a commercial installation.

4.1 Use of plastic waste

The use of plastic waste is increasing rapidly in the European countries, and the total consumption was close to 45 million tons in 2002 (APME, 2004). The numbers presented are collected and published by the Association of plastic manufacturers in Europe (APME). The data available is much more detailed for the Western European countries than the Eastern European countries. APME states that the quality and detail of the data for Eastern European countries have improved over the last years, and are expected to continue to improve. Consequently the data given here are more detailed for the Western European countries. However, it is interesting to include information on waste handling systems in the Eastern European countries, as a considerable economic growth is expected to take place.

Plastic material is used increasingly in Europe, both in number of applications and total annual consumption (Patel, 2000). In Figure 4.1, the consumption of plastic material used for plastic applications in Western Europe from 1991 to 2002 is shown. In addition to the numbers given, about 10 million tons are used for non-plastic applications, for instance textiles (APME, 2004). Western European countries dominate the European market with their 38 Mt of plastics per year (2002). In contrast the total consumption in the Eastern European countries in 2002 was 4.2 million tons (APME, 2004).

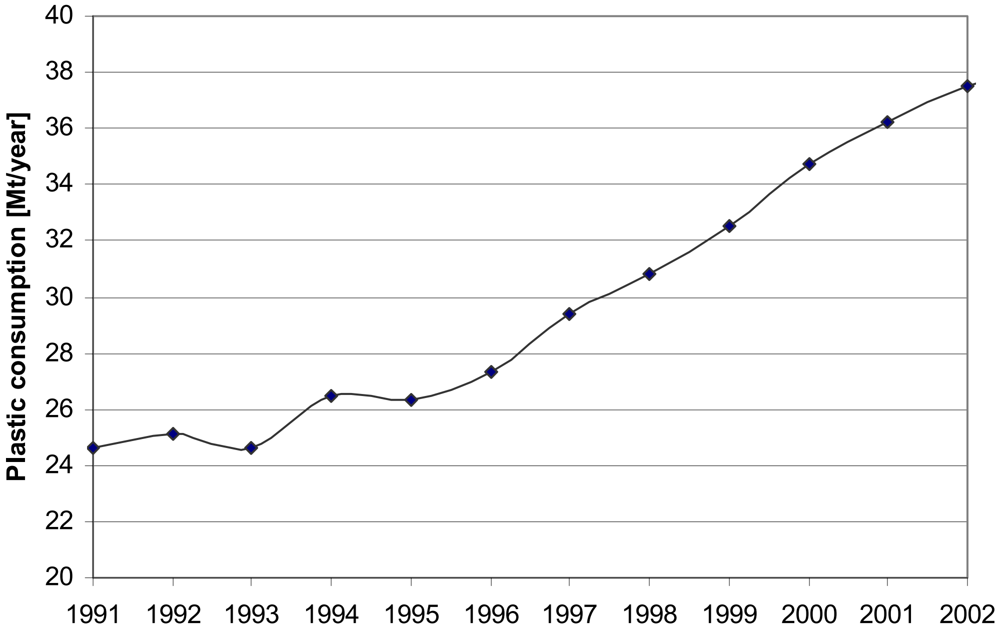

Figure 4.1: Total consumption of plastic material in Western Europe 1991-2002 (APME, 2004)

The breakdown of consumption by country in Western Europe is given in Figure 4.2. Germany is the largest consumer of plastic material in Western Europe followed by Italy, whereas Poland (~2 million tons per year) is the largest in Eastern Europe. However, six Western European countries are consuming more plastic material than Poland. From Figure 4.2 it is seen that the amount of plastic material consumed varies significantly among the countries.

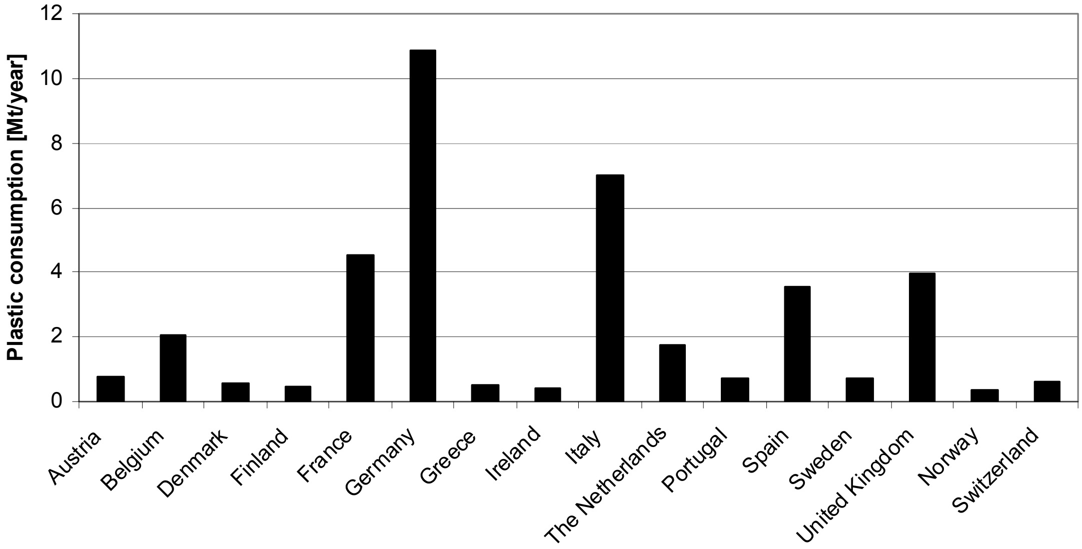

Figure 4.2: Consumption of plastic material, by country, in Western Europe 2002 (APME, 2004)

The use of plastic material for plastic applications in Western Europe is given by type in Table 4.1. Plastic materials are either thermoplastics or thermosets, where the thermoplastics PE (given as LDPE and HDPE), PP, PVC, PS and PET accounts for 75% of the total consumption. Thermoplastics soften on heating and then harden again on cooling, whereas the thermosets never soften when they have been molded (Aguado and Serrano, 1999). Thermoplastics are the dominating among the polymer families. The number of plastic types increases, and this is in particular due to an increasing number of engineering plastics. Engineering thermoplastics are defined as all thermoplastics except from PE, PP, PS and PVC (Schalles, 1991).

Table 4.1: Plastic consumption in Western Europe given by plastic type (APME, 2004).

Plastic type	LDPE	HDPE	PP	PVC	PS	PET	Polyurethanes	Others
Consumption [% of total]	19	13	15	14	8	6	6	19

In addition to the wide variety of applications, plastic materials also have different life time. The life time is to a large extent dependent on the application, ranging from a couple of weeks (e.g. plastic bags and disposable cutlery) up to 100 years (e.g. pipes and window frames). Patel et al. (2000) have studied the life time of the plastic material in use in Germany, and the results show that 30% of the plastic materials have a life time of 0-3 years, 40% a life time of 3-11 years and the remaining 30% last for more than 11 years. It is reasonable to believe that there is a similar life time distribution in other Western European countries.

4.2 Recovery of plastic waste

The use of plastic material in various applications increases, which consequently leads to increasing amounts of plastic waste. The plastic waste is a valuable source of both material and energy that should be utilized. The situation in Western Europe today, however, shows that more than 60% of the plastic waste generated is landfilled or incinerated without recovering neither the energy nor the material (APME, 2003). Out of the 40% that is recovered, the major part is recovered in the form of energy with corresponding emission of CO_2. Increased recycling of plastic waste reduces incineration and landfilling, which again reduce greenhouse gas emissions like CO_2 and CH_4, in the short and long term respectively. The utilization of plastic waste as feedstock in the chemical and energy sectors additionally saves large amounts of fossil resources like oil, gas and coal, thereby preventing CO_2 and other greenhouse gases emitting to the atmosphere both during production and use.

Increased awareness of environmental aspects such as resource scarcity, emissions and land use, have lead to EU Directives which introduce restrictions on landfilling of carbonaceous waste. In order to treat the large amounts of carbonaceous waste that is restricted from going to landfill, new waste handling technologies are needed.

4.2.1 Technologies and methods

Technologies for treatment of plastic waste cover a wide range, with disposal of the waste and direct reuse of the product as the two extremes. The term “recovery” is used to describe all activities where plastic waste is utilized as a valuable source of material and/or energy, whereas “recycling” technologies involves only those that recover the material. Recovery of both energy and material are of interest when plastic waste is treated, hence an introduction to available options for *reuse*, *material recycling* and *energy recovery* are given here. Disposal of plastic waste contributes to neither energy nor material recover, and is consequently kept outside the scope of the study.

Reuse

Reuse of the products is the direct or indirect reuse of the product in the original or a new application. Examples include reuse of parts from copy machines and other electronic equipment.

Mechanical recycling

Mechanical recycling of plastic waste, also called material recycling, is remelting of the waste into new plastic products without changing the chemical composition of the plastic. A number of operations are involved (Aguado and Serrano, 1999); separation of the plastic material, washing to remove contaminants, grinding and crushing to the desired particle size, extrusion by heat and reprocessing into new plastic products. This type of recycling is mainly restricted to thermoplastics as thermosets cannot be remolded (Aguado and Serrano, 1999).

Most polymers are incompatible with another when melted, which require separation of the various materials (Matlack, 2001). In addition other contaminants like food, metals, paper and mix of colors decrease the quality of the product. Concern about contaminants results in nonfood use only for mechanically recycled plastics in the US (Matlack, 2001). Some plastic materials can, however, be recycled together by addition of a compatibilizer (Matlack, 2001).

Chemical recycling

Chemical recycling is defined as chemical treatment which seeks to break down the polymer into low-molecular substances that can be used to manufacture new plastics (Bauer, 1991). The various methods are described briefly below (Aguado and Serrano, 1999)

1) Chemical depolymerization: Reaction with a certain agent to yield the starting monomers
2) Gasification: Partial oxidation with oxygen and/or steam to produce synthesis gas.
3) Hydrogenation: The polymer is degraded by the combination of heat, hydrogen and in most cases a catalyst.
4) Pyrolysis: Thermal decomposition of the polymer by heating in an inert atmosphere

The product gas from the methods described above is then reacted to new plastic material through several gas processing steps before final polymerization.

Feedstock recycling

Feedstock recycling is the process of converting plastic waste to other chemicals like hydrogen, ammonia and synthetic fuels. The same methods as described above for chemical recycling are used, although instead of polymerization, the process units for production of the desired chemical are used. In some literature there is no distinction between feedstock and chemical recycling.

Energy recovery

Energy recovery of plastic waste implies utilization of the energy in the material by generation of electricity and/or heat. This can be done by direct combustion or gasification/pyrolysis with subsequent combustion of the gas. The heat produced in the combustion can be used for district heating or power production by steam or gas turbine. The material in the plastic waste is not recovered, whereas the energy is utilized.

Disposal

Landfilling of the plastic waste means putting the waste at a deposit without further treatment. This option involves no recovery of the material or energy. As plastic material needs much time to degrade the material will however be available at the deposit for many years to come. Decomposition of the plastic waste forms CH_4, CO_2 and CO which is emitted to the atmosphere. Incineration without recovery of energy is also categorized as disposal, as neither the energy nor the material is recovered.

4.2.2 Comparison of recovery options

The waste hierarchy as outlined in the 1994 packaging and packaging waste directive (94/62/EC) have the following preferred order for treatment of waste:

1) Waste prevention
2) Recovery
    a. reuse
    b. material recycling
    c. energy recovery
3) Disposal

The waste hierarchy has been criticized lately as it would prevent development of more efficient waste management systems (Davoudi, 2000 and Malkow, 2004). Despite the criticism, agreement is reached that the waste hierarchy gives general guidelines for treatment of waste. More careful investigation is of course needed for each specific case. Matlack (2001) also give a general view by putting up the following priority *"Reduce, reuse and recycle in that order"*.

Björklund and Finnveden (2005) have reviewed publications which compare global warming potential and total energy use of recycling versus incineration and landfilling of various waste sources. They conclude that for most publications recycling of plastic material is preferable to landfilling and incineration. Furthermore, they report that production of materials from recycled resources is less energy intensive than from virgin resources. A comparison of material and energy recovery of municipal waste shows that, even if there is a district heating system available to utilize heat, paper and HDPE should be material recycled (Holmgren and Henning, 2004). In this thesis, focus is on material recycling and energy recovery.

One major advantage to favour chemical recycling ahead of mechanical recycling is the fact that plasticisers and stabilisers can be removed in the former. This is valuable because some of the former additives are not used in today's production and might even be prohibited by law. Mechanical recycling, on the other hand, has a lower energy demand. Due to the long lifetime of the plastic products, the waste available for recycling might have been produced more than 30 years ago. Because of this the recycling processes must be designed not only for today’s and the future plastic products, but also for the products sold more than 30 years ago.

4.2.3 Availability and recycling today

In this section the availability and the existing recycling of plastic waste in Europe is presented. The term “collectable availability” is used in the figures, which means that only the waste that is actually available for collection is included, not the total generated post-consumer plastic waste. The reasons why all the generated waste cannot be collected are hibernating stocks, pipes buried in the ground and the like. For the following numbers no distinction between chemical and feedstock recycling is used, however, all the installed capacity produces feedstock for other industries than plastic production. The total collectable available plastic waste in Western Europe (1993-2003) is given in Table 4.2 together with the recovery by various recycling alternatives.

Table 4.2: Recovery of plastic waste in Western Europe 1993-2003 (APME, 2004)

Year	Total plastic waste [kt]	Mechanical recycling [kt]	Feedstock recycling [kt]	Energy recovery [kt]	Total recovered
1993	16211	915	0	2425	**21%**
1995	16056	1222	99	2698	**25%**
1997	16975	1455	334	2575	**26%**
1999	19166	1888	346	3949	**32%**
2001	19980	2521	298	4583	**37%**
2003	21150	3130	350	4750	**39%**

The total recovery of plastic waste has increased from 21% in 1993 to 39% in 2003. Energy recovery is the largest contributor, followed by mechanical recycling. Feedstock recycling is still a minor contributor, representing only 4% of the recycled plastic. The amount of plastic going to mechanical recycling has increased with almost 250% from 1993 to 2003, whereas energy recovery has doubled over the same period. Feedstock recycling increased until 1998, when new capacity was installed mainly in Germany. The last years, no new feedstock recycling capacity has been installed (APME, 2004).

Figure 4.3 shows the availability of plastic waste and recovery in the various countries in Western Europe. There is a large difference between the various countries both with respect to plastic waste generated and the recovery rate. United Kingdom, Italy, France, Germany and Spain are the main contributors to plastic waste generated in Western Europe. Among these countries Germany, with over 50% recovery rate, and France, with close to 50% recovery rate, are in an exceptional position. For the smaller countries the recovery rate also differs, but a general trend is that the smaller countries have a high recovery rate. A trend that is observed for most countries, small and large, is that energy recovery is generally higher than material recycling.

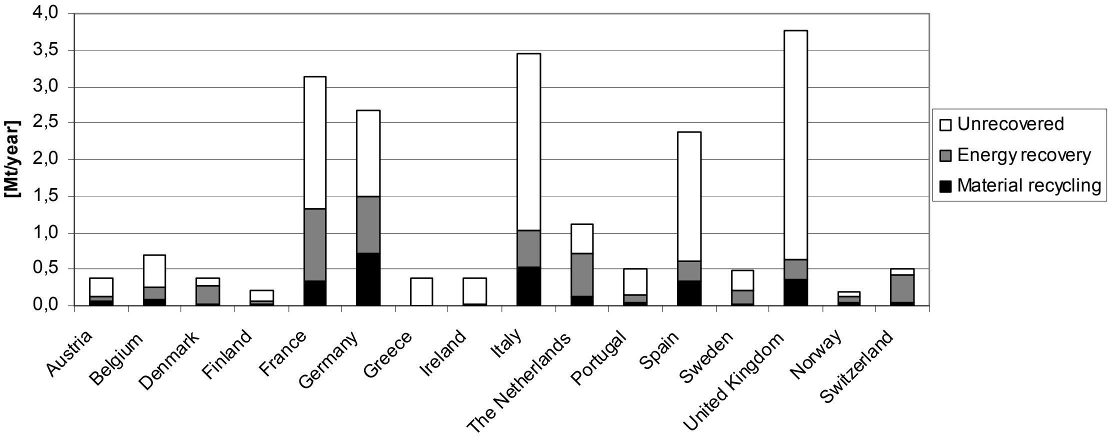

Figure 4.3: Plastic waste availability in Western Europe 2002 (APME, 2004)

Municipal solid waste, with 81.2% of the total, dominates the post-consumer plastic waste in Western Europe when divided into the various sectors. The other sectors are automotive (5.7%), electrical and electronic (5.0%), building and construction (3.7%), distribution and industry (2.5%) and agriculture (1.9%).

4.2.4 Future prospective

Section 4.1 and 4.2.3 have shown that the use of plastic increases, which result in more plastic available for recovery and recycling. Patel et al. (2000) have given two main reasons for the continued growth in available waste:

1) The amount of post-consumer plastic waste increase due to increased use in the past and the long life time of the products
2) Use of plastic material is increasing

As 70% if the plastic materials have a life time of more than 3 years (Section 4.1) today’s, waste treatment has to be designed for yesterdays, today’s and the future plastic materials.

In addition to the increased use of plastic material, the number of plastic types increases (Section 4.1). As most plastic types are not compatible with each other when melted (Section 4.2.1), either thoroughly separation of the waste or processes which can tolerated a large variety of plastic types needs to be installed. Among the sectors, municipal solid waste dominates the picture, and is likely to do so in the future as packaging and other household articles account for about 60% of today's consumption of plastic materials (APME, 2004).

Incentives and drivers for increased recovery

The general picture show higher consumption of plastic materials in an increasing amount of applications. The increased consumption leads to more waste which need treatment. The increased environmental awareness has led to several initiatives which work as drivers for increased recovery of plastic waste. EU has proposed several directives on treatment of various plastic waste. The most important directives for plastic waste are the Landfill directive (1999/31/EC), End-of-life vehicles (2000/53/EC), Waste electric and electronic equipment (2002/96/EC) and Packaging and packaging waste (94/62/EC).

The landfill directive gives targets on biodegradable waste to landfills, the implementation in Germany requires waste with an organic fraction (determined as loss on ignition) of more than 5% to be treated before it goes to landfill (Buttker et al., 2005). In Sweden landfilling of combustible waste was banned in 2002 and in 2005 organic waste was included (Eriksson et al., 2005).

The ELV directive (end-of-life vehicles) requires a recycling rate of 80% and a recovery rate of 85% by 2006, and is planned to increase to a recycling rate of 85% and recovery rate of 95% by 2015 (Buttker et al., 2005). The WEEE directive (waste electric and electronic equipment) are making producers responsible for the costs of collection and recycling of their products, but no quantified targets are given (Gottberg et al., 2006). The Packaging directive requires 60% of the total packaging waste to be recycled or energy recovered by end 2008, whereas 22.5% of the plastic waste has to be recycled back to plastic.

In addition to the EU directives, voluntary commitments like the one taken by PVC producers (ECVM - European council of vinyl manufacturers) are adding to the targets given. ECVM have launched a program which aim at installing recycling capacity to handle 200 000 tons (excluding industrial waste) of PVC by 2010. Further the lack of land available for deposit of plastic waste, and the need for new sources of organic materials will also act as drivers for increased recycling of plastic.

5 The plastic waste to plastic (PtP) concept

Purpose of the chapter:

1. *Present the recycling concept that is used as the main case study in the thesis*
2. *Present the unit operations included in the assessment*

The plastic waste to plastic (PtP) concept has been developed to produce new plastic material from waste, by chemical decomposition to synthesis gas. In addition to new plastic materials, the concept is developed to utilize the material and/or the energy in the plastic waste by production of other materials, electricity or energy carriers. The concept has been developed in cooperation with Norsk Hydro Research Centre.

5.1 The concept

A similar superstructure as the one given for natural gas in Chapter 3, has been set up for the Plastic waste to Plastic (PtP) concept in Figure 5.1. The concept offers a closed-loop system for large scale recycling of mixed plastic waste. The base line in Figure 5.1, from carbonaceous waste to new plastic materials, represents the core strategy in the concept. The possible add-ons of both input and output material given in the superstructure are introduced in order to increase the overall flexibility and material utilization. The core strategy is represented by the black arrows, whereas the add-ons are given by grey arrows.

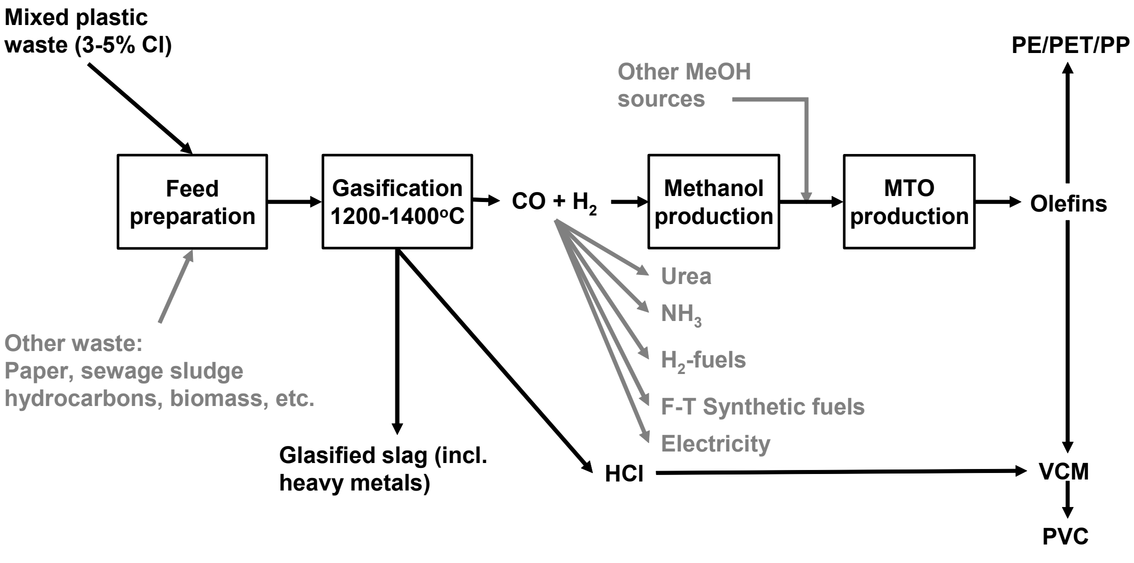

Figure 5.1*:* The Plastic waste to plastic (PtP) concept is shown schematically. The black arrows are the original PtP concept, whereas the grey arrows represent options included to increase the flexibility of the concept.

In the core strategy, plastic waste is oxidised in a gasifier, producing a high calorific synthesis gas which can be used for both energy and material purposes. Oxygen is provided by use of an air separation unit (ASU). In order to close the loop for the plastic material, the synthesis gas is converted into methanol after a water gas shift (WGS) reactor to adjust the H_2/CO-ratio followed by sulfur and CO_2 removal. The methanol is then fed to the Hydro/UOP patented MTO process (Methanol to Olefins). The olefins produced are ethene, propene and small amounts of butene. Ethene and propene are the feedstock for production of new plastic material like PE, PP and PVC. In Figure 5.1 only the material streams are given, in addition there is consumption of electricity and steam used for heating purposes. The mixed plastic waste also contains metals and other inorganics, which will be recovered in the process. Unwanted components like heavy metals and brominated flame retardants are safely removed in the gasifier. The metals that are removed can replace virgin metals and the other inorganics are recovered as a glasified slag, usable in roadbeds or in cement production.

The extended PtP concept offers increased flexibility with its possibilities for alternative feedstock and product extractions at various stages in the process chain. All carbonaceous material is a potential waste source in the concept, including paper, sewage sludge, wood, biomass and all other hydrocarbons, both renewable and non-renewable. The synthesis gas can be used to produce a number of products including, methanol, ammonia, urea, hydrogen, Fischer-Tropsch fuels and electricity. The possibility for extracting intermediates makes it possible from the single core technology (the gasifier), to add-on flexible downstream technologies that match market needs, technology developments, and existing legislation (which e.g. specifies targets for plastics-to-plastics, plastics-to-other material products, and plastics-to-energy recovery). All intermediates can also be produced from alternative feedstocks, like the introduction of methanol shown in Figure 5.1. The possibility to use alternative feedstocks provides opportunity for varying the scale of different parts of the process train. The different products in the PtP concept offer a range of carbon capture options. Production of plastics, methanol and urea all capture the carbon as part of the material itself, while production of energy, hydrogen and ammonia requires carbon capture technologies like absorption, membrane separation or a combination thereof.

The PtP concept involves several unit operations, and a short description of these core units as well as the possible add-ons are given in the next sections.

5.2 Unit operations in PtP

The units in the core PtP concept are pretreatment, the gasifier, WGS, gas cleaning, methanol production, the UOP/Hydro MTO process and plastic production.

5.2.1 Pretreatment

The pretreatment needed before the plastic waste can be recycled in a recycling process, varies strongly between the different recycling technologies. Plastic waste that has been used in different applications will contain various additives and may contain other contaminants, hence the processes need to be robust with respect to the operating conditions and the pretreatment. The pretreatment of the waste is a critical and labour-intensive part of the process. One major advantage of gasification is the possibility to treat complex mixtures without extensive separation before the gasifer. This way of operation requires, however, a flexible and thorough cleaning of the syntheses gas to fit the downstream use.

Several gasification technologies can tolerate large amounts of contaminants. This will, however, in most cases lead to more advanced cleaning of the produced syngas. In addition to removal of the contaminants, pretreatment of the waste also involves crushing of the plastic waste to the required particle size. The particle size tolerated varies widely for the gasification processes, from less than 0.5 mm to 10 mm particle size. It is of course less labour and energy intensive to produce large particles than small.

The particle size required in the entrained flow gasifier, which is the gasification technology chosen for the PtP concept, is < 0.5 mm, and one way to prepare such small particles is cryogenic grinding. Cryogenic grinding is done by mixing the plastic waste with liquid nitrogen from the ASU, resulting in fragile particles due to the very low temperatures. The fragile particles can then easily be crushed to the desired particle size (Future Energy, 2003). The waste composition is given in Appendix 1, whereas more details on pretreatment and choice of gasifier are given in Appendix 2.

5.2.2 Gasifier

Gasification is a thermal upgrading process using oxygen, air, steam, or a combination thereof, in the reaction with carbonaceous material. The product gas consists mainly of CO and H_2, normally called synthesis gas, and small amounts of CO_2, H_2O and CH_4 (Menges et al., 1992). Pure O_2 is chosen as the oxygen source in this concept instead of air; hence the following overall reaction will take place in the gasifier, Equation (5-1).

$$\left(C_xH_y\right)_n + \frac{nx}{2}O_2 \rightarrow \left(x \cdot n\right)CO + \left(\frac{y \cdot n}{2}\right)H_2 \qquad \Delta H_{rx} < 0 \qquad (5\text{-}1)$$

Total oxidation to CO_2 and H_2O will also take place in the gasifier, and the water gas shift (WGS) reaction will adjust the syngas composition to chemical equilibrium, Equation (5-2).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rx} < 0 \qquad (5\text{-}2)$$

When plastic waste is used as the carbonaceous material in the gasification, other components than carbon and hydrogen will also be present. This will of course result in additional reactions in the gasifier. During the gasification process, the plastic waste is converted to synthesis gas through a number of reactions. The detailed reactions involved in the conversion are given in Aguado and Serrano (1999).

Due to the PVC waste contained in the mixed plastic waste, chlorine will be present and HCl will be formed. A lot of concern has been given to the possible formation of the highly toxic dioxins and furans when hydrocarbons and chlorine are reacted with oxygen. Dioxins and furans have only been detected at extremely low levels in the product gases from demonstration-scale gasifiers (Yamamoto et al., 2003), well below the legal limits. A direct quench of the product gas avoids the creation of dioxins. Sulfur is contained in the waste only in small amounts, mainly as contaminants. Due to the sulfur, small amounts of H_2S will exist in the product gas (Iisa, 1992).

A high temperature in the gasifier results in a relatively high proportion of CO and a low proportion of CO_2 and hydrocarbons (Pitt and Millward, 1979). The overall energy requirement of the gasifier can be balanced by a suitable combination of exothermic and endothermic reactions, mainly through the control of the H_2/H_2O ratio by the use of the WGS reaction. The desired product gas composition depends on the actual utilization of the synthesis gas.

Several gasification technologies exists; fixed bed, fluidized bed, circulated fluidized bed, entrained flow, mowing bed and rotary kiln, which all have pros and cons. The liquidlike flow of particles in a fluidized bed allows continuous automatically controlled operations with easy handling. It is suitable for large-scale operations and the heat and mass transfer between gas and particles are high. The rapid mixing of solids in the bed leads to non-uniform residence time of solids in the reactor. For continuous treatment of solids, this gives a non-uniform product and poorer performance of the reactor. Erosion of pipes and vessels from abrasion of particles can be serious. At high temperature sintering and agglomeration of particles might occur, this might require a lowering in temperature, thereby reducing the reaction rate considerably (Kunii and Levenspiel, 1991).

Fixed beds, also called packed beds, are able to treat larger particles. The larger particles will need longer residence time in the reactor. Pressure drop over the bed is considerable, giving a lower gas velocity. Large particle beds behave different than small particle beds. The large particles can lead to large-scale uniform motion, gross circulation of bed material and severe channelling (Kunii and Levenspiel, 1991). The particles fed to the gasification reactors are about 5-10 cm, with a residence time of 15-30 minutes.

Molten polymers have high viscosity and low heat transfer (Aguado and Serrano, 1999). This can result in less favourable conditions in gasification of the waste. The problem can be solved by making a slurry, with either water or oil as the slurry medium, distributing the waste as small particles in the slurry. This is called entrained flow and used in the process developed by Future Energy (Future Energy, 2003). More details on the gasification technology are given in Appendix 2.

Due to data availability and the high quality syngas produced in the entrained flow gasifier, this is the technology chosen in this work. The gasification technology is presented in Figure 5.2.

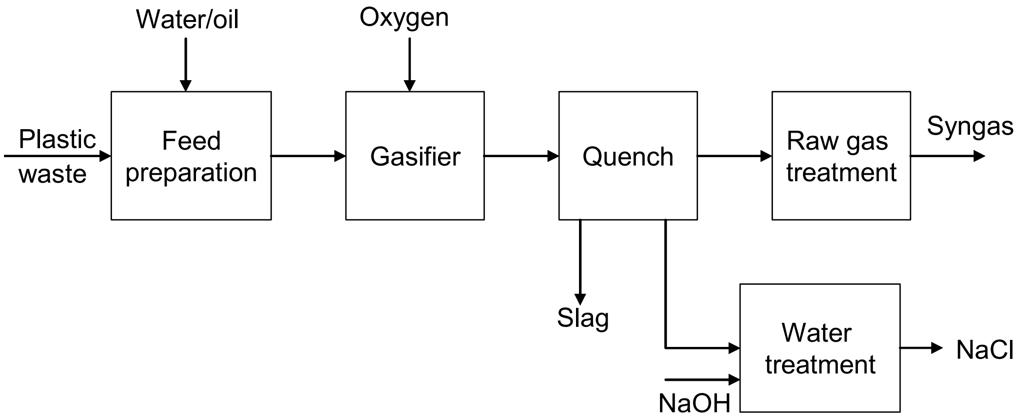

Figure 5.2: Block diagram of the gasification unit for plastic waste (Future Energy, 2003)

The grinded plastic waste is mixed with the slurry material water or oil and fed to the gasifier. In the gasifier, the slurry is reacted with oxygen and the resulting syngas is led to a direct quench to avoid dioxin formation. The quench water is treated with NaOH to remove the chlorine, whereas all other inorganics are contained in the slag leaving the gasifier. The syngas is further scrubbed and cooled before leaving the gasifier unit.

Air separation unit (ASU)

The gasifier is operated with 95% oxygen as the oxidation agent. Production of O_2 is done in an air separation unit. Air is compressed and cooled, and then separated in a cryogenic distillation column. The block diagram is given in Figure 5.3. Energy use and material flows are taken from Future Energy (2003).

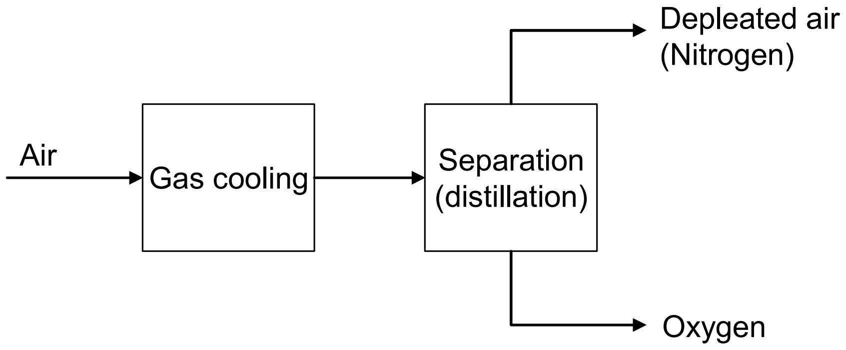

Figure 5.3: Block diagram showing production of oxygen from air by use of cryogenic distillation

5.2.3 Raw gas treatment

The raw gas from the gasifier needs treatment before it can be used in production of methanol or other chemicals. The main units are water gas shift (WGS), removal of sulfur (sulferox) and CO_2 (amine).

Water gas shift (WGS)

The syngas leaving the gasifier does not contain enough hydrogen for a high yield in the methanol production unit; hence the gas is led to the shift reactor where the H_2/CO-ratio is adjusted. In the water gas shift unit CO and H_2O are shifted towards CO_2 and H_2 over a catalyst. The reaction is slightly exothermic and is given in Equation (5-3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (5\text{-}3)$$

As the reaction is exothermic, a high yield of hydrogen is favored by a low temperature. A low temperature is, however, not favorable for the reaction kinetics, and consequently the WGS is usually a two-step reactor. The first reactor operates at high temperature (350°C) to utilize the kinetics for a fast reaction at high temperatures, the second at low temperature (260°C) to shift the exothermic reaction to the right at the more preferable low temperature. Temperatures are taken from Hamelinck et al. (2001). The block diagram of the WGS reactors is shown in Figure 5.4.

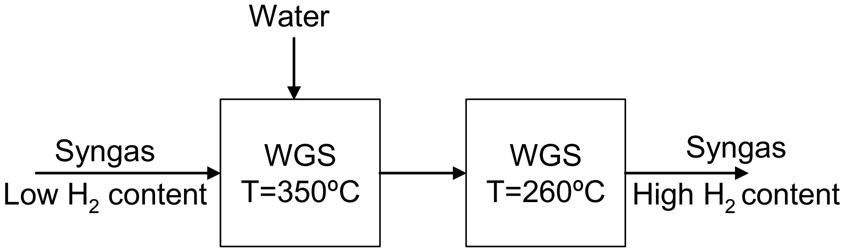

Figure 5.4: Block diagram of the water gas shift reactor system

Sulferox – removal of sulfur

The Sulferox process removes H_2S from the syngas stream. The treated gas is sent to the CO_2 removal unit, whereas the stream that contains sulfur is further treated in the Sulferox unit to produce solid sulfur (Ekbom et al., 2003). The process is shown in Figure 5.5. The absorbent used is an aqueous ferric iron chelate solution (Fe^{3+} as the active ion). The Sulferox process treats the syngas to 1 ppmv H_2S.

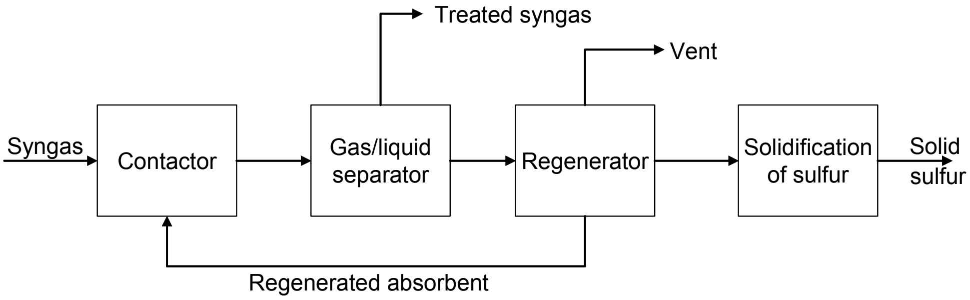

Figure 5.5: Block diagram for Sulferox, removal of sulfur from the syngas

CO_2 removal unit

Most of the CO_2 is removed from the syngas before it enters the methanol production unit. The block diagram showing the CO_2 removal unit is given in Figure 5.6. CO_2 is removed by use of amine (MEA) absorption, where CO_2 reacts with the amine in the absorber, the treated gas is then released with a low CO_2 content. The rich amine is regenerated by heating the amine in the stripper, which release CO_2 to vent or capture (Ekbom et al., 2003).

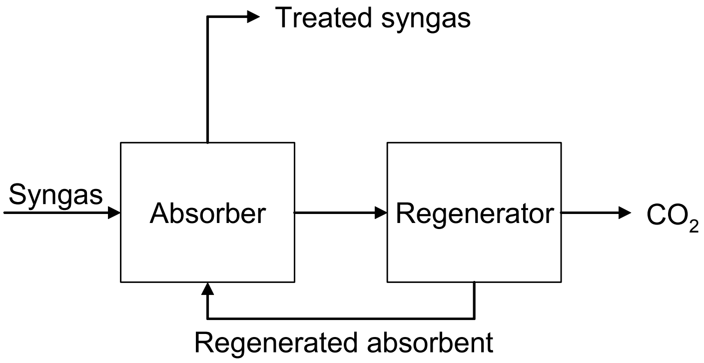

Figure 5.6: Block diagram for the process of CO_2 removal from the syngas

5.2.4 Methanol production

The next step in the concept is the production of methanol from syngas, which is achieved by a conventional methanol process. The main reactions given by Equations (5-4) and (5-5), are both exothermic. In order to obtain maximum catalyst activity, 5 mol% of the feed should be CO_2 (Moulijn et al., 2003).

$$CO + 2H_2 \rightarrow CH_3OH \tag{5-4}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{5-5}$$

The conversion in the methanol reactor is low; hence a high recycling rate of the unreacted syngas is necessary. Part of the recycle gas is taken out as a purge gas in order to avoid build up of inerts in the system. The purge gas is used as an energy source for steam generation. The methanol process given in Figure 5.7 differs from plants converting natural gas into methanol in two ways; 1) No reforming section and 2) No distillation of the crude methanol. The reforming section is replaced by the gasifier, converting plastic waste into synthesis gas. The MTO plant (next process step) tolerate crude methanol as input, which means that the separation of methanol and water in distillation columns is avoided. The mass and energy streams are based on Ekbom et al. (2003).

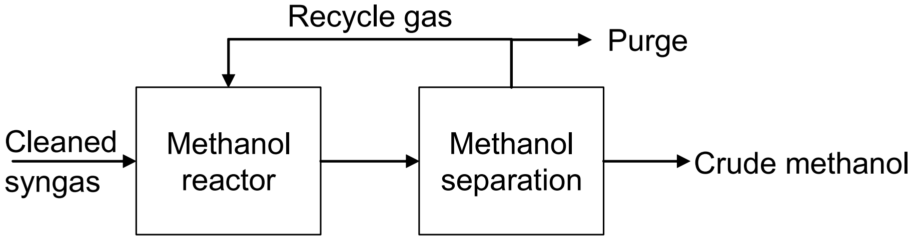

Figure 5.7: Block diagram for methanol production from the gasifier (Moulijn et al., 2003)

5.2.5 Methanol to olefins (MTO)

The UOP/Hydro Methanol to Olefins process, MTO, is designed to selectively convert methanol, either crude or refined, into olefins. Olefins are unsaturated hydrocarbons containing at least one carbon to carbon double bond, also known as alkenes. The olefins produced in the MTO process can be used in production of new plastics, including PVC, PE and PP. The process has been jointly developed by UOP and Hydro with the purpose of using natural gas as feedstock for olefins, with methanol as an intermediate. The MTO process converts methanol to ethylene and propylene at close to 80% carbon selectivity in a fluidized bed reactor. The relative yield of ethylene and propylene can be adjusted by varying the operating temperature. A block diagram of the process is given in Figure 5.8. The catalyst used in this process is based on a silicoaluminophosphate, SAPO-34. The principal reaction is given as Equation (5-6) (Kvisle et al., 2002).

$$12CH_3OH \xrightarrow{Catayst} 3CH_2CH_2 + 2CH_2CHCH_3 + 12H_2O \qquad (5\text{-}6)$$

Based on extensive testing in the demonstration plant, the MTO process can be scaled up to a single train unit with capacity of up to one million tons of light olefins per year (Kvisle et al., 2002). Basic engineering for the first planned commercial plant has been carried out. The plant will convert 2.5 million tons methanol into 400,000 tons of ethylene and 400,000 tons of propylene (Chementator, 2003). Mass and energy balances used in this thesis are taken from an SRI report (Nirula, 1994).

The MTO can be improved by adding an OCP unit (olefin cracking process) to the original MTO. In the OCP unit, C_4 and C_{5+} olefins are cracked to light olefins (C_2 and C_3), decreasing the amount of byproducts and increasing the overall carbon selectivity to ethene and propene to 90% (Kvisle, 2004). This improvement has not been included in the study.

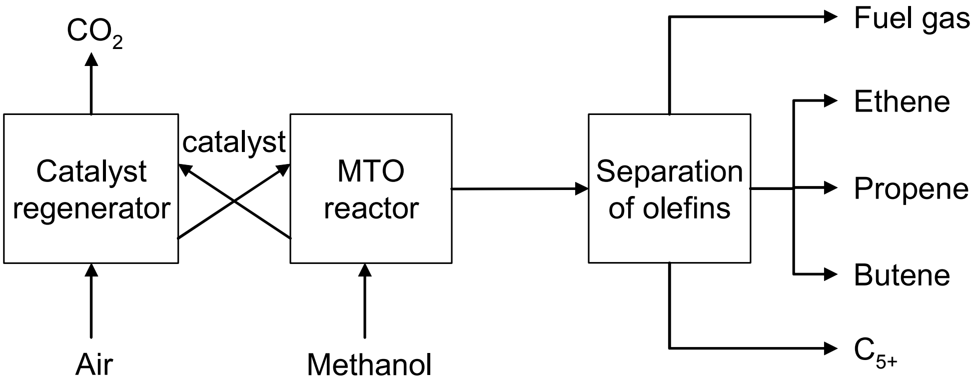

Figure 5.8: Block diagram for the MTO unit (Kvisle et al., 2002).

Methanol is reacted to olefins in the MTO reactor. Due to degrading of the catalyst (coke formation), the used catalyst is sent to the catalyst regenerator where the coke is burned off with air. The product gas from the MTO reactor is sent to the separation section, where the different products and by-products are separated in distillation columns.

5.2.6 Plastic production

The block diagrams for production of HDPE and PP by use of the Borstar technology (Borealis, 1998) are shown in Figure 5.9 and Figure 5.10, respectively.

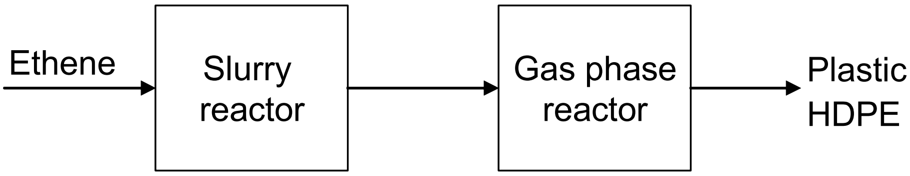

Figure 5.9: Block diagram of Borstar technology for production of HDPE from ethylene (Borealis, 1998)

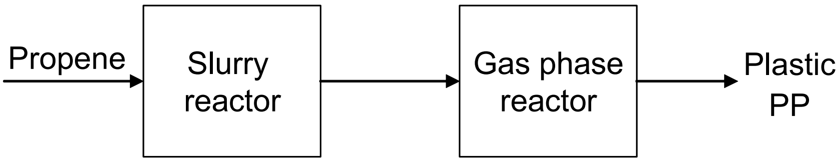

Figure 5.10: Block diagram of Borstar technology for production of PP from propylene (Borealis, 1998)

The Borstar process combines a loop reactor using supercritical propane as the polymerisation medium, placed in series with a gas phase reactor where the second stage of the reaction takes place. Lower molecular weights are formed in the loop, while high molecular weights are formed in the gas phase reactor, leading to a flexible process with regard to molecular weight and density of the polyolefin products.

5.3 Unit operations in the extended PtP

The core idea in the PtP concept is to convert plastic waste into new plastic materials. However, to increase the flexibility of this system as well as to improve its efficiency, production of other chemicals, electricity and energy carriers were introduced in Figure 5.1. In addition, various intermediates can be introduced in order to increase the flexibility with respect to scale of the various units and additional unit operations can be added, as indicated in Figure 5.11. The extended PtP concept is evaluated in Chapters 6 and 7. The possible unit operations within the extended PtP concept is, however, presented here, together with the unit operations in the core PtP concept.

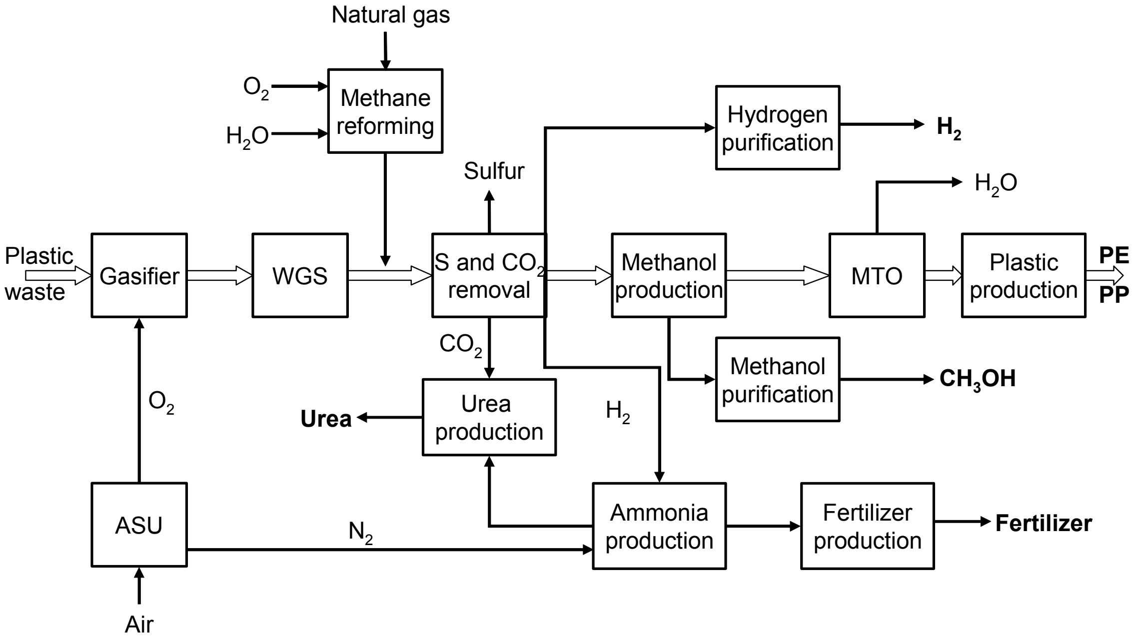

Figure 5.11: Available options in the extended PtP concept

Again, the base line in Figure 5.11, from carbonaceous waste to new plastic materials, represents the core strategy in the concept (represented by block arrows). The key unit in the superstructure is the gasifer which converts the plastic waste into synthesis gas. The synthesis gas produced can be used both as feedstock for chemicals production and as an energy carrier. The synthesis gas is highly flexible regarding the final output, since the use of different catalysts gives different products (Holmen, 1996). This is shown in Equation (5-7) below.

$$\begin{aligned} CO + H_2 &\xrightarrow{Ni} CH_4 \\ &\xrightarrow{ZnO} CH_3OH \\ &\xrightarrow{Fe,Co} Hydrocarbons \\ &\xrightarrow{ZrO_2} C_4H_8 + CO_2 \end{aligned} \tag{5-7}$$

The additional units involved in the extended PtP concept are described in this section. The section ends with a discussion about various reformer options for production of hydrogen rich syngas from natural gas that can be included in the PtP concept.

5.3.1 Methanol purification

As the production of crude methanol is one of the intermediate steps in the core concept, pure methanol can be produced by adding a separation sequence to the methanol unit. In order to produce pure methanol, water and methanol have to be separated. This is done by distillation of crude methanol using three columns. More details can be found in Moulijn et al. (2003).

5.3.2 Ammonia production

Ammonia is produced by the exothermic combination reaction, Equation (5-8), requiring a hydrogen-nitrogen ratio of 3:1.

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \tag{5-8}$$

Hydrogen is usually provided by steam reforming of natural gas followed by autothermal reforming with air (Moulijn et al., 2003). By use of air, the nitrogen needed in the reaction is introduced to the reactor and at the same time there is no need for air separation. If ammonia production is to be included in the PtP concept, hydrogen is taken from the syngas, whereas the nitrogen is provided by the ASU.

5.3.3 Urea production

The ASU produces relatively pure nitrogen as a by-product in the oxygen production. Nitrogen is an important constituent of fertilizers, where H_2 and N_2 are reacted over a catalyst to produce the intermediate product ammonia (NH_3). Ammonia is also the feedstock for urea, which is produced through a two step exothermic and uncatalyzed equilibrium reaction. The overall reaction, Equation (5-9), is given below. Urea is used as fertilizer and in the manufacture of livestock food (Moulijn et al., 2003).

$$2NH_3 + CO_2 \leftrightarrow H_2NCONH_2 + H_2O \tag{5-9}$$

5.3.4 Hydrogen production from syngas

Hydrogen is one of the main components in the synthesis gas, and the amount can be further increased by shifting the gas, Equation (5-3), with steam to yield H_2 and CO_2. The resulting gas is then separated by membranes or adsorption to provide high purity hydrogen.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5-3}$$

5.3.5 Steam methane reformer (SMR)

The reformer unit given in Figure 5.11 can be a steam methane reformer (SMR), an autothermal reformer (ATR) or a CO_2 reformer.

In an SMR, natural gas (methane) is reacted with steam over a nickel catalyst to produce syngas, given by Equation (5-10). The reaction is endothermic, and heat is added by heat transfer to the reactor. The reforming takes place in tubes packed with catalyst and arranged vertically in gas-fired steam reformers. The heat is provided by combustion of natural gas.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{5-10}$$

The molar composition, on water free basis, of the syngas from the SMR is given in Figure 5.12 for various operating conditions (pressure, temperature and steam/carbon ratio). Unconverted methane is reduced with decreasing pressure, increasing steam/carbon ratio and increasing temperature. Another undesired element, CO_2, decreases with increasing temperature and decreasing steam/carbon ratio, whereas the pressure does not influence the amount of CO_2 produced.

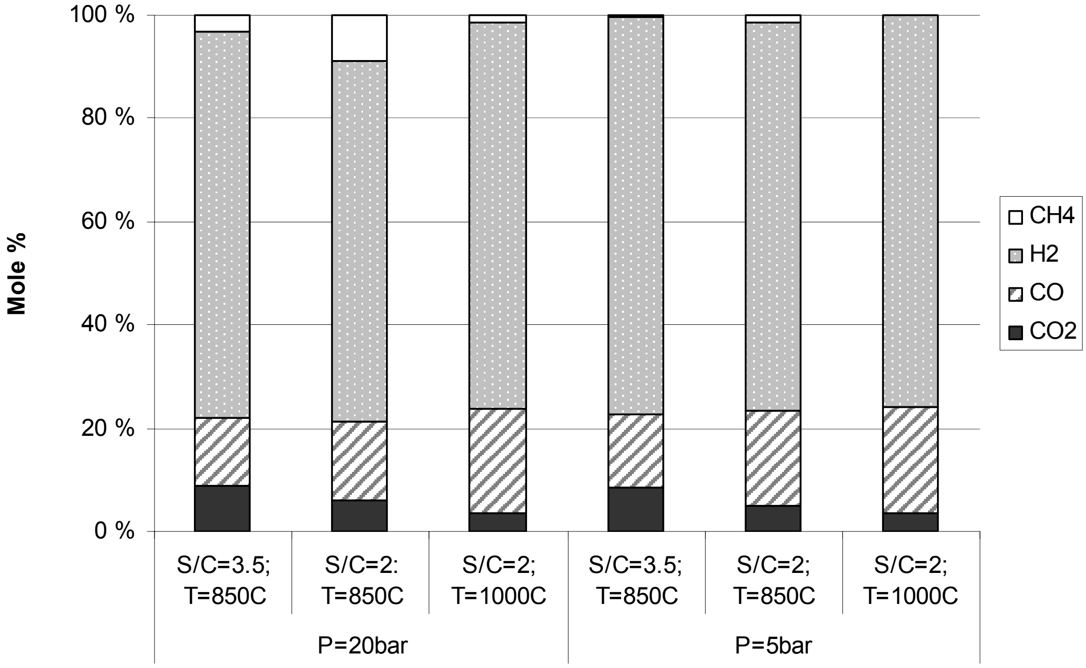

Figure 5.12: Molar composition on water free basis of the product gas from the SMR, with change in pressure, temperature and steam/carbon ratio (S/C).

5.3.6 Autothermal reformer (ATR)

The autothermal reformer, ATR, combines the endothermic reaction between methane and steam, Equation (5-10), and the exothermic reaction with oxygen, Equation (5-11). The reactions are given below, together with the WGS reaction, Equation (5-3).

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{5-10}$$

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2 \tag{5-11}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5-3}$$

The product gas consists mainly of CO and H_2, normally referred to as synthesis gas, and small amounts of CO_2, H_2O and CH_4. The synthesis gas composition for an ATR is normally a H_2/CO-ratio of 2-3 (Menges et al., 1992). To avoid total oxidation to CO_2 and water, the oxygen content in the reactor must be kept low. The overall energy requirement of the reformer can be balanced by a suitable combination of exothermic and endothermic reactions, mainly through the control of the steam/carbon ratio. Total oxidation is more exothermic than the partial oxidation. A high temperature in the reformer hence results in a relatively high proportion of CO and a low proportion of CO_2 and hydrocarbons (Pitt and Millward, 1979).

In Figure 5.13 the molar composition of the product gas from an ATR is given. Again elevated temperature decreases unconverted methane. All results for the ATR are shown for a pressure of 20 bar.

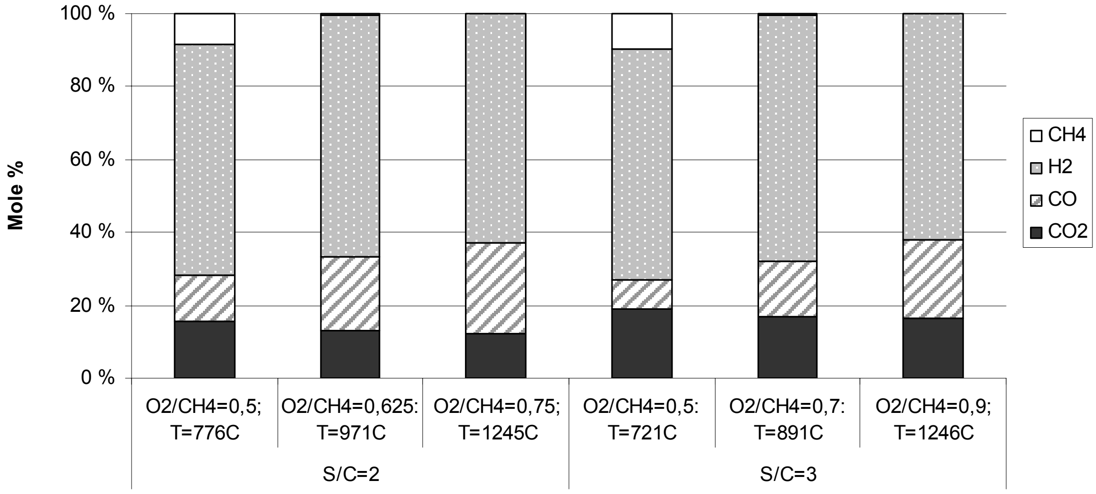

Figure 5.13: Molar composition on water free basis of the product gas from the ATR, with change in O_2/CH_4 ratio and steam/carbon ratio (S/C) [No heat added, the corresponding temperature given].

5.3.7 CO_2 reformer

In the CO_2 reformer, natural gas is reacted with CO_2, given by Equation (5-12). The reaction is endothermic, and heat is provided by the exothermic reaction with oxygen, Equation (5-11).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{5-12}$$

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2 \tag{5-11}$$

In the PtP system, there are large amounts of surplus CO_2, which make CO_2 reforming an interesting option. However, the H_2/CO-ratio of the produced syngas (typically 1.2-1.6) in this option is lower than the required ratio of ~2 in the methanol reaction, which means that the syngas has to be shifted in a water gas shift reactor in order to obtain the desired H_2/CO-ratio.

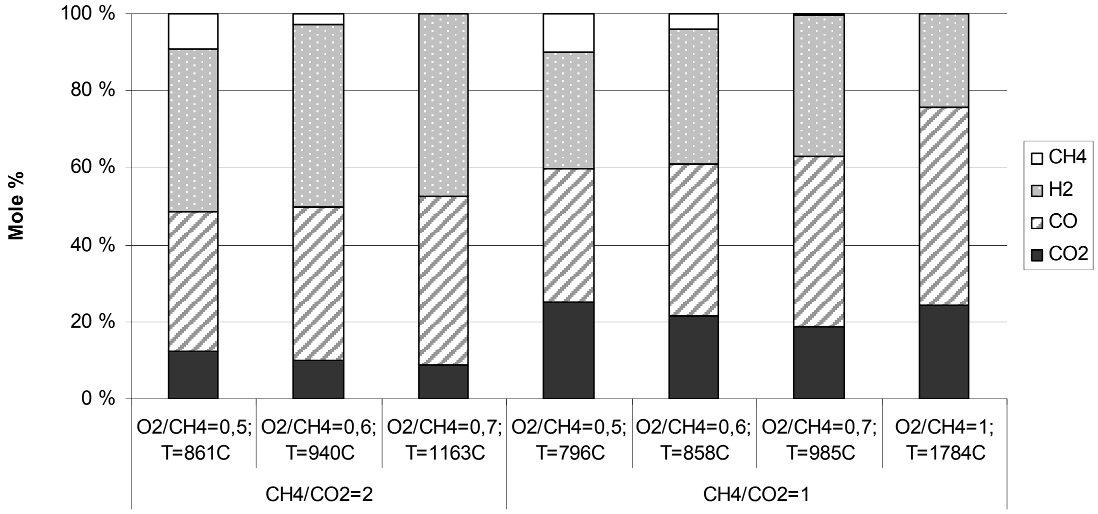

Figure 5.14: Molar composition on water free basis of the product gas from the CO_2 reformer, with change in O_2/CH_4 ratio and CH_4/CO_2 ratio [No heat added, the corresponding temperature given].

The general trends in the molar composition of the syngas leaving the CO_2 reformer are given in Figure 5.14. The amount of CO_2 in the product increases with decreasing CH_4/CO_2-ratio fed to the reactor, whereas the amount of hydrogen is increasing with increasing CH_4/CO_2-ratio. Unconverted methane is decreasing with increasing temperature, and the hydrogen content goes through a maximum with increasing temperature.

5.3.8 SMR, ATR or CO_2 reformer

In addition to the different ways of providing heat for the reaction, a major difference between these reformer options is the H_2/CO-ratio in the product gas. As can be seen from Equation (5-10), 3 moles of H_2 are produced per mole of CO. For the reaction with oxygen, Equation (5-11), only 2 moles of H_2 are produced per mole of CO. Equation (5-12), with CO_2, results in a H_2/CO-ratio of 1. This means that the synthesis gas produced in the SMR has a higher H_2/CO-ratio than what is the case in an ATR, whereas the CO_2 reformer produces an even lower ratio than the ATR. Typical ratios for SMR and ATR are 3-4 and 2-3, respectively (Moulijn et al., 2003), the ratio expected from a CO_2 reformer is 1-2. Table 5.1 summarizes the major differences between ATR, SMR and CO_2 reformers.

Table 5.1: Characteristics of SMR, ATR and CO_2 reformer (Moulijn et al., 2003)

	SMR	**ATR**	**CO_2 reformer**
Energy	External heating of the reactor	Exothermic reaction with O_2	Exothermic reaction with O_2
Temperature [°C]	< 1000°C	< 1200°C	>1000°C
Pressure [bar]	5-30 bar	20-100 bar	20 bar
H_2/CO-ratio	3-4	2-3	1-2

The low H_2/CO-ratio in the product from the CO_2 reformer means that a WGS is needed to shift the syngas to the required H_2/CO-ratio for the methanol reactor. This alternative has, nevertheless, been temporarily included as it allows part of the CO_2 to be recycled in the system.

The various reformer options are modelled as Gibbs reactors in Hysys, to look at product compositions at various conditions. Both steam reforming and partial oxidation of methane are hindered by elevated pressure, due to the increase in number of moles in the reactions. The H_2 and CO content of the equilibrium gas increase with temperature, whereas CO_2 goes through a maximum. H_2 and CO are formed mainly by endothermic reactions, which explain the beneficial high temperature. CO_2, on the other hand, is formed in exothermic reactions only, and is a reactant in endothermic reactions. At low temperatures exothermic reactions are dominating resulting in large amounts of CO_2, whereas at higher temperatures the endothermic reactions become more and more important, which reduces the CO_2 produced. In general it is said to be economically advantageous to operate at the highest possible pressure and temperature (Moulijn et al., 2003). Generally, most downstream applications require syngas at elevated pressure, which means that the higher pressure that is tolerated in the ATR is beneficial. However, most reforming units installed are using steam reforming rather than autothermal reforming due to the large investment costs for an ATR.

In order to choose between the SMR and the ATR with respect to environmental performance, the CO_2 emissions from the reactor itself is important as well as the emissions from production of oxygen and heat. In Section 2.5 the concept of impact categories within LCA was introduced, and the impact category of greenhouse gas emissions are used to evaluate the SMR and ATR with respect to global warming potential. All emissions that contribute to the greenhouse gas emissions are summarized by use of Equation (5-13). The use of the equation is discussed further in Chapter 6.

$$CO_2\text{-equivalent} = CO_2 + 56 \cdot CH_4 + 280 \cdot N_2O + 4300 \cdot HCFC \qquad (5\text{-}13)$$

The CO_2 equivalents (CO_2-eqv) for various operations of the SMR are shown in Table 5.2. “CO_2 from process” is CO_2 formed in the SMR due to thermodynamic equilibrium. “CO_2 from heating” is CO_2 formed in combustion of methane to provide heat for the endothermic reaction. For all cases, except the most promising (S/C=2, T=1000°C), CO_2-eqv from the process is the major contributor. CO_2 from heating increases with temperature, S/C-ratio and pressure. CO_2-eqv from the process decreases with increasing temperature, decreasing S/C-ratio and decreasing pressure. Unconverted methane dominates the CO_2-eqv from the process. Production of steam is not included in the numbers given.

Table 5.2: CO_2 equivalents from the SMR process and production of heat

Test	**Pressure = 20 bar**			**Pressure = 5 bar**		
	S/C=3.5 T=850°C	**S/C=2 T=850°C**	**S/C=2 T=1000°C**	**S/C=3.5 T=850°C**	**S/C=2; T=850°C**	**S/C=2; T=1000°C**
CO_2 from heating	0.55	0.40	0.50	0.42	0.37	0.42
CO_2 from process	7.68	16.68	3.24	1.10	3.37	0.36

In Table 5.3 the CO_2 equivalents from the ATR are given. Again, “CO_2 from the process” correspond to the CO_2 produced in the reactor due to thermodynamic equilibrium. “CO_2 from oxygen production” is CO_2 released from the production of electricity consumed in the ASU. The CO_2-eqv from the process dominates the overall CO_2 emissions in the ATR unit. CO_2-eqv from process decreases with increasing temperature and decreasing S/C-ratio. CO_2 from oxygen production increases with temperature as temperature is controlled with increasing oxygen flow. Production of steam is not included in the numbers given.

Table 5.3: CO_2 emissions from the ATR process and production of oxygen

Test	**Steam/Carbon = 2**			**Steam/Carbon = 3**		
	O_2/C=0.5 T=776°C	**O_2/C=0.625 T=971°C**	**O_2/C=0.75 T=1245°C**	**O_2/C=0.5 T=721°C**	**O_2/C=0.7 T=981°C**	**O_2/C=0.9 T=1246°C**
CO_2 from O_2 production	0.07	0.09	0.11	0.07	0.10	0.13
CO_2 from process	13.50	0.86	0.34	15.37	1.40	0.43

A comparison of Table 5.2 and Table 5.3 shows that the overall CO_2 emissions are, in general, lower for the ATR than the SMR. For both reactors, CO_2 and unconverted methane from the process dominates. Further, unconverted methane has a high global warming potential, the CO_2 equivalents are dominated by unconverted methane when this is present in the product gas. While CO_2 from heating is only a local contribution, CO_2 formed in the reformer results in higher consumption in downstream processes. In addition, CO_2 from heating of the SMR can be reduced, or even avoided, if excess heat is available in the system. The heating requirement is subject for process integration in Section 7.2, where also the production of steam will be included.

An additional issue is to avoid coke to form in the reactor. Coke formation can lead to catalyst deactivation, creation of hotspots and lower selectivity. It can be avoided by increasing the steam/carbon ratio (mole basis) to 2.5-4.5, which is significantly higher than the stoichiometric amount given by Equation (5-10). Coke formation is a more frequent problem in the SMR than the ATR.

In summary, ATR, SMR and the CO_2 reformers all show promising features. The low H_2/CO-ratio produced in the CO_2 reformer does, however, not fulfill the requirement of increasing the H_2-content in the syngas from the gasifier and is not included in the later assessments. It is not possible to recommend one of the other two reactors without evaluation of the total CO_2-eqv from the PtP system. In general, it is important to keep unconverted methane as low as possible, which can be done by increased temperature. The various reformer reactors are tested within the PtP concept in Section 7.2.

6 System evaluation of the PtP concept

Purpose of the chapter:

1. *Present results from the various system evaluations*
2. *Show the potential of the PtP concept*
3. *Compare plastic waste with biomass*
4. *Comparison with alternative process routes (virgin production and other recycling alternatives)*
5. *Demonstrate the need for combination of methods*

This chapter gives a qualitative and quantitative analysis of the PtP concept. The chapter starts with an evaluation of the chemical integration potential within the PtP concept, by use of substance flow analysis. In Section 6.2 the core PtP concept is evaluated by use of LCA, whereas Section 6.3 shows how the core PtP concept can be improved by process integration. The chapter closes with a comparison between the PtP concept and other available options for treatment of plastic waste and production of plastics. The mass flows used in LCA and process integration are given in Appendix 3, with one exception for the LCA; the MTO product mix. For the LCA case, the MTO product mix is 68% ethene and 32% propene, compared to the 61% ethene and 39% propene in the process integration case.

6.1 Chemical integration

Chemical integration was introduced in Section 2.4 and defined as “Systematic methods for designing integrated production systems with special emphasis on high atom utilization”. In order to obtain high atom utilization within a system two strategies were identified, dependent on the type of reaction involved in the system; 1) avoid the production of by-products or 2) utilize the by-products. Within the PtP concept all three reaction types are present, and consequently it is a need for both approaches.

The core strategy, taking plastic waste back to plastic materials, is shown in Figure 6.1. All grey components in the figure are inputs to or outputs from the system, whereas the black components are intermediates. In the core strategy, the final product is the plastic material (PE and PP). More details about the core strategy are given in Section 5.1 and 5.2, and Kaggerud et al. (2005a). From Figure 6.1 it can be seen that there are 3 main challenges that have to be evaluated:

1) CO_2 produced in the WGS in order to increase the H_2/CO-ratio to satisfy the higher hydrogen content of the methanol (carbon loss)
2) Water emitted from the MTO reactor, which is a by-product in the reaction (hydrogen loss)
3) The length of the process train which requires a high unit efficiency

All materials that are leaving the system except in the form of final product is decreasing the atom utilization within the core PtP concept, in Figure 6.1 it is shown that CO_2 and H_2O are leaving the system without adding value to the final product.

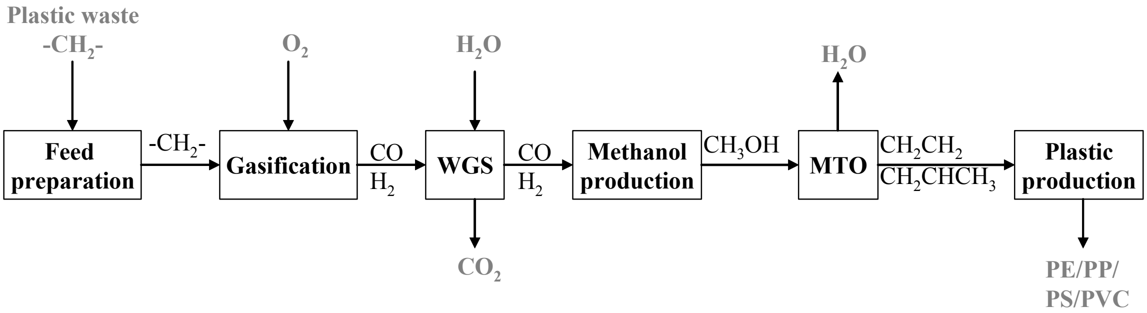

Figure 6.1: Flow of key substances in the core PtP concept.

The first challenge, which is the CO_2 formed in the WGS reactor in order to increase the hydrogen content is a result of system restrictions. As the methanol unit requires a higher H_2/CO-ratio than produced in the gasifier, CO_2 is emitted in an attempt to increase the hydrogen content. The WGS reaction is an example of a displacement reaction, and from the discussion in Section 2.4 it is known that displacement reactions yield by-products. In order to increase the atom utilization, either the reaction must be replaced or the by-product utilized. Replacement of the reaction is discussed in Section 6.1.1, whereas utilization of the by-product is discussed in Section 6.1.2.

The second challenge, which is water emitted from the MTO reactor is a result of the decomposition reaction taking place. Again, either the reaction must be replaced or the by-products utilized to increase the atom efficiency. Utilization of the by-product is evaluated in Section 6.1.1, whereas replacement of the reaction is discussed in Section 6.1.2. The third challenge, which is the decrease in efficiency due to the long process train, is discussed in Section 6.1.1.

6.1.1 Substance flow analysis (SFA)

SFA was introduced in Chapter 2.6, and is used to calculate the carbon and hydrogen efficiencies within the PtP system. By looking at ideal units with stoichiometric reactions within each unit, calculations in the SFA are used to show the potential, with respect to carbon and hydrogen efficiencies, of various process routes. In this approach, the origins of pollution and the fate of the substances in focus are mapped. This can be used to understand the strengths and weaknesses of the system in the early design phase.

The core concept, shown in Figure 6.1, has been evaluated with respect to carbon and hydrogen efficiency in the various steps. Definition of the carbon and hydrogen efficiencies, η_i, for step *z* is given by Equation (6-1):

$$\eta_i^z = \frac{\left(N_i\right)_{out}^z}{\left(N_i\right)_{in}^z} \tag{6-1}$$

The carbon and hydrogen efficiencies for the entire concept are defined as the number of carbon or hydrogen atoms contained in the raw materials that is recovered in the final product. In Equation (6-2) the efficiency is defined for any atom *i*:

$$\text{Efficiency (i)} = \frac{\text{number of i atoms in final product}}{\text{number of i atoms in raw materials}} \tag{6-2}$$

The evaluation of the core PtP concept has been done by using the stoichiometric reactions given as Equations (5-1), (5-3), (5-4) and (5-6). For simplicity Equation (5-5) is omitted. In order to show the theoretical maximum for the core concept, all unit efficiencies are set to 1. In Figure 6.2 and Figure 6.3 the stepwise decrease in carbon and hydrogen efficiency, respectively, for various H/C-ratio feed compositions is given.

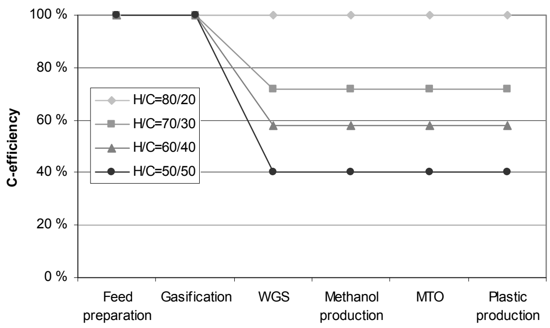

Figure 6.2: Stepwise decrease in carbon efficiency for various feed compositions.

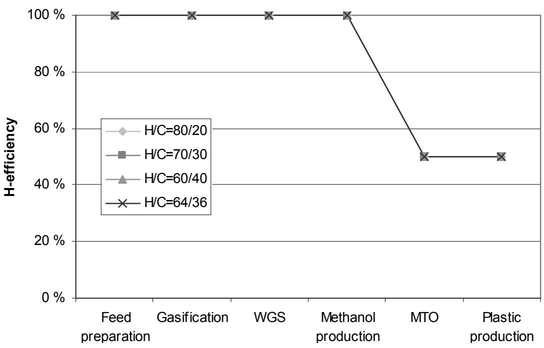

Figure 6.3: Stepwise decrease in hydrogen efficiency for various feed compositions.

As can be seen from Figure 6.2, for all feed compositions lower than 80/20 the carbon efficiency drops in the WGS. The reason for this is the low hydrogen content in the waste compared to methanol (CH_3OH); hence CO in the syngas has to be shifted to hydrogen by use of the WGS-reaction (Equation 5-3), producing equal amounts of CO_2. A high H-content in the feed gives higher carbon efficiency due to the high H/C ratio needed in the methanol production. For an H/C feed composition of 80/20 there is enough hydrogen available in the waste material to produce methanol without shifting the synthesis gas stream towards more hydrogen, hence no drop in efficiency will take place. Plastic waste will typically have an H/C ratio of 60/40-70/30 (H/C=64/36 is used in the subsequent calculations), hence a drop in efficiency will occur in the WGS/methanol production. Various ways to decrease this drop in carbon efficiency is discussed later in this section. In Figure 6.3 the H-efficiency through the concept is given. Independent of the waste composition, the hydrogen efficiency drops to 50% in the MTO reactor. The drop in efficiency is due to the water produced as a by-product in the production of olefins from methanol. Independent of hydrogen content in the waste, the H/C ratio from the methanol unit is 4/1, while in the olefins produced in the MTO unit, have an H/C ratio of 2/1.

As the unit efficiency drops (defined as the internal efficiency in the process) the total carbon and hydrogen efficiency will of course drop as well. For calculations where the H/C ratio is set to 70/30, the total carbon efficiency will drop from 0.72 at unit efficiency 1 to 0.43 at unit efficiency of 0.9. Due to the long process train, a small decrease in unit efficiency will result in a large drop in the total carbon efficiency. The main drop in efficiency is still the methanol production, for the same reasons as explained above. However; as the unit efficiency drops substantially, the other steps in the process will contribute more to the efficiency drop. For a unit efficiency of 0.85 the total carbon efficiency is as low as 0.32. For such low unit efficiencies the drop in carbon efficiency is spread more uniformly along the process train. The same trend is valid for the hydrogen efficiency.

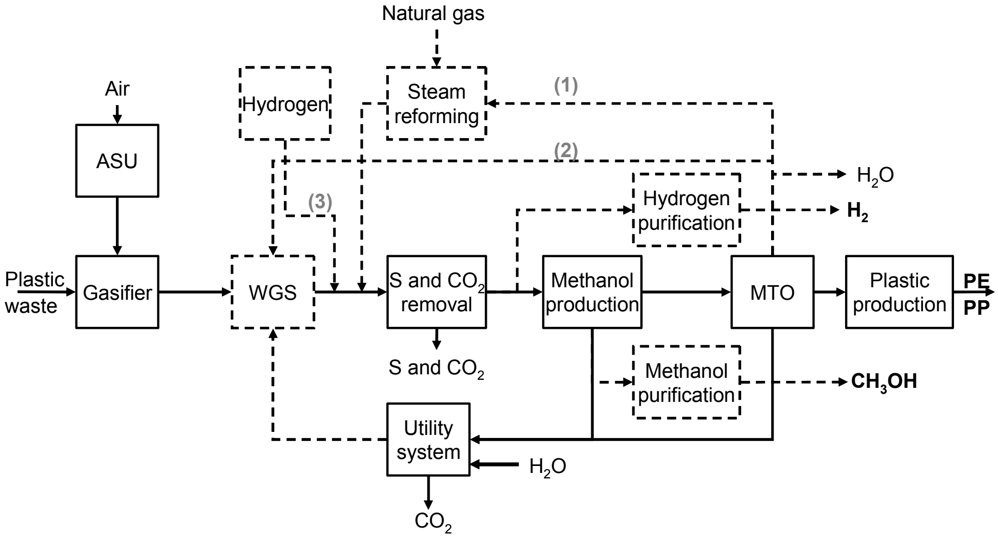

Figure 6.4: Superstructure of the Plastic waste to Plastic (PtP) concept.

Various actions can be taken to overcome the carbon and hydrogen efficiency drop in the PtP concept for production of plastic materials. The reason for the large drop in carbon efficiency in the methanol reactor is the need to increase the hydrogen content in the syngas by use of a WGS reactor. Production of hydrogen in the WGS reactor produces equal amounts of CO_2, which lower the overall carbon efficiency. In order to increase the carbon and hydrogen efficiencies, alternative ways of increasing the hydrogen content in the syngas and utilization of the water from the MTO have been evaluated. The approaches are given below:

(1) Add steam reforming of natural gas, using water from the MTO unit as water source.
(2) Add pure hydrogen to the syngas
(3) Recycle water from the MTO unit to the WGS

Alternative 1 and 2 eliminates the need for the WGS reactor, whereas alternative 2 is an approach to increase the hydrogen efficiency. The pure hydrogen added to the syngas could be taken as excess H_2 from a chlorine production or an oil refinery. The three approaches are shown in Figure 6.4, where the numbers in brackets correspond to the numbered alternatives. The solid-drawn arrows represent mandatory streams and units, whereas the dotted lines represent the various alternatives.

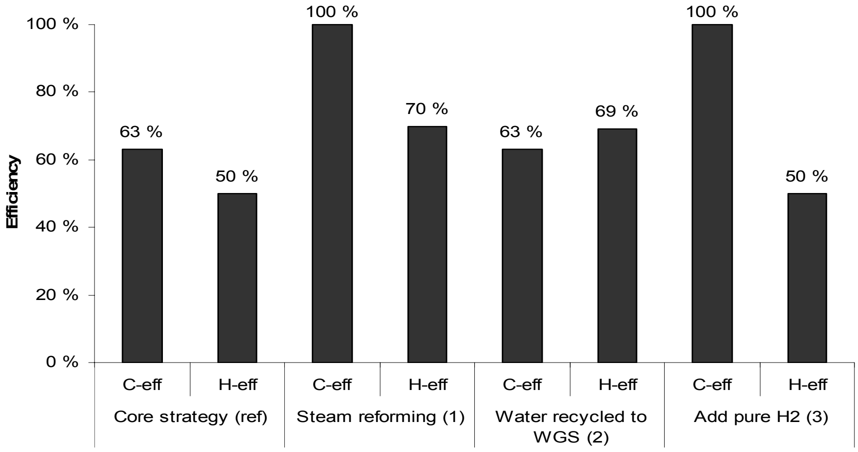

Figure 6.5: Carbon and hydrogen efficiencies for various production schemes for plastic production by the PtP-concept

In Figure 6.5 the carbon and hydrogen efficiencies are given for the core strategy (used as reference) and the various approaches for improvement of the system. The efficiency is calculated from Equation (6-2). All raw materials are included in the denominator (plastic waste, natural gas, H_2O and H_2). The results show that adding a steam reforming unit increases both carbon and hydrogen efficiencies significantly. Recycling of water from MTO to the WGS increases the hydrogen efficiency, whereas the carbon efficiency is unchanged. In the last approach where pure hydrogen is added, all the carbon atoms are recovered, whereas only 50% of the hydrogen atoms are contained in the plastic product. From this point of view the approach with a steam reformer looks interesting. This approach is, however, the most capital intensive of the suggested improvements, whereas the approach with recycle of water from MTO to WGS requires the process train to be located at the same site.

6.1.2 Chemical integration potential in the PtP concept

There are several possibilities for chemical integration within the PtP concept. Alternative configurations to the core PtP concept, can be set up. The H_2O produced in the MTO unit can be recycled and used as the steam input to the WGS reactor. The configuration with a WGS reactor produces equal amounts of CO_2 when CO is shifted to H_2 by steam. To avoid the need for a WGS, H_2 rich syngas or pure H_2 can be added to the system. Hydrogen rich syngas can be produced by reforming of natural gas. Pure H_2 can be produced by electrolysis of water, reforming of natural gas with consecutive

WGS, or it can be found as a by-product in chlorine production and oil refineries. If steam reforming of natural gas is chosen, the H_2O from the MTO unit can be favourably fed to the reformer, and due to the high H/C ratio in the output from a steam reforming unit, this can be combined with the synthesis gas from the gasifier. If electrolysis of water is used as the H_2-source, the water from the MTO unit can be utilized; likewise the O_2 produced in the electrolysis should be used in the gasifier. The various options are summarized in Figure 6.6.

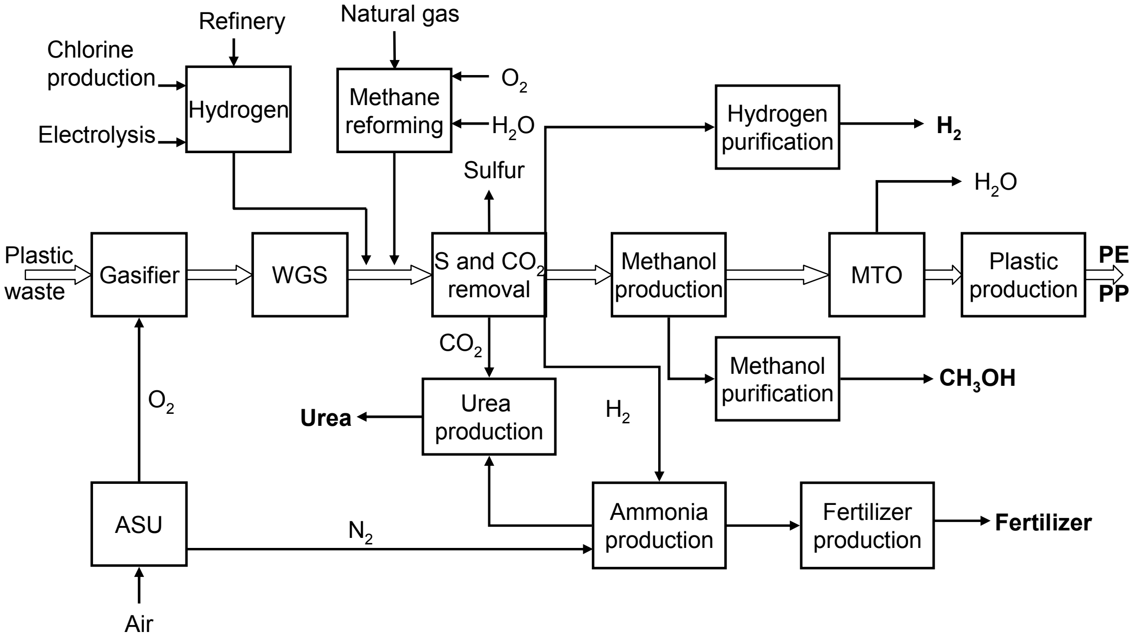

Figure 6.6: Available options in the extended PtP concept (copy of Figure 5.11)

Utilization of the water released in the decomposition reaction in the MTO reactor should be investigated further, as equal amounts of water is produced in the production of olefins. The water cannot be utilized chemically in the MTO reactor, hence for maximum atom utilization, the water should be recycled to the syngas as an important hydrogen source. This can be done by a recycle to the WGS reactor, input to a methane reformer, feed to water electrolysis or as the water slurry in the gasifier.

In addition to the various process configurations for production of new plastic materials, various products can be produced as shown in Figure 6.6. The potential carbon and hydrogen efficiencies for some of the alternative products in the PtP-concept are given in Table 6.1. The carbon efficiency for production of plastic and methanol is equal, as the drop in efficiency comes from the CO_2 that is released in the water gas shift (WGS) prior to the methanol production unit. Clearly the carbon efficiency for both ammonia (NH_3) and hydrogen (H_2) is zero, as no carbon is contained in the final product. For both ammonia and hydrogen, the carbon is released as CO_2 which of course can be captured, but this does not contribute to an increased carbon efficiency as it is defined in Equation (6-2). For hydrogen, the picture is different, with a 100% yield for methanol, ammonia and hydrogen, but only 50% for plastic. The reason for the lower efficiency in production of plastic is the water released in the MTO unit (Figure 6.1).

Table 6.1: Carbon and hydrogen efficiency of various products in the PtP concept

Product	Plastic	Methanol	Ammonia	Hydrogen
C-efficiency	63%	63%	0%	0%
H-efficiency	50%	100%	100%	100%

As can be seen from Table 6.1, neither of the products have both a high hydrogen and carbon efficiency. In order to increase the efficiencies further, chemical integration through utilization of by-products as well as avoiding the by-products to form are suggested. The ideas are given in Figure 6.6, and are similar to the ideas described in Section 3.1 for utilization of natural gas. Nitrogen that is a by-product in the air separation unit can be used in production of ammonia, which is an intermediate in production of both urea and other fertilizers. CO_2 formed in the gasifier and WGS can be used in production of urea.

From Figure 6.1 it is known that the water emitted in the MTO as well as the CO_2 in the WGS are the main obstacles to high atom utilization within the system. Even though this thesis is limited to studying the extended PtP concept as it is given in Chapter 5, it is worth noting that alternative configuration might exists that can improve the hydrogen and carbon efficiency in chemical recycling of plastic waste.

It is clear that co-localization of part or the entire process train will add benefits with respect to chemical integration, especially with respect to utilization of the by-product water in the MTO and the possibility for increasing the hydrogen content in the syngas by adding a reformer unit for natural gas. It is, however, important to remember that atom utilization is only one out of several approaches that are important in development of environmentally friendly processes. A broader discussion of the environmental performance is presented next, as the core PtP concept is subject to life cycle assessment.

6.2 Life cycle assessment of PtP

Life cycle assessment, LCA, is presented in Chapter 2.5. In this section, the method is applied to the core PtP concept.

6.2.1 System boundaries and allocation

The system boundaries are to be set in order to include all important burdens in the system, and avoid all the insignificant streams, the latter for simplicity of the model. Azapagic and Clift (1999b) have used a cradle to gate approach for their study on boron production, as the use and disposal phase will not affect the optimum production routes for the products. This is true as long as there is a demand for all products, or the products cannot substitute each other in the use phase. In this thesis, the system boundaries include all activities from the plastic waste source to the final product at the plant gate, which means that the use of the product is not included. The use phase is important to include in traditional LCA studies mainly for two reasons; comparison of various products which fulfil the same function and identification of which part of the life span that dominate the overall environmental impact. The first is not prevailing for LCA applied to processes. The second factor should always be considered, however, in the present study the process is in focus, and this is why the use phase has been ignored. Production of utilities and feedstock is included as well as transport of the waste. For simplicity, the manufacturing of equipment is not included. Inclusion of this impact could change the overall findings, however, the *methodology* is not influenced by this exclusion. The minimization in number of units will of course work as a rule of thumb with respect to environmental impact from the construction of units, when all other conditions are the same.

Figure 6.7 gives the system boundary for the LCA study. The units within the system boundary take the form of a superstructure to be optimixed. The approach taken here, however, is to do a case based simulation of each of the feasible configurations rather than application of optimization. In Chapter 8, some initial ideas on how to use optimization is given. Clearly some of the alternatives in the superstructure exclude others; one example is adding of hydrogen as a by-product from chlorine production or a refinery combined with production of hydrogen. In addition to the material streams shown in Figure 6.7, heat and electricity is needed in many of the units; details on energy use are given in Chapter 5 and Section 6.3. Production of heat and electricity are not given in the figure, but included in the system boundaries.

Baumann and Tillman (2004) define studies which only include a gate-to-gate perspective as environmental flow models of industrial plants rather than complete life cycle assessment. As transport of waste material is taken into account as well as electricity production, the term LCA is used in this thesis for evaluation of the system even though it is close to a gate-to-gate perspective.

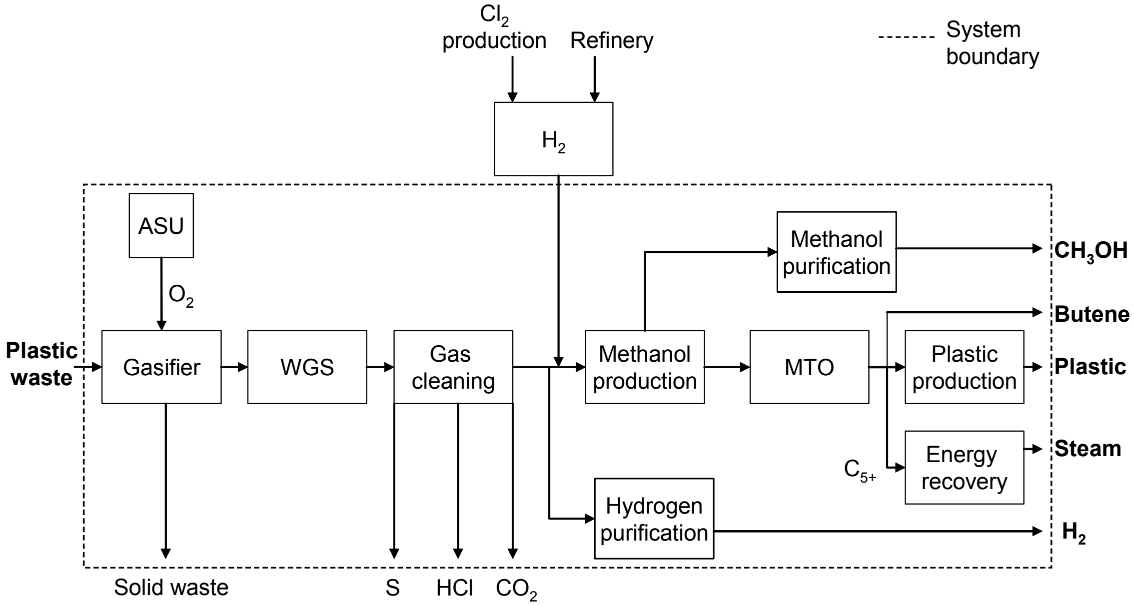

Figure 6.7: System boundary used in the LCA

In addition to the system boundary, allocation of the environmental burdens within the PtP system has to be defined. There are two challenges to take into account, allocation among products in the PtP concept and whether to allocate any of the burdens from the production and use of the virgin plastic. The virgin plastic is the life of the plastic before it enters PtP as waste/input. PtP is a recycling process, hence the question of which of the environmental burdens in virgin plastic production should be allocated to PtP need to be answered. It can easily be argued that the virgin production should get part of the benefit of producing a recyclable product, which means that part of the burden should be allocated to the PtP. However, in this thesis it is argued that as the plastic waste already exists, all the burdens from the production and use of the virgin plastic should be allocated to the virgin plastic. This means that the virgin production will not be included in the PtP evaluation. In addition, there is no need for including the use phase as the focus is on the production processes.

Allocation of environmental burdens between the products is done by mass. However, only PE, PP, methanol and hydrogen have been assigned with environmental burdens, leaving the by-product, butene, without any burden. Butene has not been credited avoided burdens. Credit for avoided burden is often given to the system that produces a valuable by-product.

In addition to allocation of burdens among the various products, assignment of burdens to the different units is important. The assignment is discussed in Appendix 4. The conclusion from that discussion is that it is beneficial for the understanding and search for improvement within the system, to assign emissions to where they are formed.

6.2.2 Functional unit

The PtP concept offers opportunities to produce various chemicals as well as electricity from the plastic waste. From an environmental point of view, the product mix with the lowest environmental impact should be selected. Assume that 300.000 tonnes of plastic waste is available; what could be done with it within the PtP concept? According to the discussion in the previous section, such an evaluation should be done in a holistic system perspective. LCA is a methodology that takes this into account.

In addition to the environmental impact one should also take into account the product demand and production costs. The main objective of the evaluation is accordingly:

Minimize environmental burden in the PtP concept, while maximizing production to meet product demand, and keeping the production costs at a minimum.

To investigate the various process alternatives, the functional unit has been set to:

Production of 1 kg plastic material (0.68 kg PE and 0.32 kg PP).

In order to compare production of various products (plastic compared to methanol and H_2) the functional unit is changed to:

Production of maximum amount of selected product based on the amount of plastic waste needed to produce 1 kg of plastic material in the base case.

This functional unit can be used since this LCA study only takes the process into account, not the use phase.

6.2.3 Data availability and quality

The PtP concept is a large system, which requires considerable amounts of data for the inventory assessment. There are two main challenges regarding data quality in the assessment of the PtP concept: 1) Different state of development of the various units and 2) use of databases with average numbers. The different state of development of the various processes within the concept implies challenges with comparison of various alternatives. Production of plastic material, WGS, gas cleaning and generation of methanol are mature processes with operating plants. On the other hand MTO is still under detailed engineering for construction of the first commercial plant based on stranded gas (Chementator, 2003), while the process for gasification of plastic waste is based on a feasibility study. Data for electricity production can be found in databases, however, a new problem rises as the quality of data in databases differs from data obtained from real processes. Baumann and Tillman (2004) report that using average numbers for background processes like electricity production and real numbers for foreground processes is normal practice within LCA studies.

The data used in the LCA of the PtP concept is taken from various sources. Details and references are given in Section 5.2 and Appendix 6. To allow for change in the scale of the units, energy use is adjusted linearly with mass flow. Electricity is based on the EU-mix given in Appendix 5. In order to minimize the impact of the uncertainties in data used in the study, sensitivity tests are done for the most important inputs in Chapter 7.3. The mass and energy streams in the system are based on the Biomeet report (Ekbom et al., 2003). The report describes a system for conversion of biomass to methanol. As the study was initially done in order to compare the results with a biomass based system (see Section 6.4.3) the same data sources was chosen for both systems. Unfortunately the Biomeet report does not give details about all mass streams, but the combustion of off-gases in the methanol unit is said to cover the steam demand in the WGS, gas cleaning and methanol unit for the biomass case. For simplicity in the first evaluation, this has also been used for the PtP case. This is discussed further in Section 6.5. The combustion of off-gases to produce steam is called "steam island". Further, the combustion of off-gases from the MTO unit is covering the need for steam in the MTO unit, whereas the emissions from production of steam needed in the plastic production is calculated by use of the Econinvent database (2004), by use of the unit "production of steam in chemical processes, at plant".

6.2.4 Process model and simulations

HYSYS has been used to simulate the waste to plastic routes via syngas, methanol and olefins. The model is given in Figure 6.8 (more details in Appendix 6). The steps in the HYSYS model are the following:

1) Syngas from the gasifier is imported and water is removed.
2) Water gas shift (WGS) as a two stage process with addition of steam to obtain a H_2/CO-ratio of 2 after the WGS.
3) Removal of sulfur is modeled as a component splitter using the same split fraction for all scenarios. The split fraction and utility use are given by Ekbom et al. (2003).
4) Removal of CO_2 is modeled as two component splitters, where the first one separates recycle gas and the second one separates flue gas. For plastic waste, the output from the first and second splitter is classified as flue gas since no recycle gas is needed in the gasifier. The same split fraction is used for all scenarios. The split fraction and utility use are given by Ekbom et al. (2003).
5) Reaction of cleaned syngas to methanol at total conversion of 92% (Ekbom et al., 2003). The reactor is followed by a component split of methanol, water and non-reacted syngas. The unreacted syngas (small amounts) is used as fuel gas in the steam island.
6) The CO_2 emissions from the steam island are calculated by combustion of the flue gas from the methanol reactor.

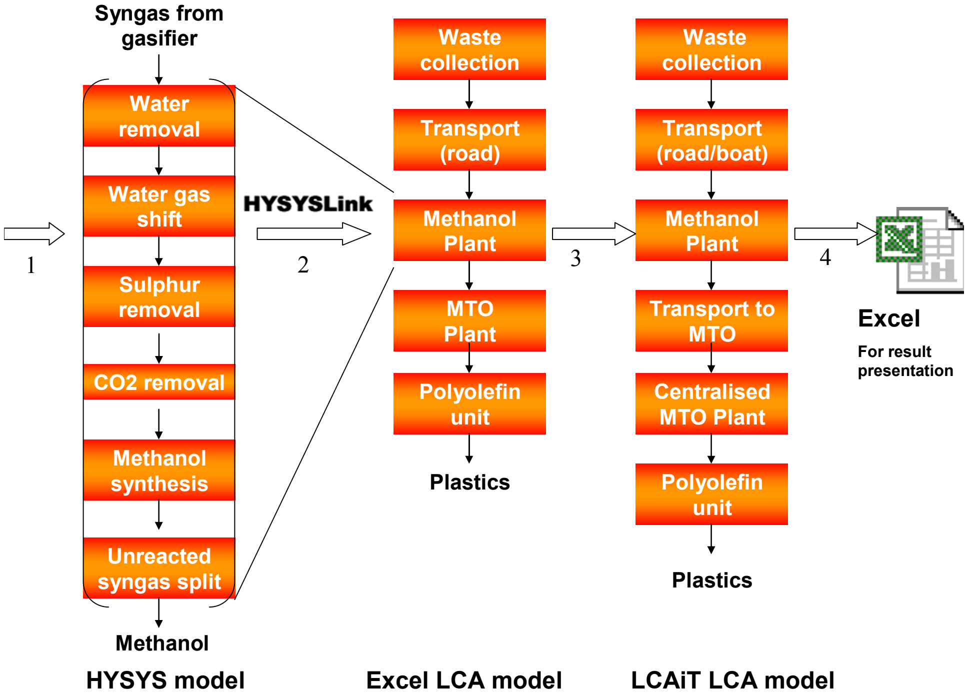

Figure 6.8: LCA-process modelling integration for the waste-to-plastics case study

The results from the HYSYS model were then exported (see Figure 6.8) to an Excel LCA model which includes input, output and emissions for each process step, normalized to the functional unit (1 kg of plastic material). The process units gasification, MTO, ASU, transport and plastic production were not modeled in HYSYS, but modeled directly in the Excel model. In the MTO process, the CO_2 emissions from combustion of the flue gases are calculated by complete combustion in HYSYS, whereas the CO_2 emissions from regeneration of the catalyst are adjusted linearly by the amount of methanol reacted. Production of plastic material is modeled by use of material and energy balances given in the Borealis Borstar technology (Borealis, 1998).

Transport of the waste material by truck to the plant has been included in the model. Transport by truck for 200 km with empty return is used. This transport distance is chosen based on work published by Björklund et al. (2005). The LCI data for the transport of plastics are taken from Baumann and Tillman (2004). The fuel used in transportation is based on fossil resources. Transport of the products is not included in the study. Transport of methanol is, however, included in the LCA-iT model (Figure 6.8), and the results from this approach are given in Nouri and Kaggerud (2006).

The Excel model was used to calculate the CO_2 equivalents emitted from the system, both renewable and non-renewable. The mass flows were then exported to the LCA-iT software (see Figure 6.8) to calculate the other environmental impact categories of the various scenarios using LCA-iT databases. Finally, the impact assessment graphs together with the Life Cycle Inventories, LCI, were exported to Excel files for LCA results presentation.

6.2.5 Results

Only the greenhouse gas emissions are given here since they are of particular interest when carbonaceous material is evaluated. Results for the other impact categories are given in Nouri and Kaggerud (2006). The results from the LCA of the system are given in Figure 6.9. The numbers are normalized, relative to the core strategy, and all improvements evaluated one at a time, using the core strategy as the reference. The CO_2-emissions are broken down into those related to the processes and those related to the use of utilities. This approach is based on the definitions given by Smith and Petela (1991):

<u>Process waste:</u>
Reactor: Unreacted feed, waste by-products, feed impurities, catalyst degradation
Separation and recycle: imperfect recovery and recycling
Start-up and shutdown

<u>Utility waste:</u>
Hot utilities: Furnace, steam boiler, gas turbine, diesel engines
Cold utilities: cooling water and refrigeration
Electricity

Compared with the definition of foreground and background processes referred to in Section 2.5.1, the division into process and utility waste differ in some essential ways. The difference is that the foreground system might also include steam and cooling water, whereas these utilities are treated separately from the rest of the process by the definition given by Smith and Petela (1991). The core strategy is shown as the reference case in the first two columns, whereas the other approaches are based on the core strategy with changes as described in Figure 6.4. The functional unit is production of 1 kg plastic material (0.68 kg PE and 0.32 kg PP). For production of hydrogen and methanol the functional unit is treatment of the same amount of plastic waste as in the core strategy. The transport of waste and products is not included in Figure 6.9 as the contribution is negligible compared to the other activities. This is in agreement with other studies (Bjørklund and Finnveden, 2005). Sulfur and CO_2 removal is included in the WGS, since the numbers are negligible compared to the rest of the contributions.

All CO_2 emissions and other components that contribute to greenhouse gas emissions (CH_4, N_2O and HCFC) are calculated and summarized as CO_2 equivalents on mass basis, Equation (6-3) (Baumann and Tillman, 2004). The potential is given for a 20 year time frame, and provided by the Intergovernmental Panel for Climate Change (IPCC).

$$CO_2\text{-equivalent } = CO_2 + 56 \cdot CH_4 + 280 \cdot N_2O + 4300 \cdot HCFC \qquad (6\text{-}3)$$

The unit on the y-axis of Figure 6.9 is kg of CO_2-eqv per kg of produced functional unit.

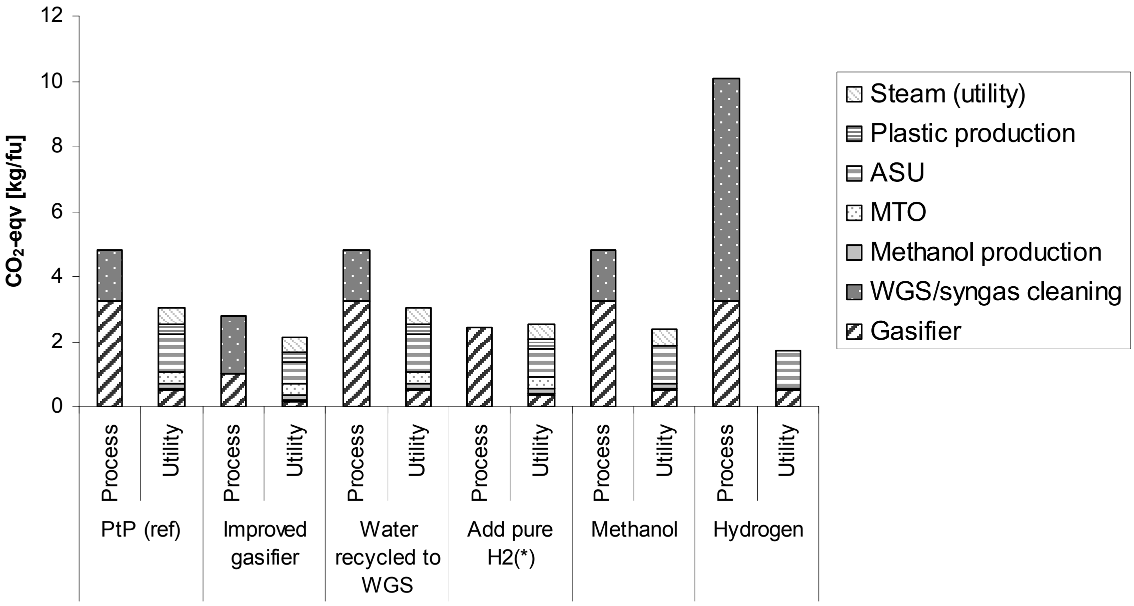

Figure 6.9: Normalized CO_2-eqvivalents for the various approaches in the PtP concept.
(*)Production of hydrogen not included.

In the core strategy, the gasifier, ASU and WGS are the main contributors to the CO_2 emissions. The first approach to increase the performance of the system is to use an improved gasifier. Smith and Petela (1991) claim that the waste streams created by the utility systems tend to be less environmentally harmful than process waste, and further suggest to start at the reactor when considering waste minimization. Starting at the reactor, an improved gasifier which yields a higher quality syngas is used, resulting in lower emissions both from the process and the utilities as more of the plastic waste is converted to valuable products. Two of the approaches for improvement of the system, given in the SFA section, are also evaluated: Recycling of water from the MTO to the WGS and addition of pure hydrogen. Recycling of water from the MTO to the WGS does not contribute to any decrease with use of the GHG impact category, as the water available from the MTO needs to be evaporated to provide steam, hence it is only a way to increase the atom utilization.

Addition of pure hydrogen decreases the total CO_2 emissions in this study. It is important to note, however, that production of hydrogen is not included in the results, since it is taken as a by-product from chlorine production or refineries. If production of hydrogen was included, the total CO_2 emissions would exceed the emissions from the core strategy. Production of methanol reduces the overall CO_2 emissions slightly, compared to the core strategy. Emissions from the MTO and plastic production are avoided, whereas additional purification of the methanol is needed. For hydrogen, no carbon is captured in the final product, resulting in larger CO_2 emissions. The purity of the hydrogen produced is 80 mol%. Capture of the CO_2 emitted in the system is not included, hence all CO_2 that is produced will be emitted. The total CO_2 equivalents per functional unit for the various alternatives are summarized in Table 6.2.

Table 6.2: Total CO_2-eqv per functional unit for the various process concepts

Case [kg CO_2–eqv]	Process	Utility	Total
PtP (ref)	4.8	3.0	7.8
Improved gasifier	2.8	2.1	4.9
Water recycled to WGS	4.8	3.0	7.8
Add pure H_2(*)	2.4	2.6	5.0
Methanol production	4.8	2.4	7.2
Hydrogen production	10.1	1.7	11.8

(*)Production of hydrogen not included

The introduction of a reformer unit is evaluated in Chapter 7. In the next section of this chapter, the core PtP concept is evaluated with respect to process integration potential.

6.3 Process integration (PI)

Process integration as a method is presented in Section 2.3. In this section, the core plastic waste to plastic concept is evaluated with respect to process integration possibilities. The potential for process integration along the production train has been identified, both within the different processes and between them. The grand composite curve (GCC) has been constructed for each unit in order to look at the potential for integration. Design of heat exchanger networks is not part of the study, as the aim is to look at the overall targets and potential within each unit as well as the entire process train. The units are shown with corresponding flowsheets and a brief discussion of the energy sources and energy sinks within each of the units is given. The potential for both process and chemical integration between the different units is important information for deciding whether the complete process train should be co-localized or allowing transport of feedstock and intermediate products.

Two different approaches have been investigated for the core PtP system. In the first approach, the process integration within each unit is maximized, whereas in the second approach all surplus steam and off-gases are sent to a central utility plant which provides utilities for all units. There is, of course, also possible too choose solutions between these two extremes.

The process integration opportunities depend on the quality of the heat available in the process. Construction of the GCC for the process helps identify where heat can be recovered within the process. In addition there is often a need for a utility cooling and/or heating. In general, there are four different situations that need to be taken into account:

1) Threshold problems with a surplus of heat:
   If the heat is available at high temperatures, steam can be produced and utilized for power generation within the unit, or exported to a common utility plant. For processes with heat available at low temperatures, no steam can be produced and cooling water is required for cooling of the processes.

2) Threshold problems with a deficit of heat:
   Heat needs to be supplied to the unit, either by external utilities or the common utility plant.
3) Processes with a pinch point at high temperatures:
   Steam can be produced below pinch and used in power generation within the process or exported to the common utility plant. Heating is required above pinch, which can be provided either by external utilities or the common utility plant.
4) Processes with a pinch point at low temperatures:
   For processes with a low pinch point, no steam can be produced below pinch, and cooling water is required for cooling of the process. Heat is again required above pinch, which can be provided either by external utilities or the common utility plant.

In addition to steam and heat from the process streams, there are combustible off-gases available from the methanol unit and the MTO unit. In the methanol unit this off-gases are called purge gas, whereas in the MTO unit they are called tail gas.

The *first approach* investigated is to utilize the available steam, off-gases and process streams for process integration within each unit only. Both process to process heat integration and power production by use of a single shaft compressor powered by a steam turbine are investigated. First step is to cover the heat required for heating within the process, then excess heat (steam and off-gases) are used for power production. Only the steam and off-gases available within each unit is utilized in the production of power by expansion of steam, including superheat and reheat. In other words, no external heating or firing in the power production. The power production is maximized, but only to the point where the power required within the process is covered, no excess power can be supported to the other units. Excess steam and heat available are then made available for the other processes.

The *second approach* investigated, is to send all available steam and off-gasses to a common utility system, which provide utilities for all units. This approach is a practical version of the total site analysis introduced in Section 2.3. In this approach, all process to process heat recovery is carried out within the unit first, and only steam and off-gases are sent to the common utility system. The reasons for not looking at process to process integration between the units are the controllability, piping and other operational considerations. The common utility plant produces power and steam at various qualities which can be exported to all units via the electricity grid and pipes, respectively.

The power production by expansion of steam is a complicated task with many degrees of freedom: Steam mass flow, pressure level, superheat and reheat temperature and number of stages in the expansion. The choices vary for each situation and more details on the power production are given in Appendix 3.

Each unit, with corresponding block diagram, is presented in Chapter 5. In this section a more detailed description of energy related issues is given. Production of plastic material from olefins is not included in the process integration study, as the possibilities for integration of the well established plastic production units with the other units in the PtP chain are limited. The ASU and gas cleaning processes are also omitted from the process integration study, this is mainly due to data availability and the fact that the ASU is already heavily heat integrated. All GCCs are given for a ΔT_{min} of 10°C and the temperatures in the GCC are given as modified temperatures, T'. Modified temperatures are used in order to represent hot and cold streams as well as utilities in the same diagram. Modified temperatures for hot streams and hot utilities are given by Equation (6-4):

$$T_{hot}^{'} = T_{hot} - \frac{1}{2}\Delta T_{\min} \tag{6-4}$$

Correspondingly, modified temperatures for the cold streams and utilities are given by Equation (6-5):

$$T_{cold}^{'} = T_{cold} + \frac{1}{2}\Delta T_{\min} \tag{6-5}$$

More details from the process integration study are given in Appendix 3.

6.3.1 Gasifier

The flowsheet for the gasification unit is given in Figure 6.10. Air is separated in an ASU providing oxygen to the gasifier. The corresponding nitrogen is liquefied and used in cryogenic grinding of the plastic waste to allow for the small particle size required in the gasifier. Cryogenic grinding is energy intensive, and alternative preparation of the waste should be investigated, this is, however, not included in this thesis. After the grinding, the plastic waste is mixed with the slurry medium, water or oil, and fed to the gasifier. In the base case, water is used as the slurry medium. The slurry is reacted with oxygen in the entrained flow gasifier.

A cooling screen surrounding the reactor controls the temperature of the exothermic reactions and liquefies the ash and other inorganics. After the gasifier, the product gas is led through a direct quench where the gas is cooled instantly to avoid the formation of dioxins (Lightly and Veranth, 1998). In addition chlorine, slag and particulates are transferred to the quench water. The syngas leaving the quench has a temperature slightly above 200°C. To remove the remaining chlorine, the syngas is scrubbed before cooling in the LP steam generator and a cooler. The raw gas leaving the gasification section has a temperature of 35°C. The waste water has a temperature of 200°C when it leaves the quench. The waste water is treated with NaOH to remove chlorine, producing NaCl.

The reactions involved in the gasification of plastic waste are exothermic, giving a surplus of energy from the process. The energy contained in the high temperature synthesis gas is transformed to the low temperature quench water at temperatures around 200°C. The other streams in the gasification unit do not involve large temperature changes. The oxygen for the gasifier is produced by cryogenic distillation in the air separation unit (ASU). The cryogenic process route is the preferred one today, whereas advanced concepts for heat integration can favour the use of membranes or chemical separation in the future (Smith and Klosek, 2001). The ASU is not included in the grand composite curve for the gasification unit, neither is the cryogenic grinding of the waste plastic.

The gasifier is equipped with a cooling screen which allows the ash and other inorganics to become liquid and flow downward to exit the reactor through the quench. The cooling screen consists of tubes where pressurized water is circulated in a closed loop. The temperature of the cooling screen is not given, but it is assumed that the water is too cold for a profitable production of steam. No details are given for steam production or heat released in the gasifier, hence this has not been included in the calculations. From the calculations in Appendix 2 it can be seen that the majority of the available heat is included, since the cooling of the product gas constitute 84% of the available heat.

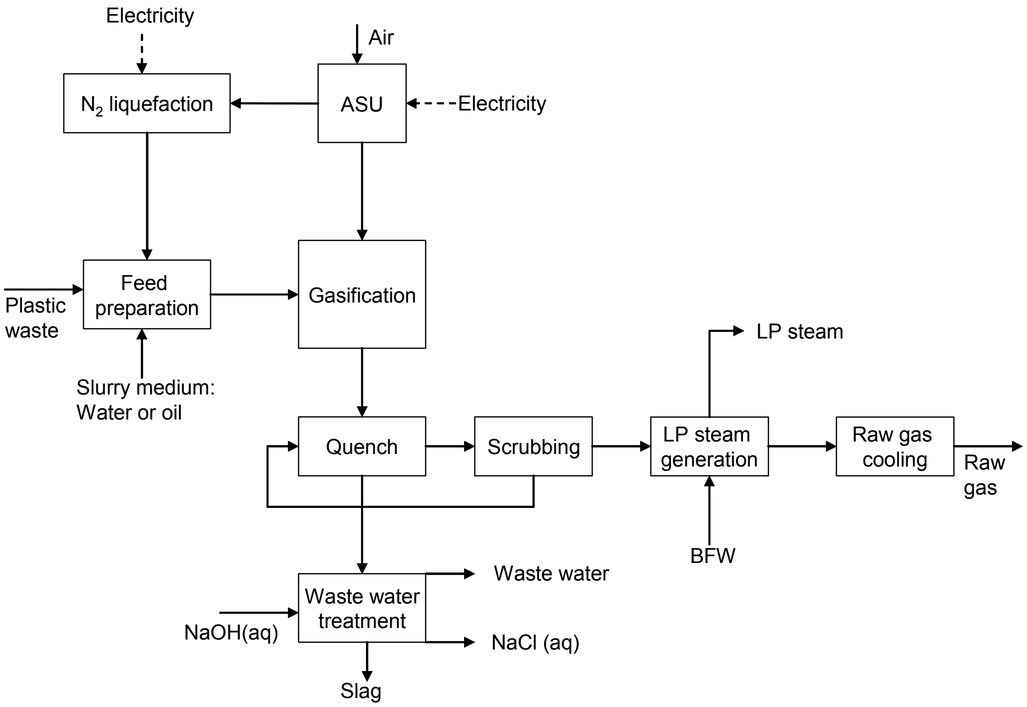

Figure 6.10: Flowsheet of the gasification unit (Future Energy, 2003).

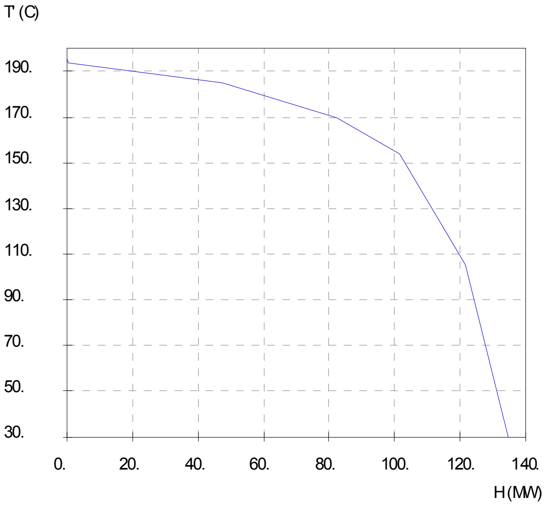

Figure 6.11: Grand **c**omposite curve for the gasification unit with quench

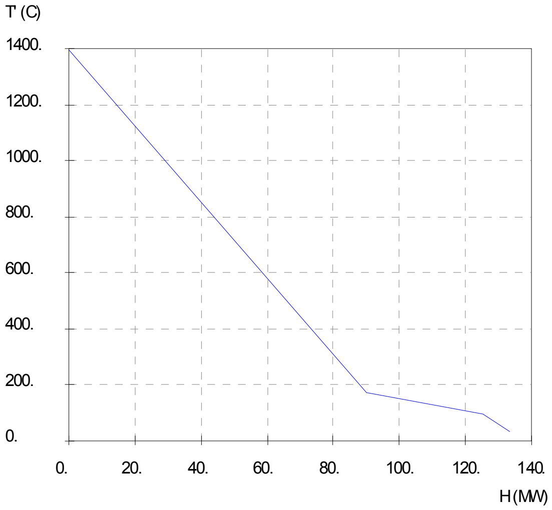

Figure 6.12: Grand composite curve for the gasification unit without quench

The grand composite curve for the gasification unit with quench is given in Figure 6.11. The gasification unit has no significant cold streams, and is an example of a threshold problem with a surplus of heat. There is a considerable amount of low temperature heat available at 200°C in the quench water, and the possibility to produce high temperature steam is limited. The temperature in the gasification reactor is 1400°C, which is a more favourable temperature from a heat and power point of view. One obvious improvement of the energy utilization for the gasification unit is to avoid the quench in order to utilize the high temperature of the product gas. The grand composite curve of the potential energy available, without the use of a direct quench, is shown in Figure 6.12. For both cases, the cooling demand is 135 MW. The option within the use of a quench has not been investigated further, as the quench is today's choice of technology for avoiding dioxin formation. The GCC is, however, included in order to illustrate the large potential for heat recovery that exists if such a solution was available.

In addition to the cooling demand, the process requires 10 MW of electricity. This number includes power demand in the gasifier and pre-treatment of the plastic waste. In addition, the electricity needed in the ASU and nitrogen liquefaction amounts to 40 MW.

6.3.2 Water gas shift and gas cleaning

Next, the syngas is reacted with steam in the water gas shift reactor (WGS), given in Figure 6.13. The WGS is a two step reactor, the first operating at high temperature (feed at 350°C) and the second at low temperature (feed at 260°C). The syngas is heated to the operating temperature before it enters the first WGS, whereas steam needed as reactant in the reactors is produced by cooling the product gas between the reactors. After the syngas has left the WGS section, the product gas is further cooled before it enters the gas cleaning section (50°C). When the cleaned syngas leaves the gas cleaning section, the temperature is 38°C. Process integration opportunities within the gas cleaning section are not included in the study. The total energy requirement is, however, included in later calculations of energy use.

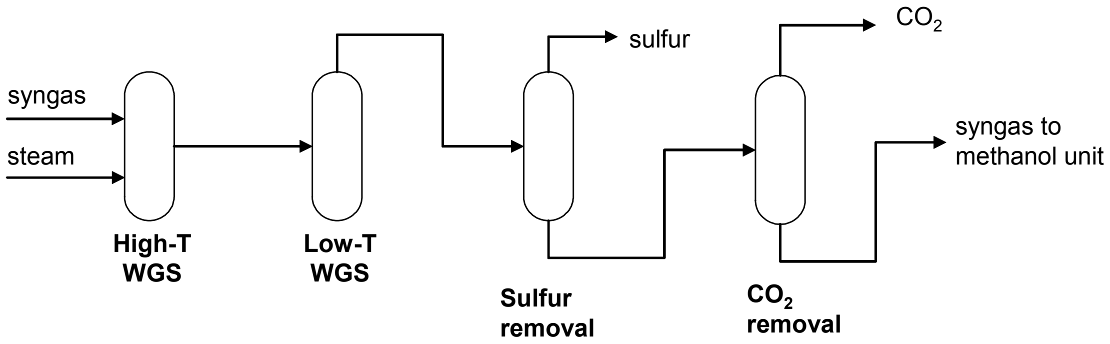

Figure 6.13: Water gas shift reactors and gas cleaning

The grand composite curve of the WGS section is given in Figure 6.14, showing a threshold problem with a deficit of heat. The utility heating requirement is 1.2 MW. The process is able to provide most of the heat required for production of the steam needed in the reactors. If production of steam is not included in the WGS, but provided by a utility system or other processes, the WGS will have a surplus of heat.

The shape of the GCC, with a pocket, indicates that utilization of the temperature difference within the pocket by inclusion of a back pressure turbine could be beneficial. The pocket is, however, considered too small for a profitable utilization of the temperature difference and consequently not included in the study.

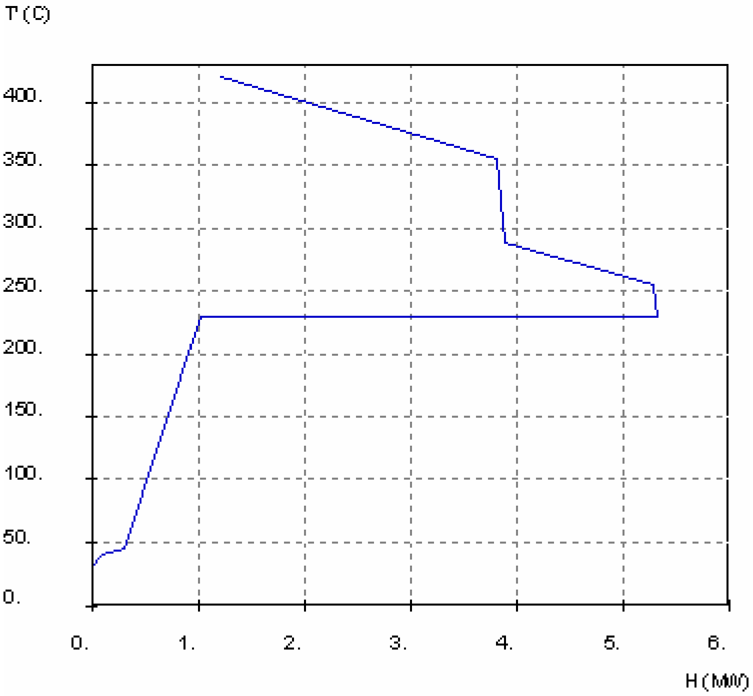

Figure 6.14: Grand composite curve of the WGS reactor system

6.3.3 Methanol production

The production of methanol is an exothermic reaction, and the heat can be recovered in a water jacket which produces saturated steam. The reactor operates at 250°C. The conversion in the methanol reactor is low; hence a high recycling rate of the unreacted syngas is necessary. The methanol production given in Figure 6.15 differs from plants converting natural gas into methanol, since it does not include steam reforming of natural gas. In addition, the MTO plant tolerates crude methanol as input, which means that the separation of methanol and water in distillation columns is avoided. As a result, all the cold streams in a normal methanol unit are removed, and the process integration opportunities within the methanol unit are limited. There are, however, considerable amounts of low temperature heat available from the methanol unit. In addition to the steam produced in the reactor section, heat is available from cooling of the syngas after the compressor and cooling of the product stream before it enters flash 1. The purge gas from flash 1 and 2 in Figure 6.15 can be utilized as an energy source. A compressor with duty 6.3 MW is used to compress the syngas fed to the methanol reactor. In Appendix 3, the compressor has been divided into two units, where one is used for compression of the recycled syngas and the other one for compression of the fresh syngas feed.

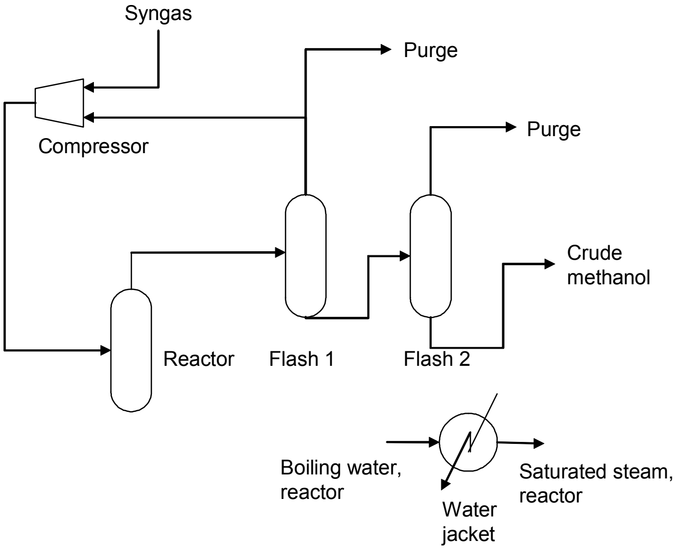

Figure 6.15: Flowsheet for the methanol unit (Moulijn et al., 2003)

The grand composite curve of the methanol production unit is given in Figure 6.16, showing a threshold problem with surplus of heat. The horizontal line is the 26 MW of latent heat available by cooling of the reactor at 250°C. In addition to production of saturated steam in the water jacket surrounding the reactor, various steam levels can be chosen for the production of steam in the GCC. At 200°C, 4.1 MW of steam is available, whereas at 175°C, 6.2 MW of steam can be produced. The steam level chosen depends on the needs in the process. Combustion of the purge streams is not included in the GCC. The methanol unit requires 6.3 MW of power for the compressor, and this can be produced by expansion of the available steam from the water jacket. This option is evaluated in Appendix 3, showing that the required power can be produced by expansion of the steam, using the heat available from the methanol process (given in Figure 6.16) for reheat and part of the heat available from combustion of purge gas for superheat of the steam.

The introduction of heating in the power production gives a pinch point at 250°C /240°C, and there is now a need for utility heating and cooling (a process with a pinch point at high temperatures). The 2.27 MW of heat needed above pinch (superheat of the steam) can be provided by the combustion of purge gas. By integrating the methanol background process with the power production, utility cooling required is 37.2 MW, whereas no utility power is required in the compressors. In addition, 4.71 MW of the heat available in the reactor where the purge gasses are combusted can be utilized in other processes. The GCC for the methanol production with power production is given in Figure 6.17.

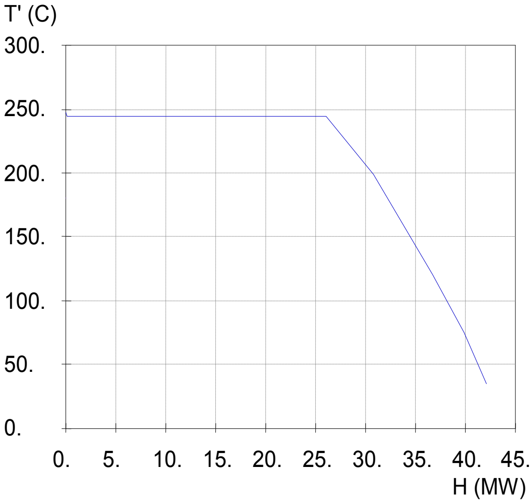

Figure 6.16: Grand composite curve of the methanol unit, without power production

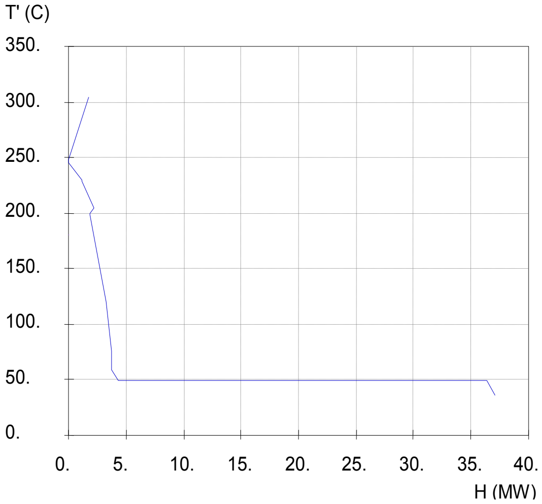

Figure 6.17: Grand composite curve of the methanol unit, with power production

6.3.4 MTO

The main products in the MTO unit are ethene and propene. Depending on the market, the other products shown in Figure 6.18 can be sold or used as fuel gas; here only the tail gas is utilized as fuel. In the MTO process (Figure 6.18), the exothermic reaction takes place at 400-500°C and 1-3 bars, and the catalyst regeneration reactor operates at 500-700°C. One possibility to utilize the energy released in the reactors is to produce saturated steam (40 bars and 250.4°C) in water jackets.

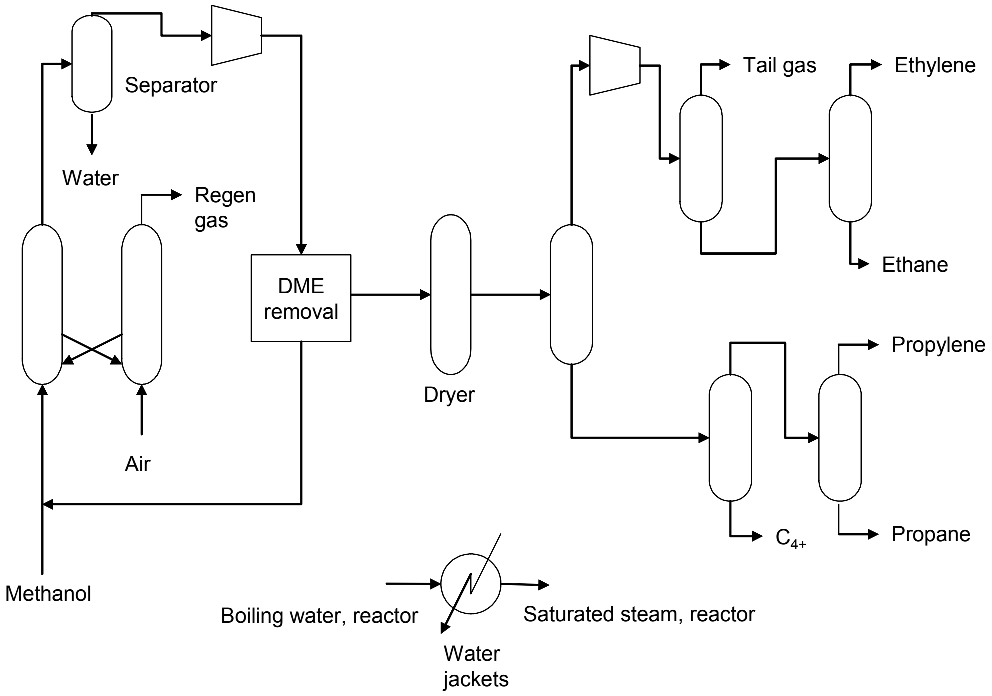

Figure 6.18: Flowsheet for the MTO unit (Kvisle et al., 2002).

The product stream leaving the MTO-reactor is compressed before it enters the separation sequence, and the work needed in this compressor is significant. In the separation sequence, refrigeration cycles are needed. A vapour recompression cycle is used to separate the products in the propene column (C_3-splitter). The grand composite curve of the MTO background process is constructed and given in Figure 6.19. The background process is defined as the process without distillation columns. The saturated steam from the water jackets is not included in the first part of the analysis. The reason is that this steam should be regarded as a utility stream that could be used for heating purposes in the process or for power production in a steam turbine. The intercooling in the 3 stage compression of the product stream (compressor before DME removal) is on the other hand included. The refrigeration section is a utility system, and consequently not included in the background process.

The MTO background process includes both hot and cold streams, which results in considerable internal heat recovery options above pinch. There is a heat deficit of 2.1 MW above pinch. At low temperatures, however, there is a large surplus of heat, 7.8 MW. The MTO process is an example of a process with a pinch point at low temperatures, where no steam can be produced below pinch. In addition to the background process included in the GCC, 14.3 MW of steam is available from the water jackets of the two reactors. The shape of the GCC indicates that the integration of a heat pump at pinch could be interesting, however, this option is not included in the analysis.

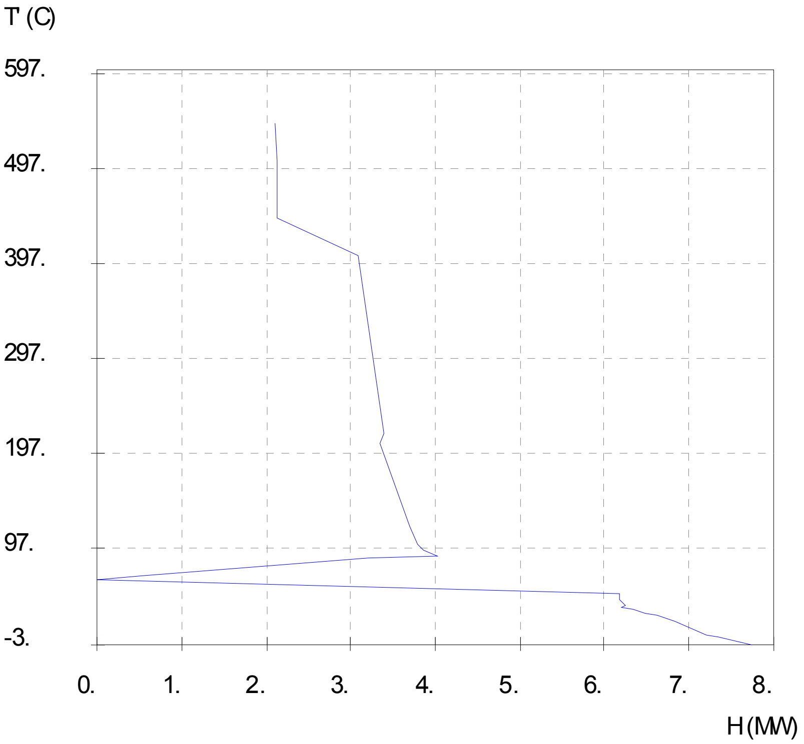

Figure 6.19: Grand composite curve for the background process of the MTO unit

The background process needs 2.1 MW of utility heating at 60°C to 80°C and 7.8 MW of utility cooling at 60°C to 2°C. The refrigeration cycle provides cooling of the cold end of stream 12 and 8 (Figure A3.8), taking them down to 10°C and 2°C, respectively. Reboilers IV and VI are integrated with the background process as shown in Figure A3.9, leaving a cooling demand in the background process of 4.3 MW. The condensers in the distillation columns are integrated with the refrigeration cycle as given in Figure A3.11, leaving a heating demand of 5.2 MW and cooling demand of 5.5 MW in the separation section. The heat demand can be covered by the steam from water jacket 1 (5.2 MW at 250°C), whereas the cooling is provided by use of cooling water. The refrigeration section needs 2.9 MW of external cooling, which is done at elevated pressure against cooling water.

In addition to heating and cooling, there is a need of power in the MTO process. The total power duty needed is 2.7 MW, which is covered by expansion of part of stream 14 (Water jacket 1 in Figure A3.8). Superheat and reheat in the power production is covered by combustion of tail gas and the steam available from water jacket 2. There is a surplus of 2.26 MW of high temperature heat from the combustion of tail gas, and this heat can be used to cover the 2.1 MW of heating needed in the background process (60°C to 80°C).

6.3.5 Process integration between the units

Sections 6.3.1 to 6.3.4 have shown how process integration can be maximized within each unit by process to process heat integration, and utilization of the surplus heat and combustible off-gases for internal power production. Table 6.3 summarizes the heat surplus, heat deficit and power demand in the processes with this approach, termed “first approach” in the introduction to Section 6.3. The integration within each unit is maximized, and only the demands *after* process integration are included in the table. The second column shows the available heat above 200°C within each unit, whereas the third column represents the total surplus heat within each unit. The fourth column gives the total heat deficit of each process and the fifth column is the total power required within each unit after process integration. The last column is the surplus heat available from combustion of off-gases and steam produced in the water jackets. The surplus heat given in the last column is in *addition* to heat available shown in columns two and three.

Table 6.3: Summary of the utilities needed in the *first approach* (maximize PI within each unit)

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10[1]	0
WGS	0	0	1.2	0	0
Methanol	2.1	37.2	0	0	4.7
MTO	0	20.9	0	0	0.2

[1] ASU not included

For the gasifier, the configuration with quench is used, and the power demand in the ASU is not included in the numbers. By use of the *first approach* the possibilities for further process integration between the units are limited. The heat deficit in the WGS can, however, be covered by the available heat in the methanol unit. Whereas the power required in the gasifier can not be covered by expansion of the available steam from the other processes. There is a large surplus of low temperature heat in the system, which can not be utilized with the current configuration. Steam can be produced in the gasifier, 47 MW at 180°C (10 bars), but the limited amount of high temperature heat for superheat and the low pressure of the steam produced makes power production from this steam not attractive.

The approach so far has been to utilize the available steam, off-gases and process streams for process integration within each unit. The *second approach* investigated, is the other extreme, by sending all available steam and off-gases to a common utility plant after process to process heat recovery have been maximized within each unit. The common utility plant can provide utilities, like power and steam, for all units. With a common utility system for all units, power is produced centrally and electricity is sent to the grid to power the compressors. This is in contrast to the single shaft compressor which can be used when the steam is utilized within each unit. The main advantage with a common utility system, is the ability to use a larger steam turbine which has a higher efficiency.

After the internal process to process heat recovery has been maximized for each unit. The steam and off-gases from the methanol unit, MTO and the gasifier are sent to the common utility plant where production of electricity and extraction of steam can be done to fulfill the needs within the entire process train. The heat and power required as well as available heat from the processes are summarized in Table 6.4. Negative numbers represent a need for power or heat, whereas positive numbers are available heat.

Table 6.4: Heat and power available and required after internal process to process heat recovery

Unit	Heat [MW]	T [°C]	P [bars]	Power [MW]	Comment
Gasifier	47.4	180	10.0		Cooling of process
Gasifier	11.6	175	8.9		Cooling of process
Gasifier				-10	Without ASU
WGS	-1.2	25-224			Heating of process
Methanol	26	225	25.5		Water jacket
Methanol	4.1	200	15.5		Cooling of process
Methanol	2.1	175	8.9		Cooling of process
Methanol				-6.3	Compressor
MTO	11.6	250.4	40		Water jacket
MTO	2.7	250.4	40		Water jacket
MTO	-2.1	60-80			Background process
MTO	-5.2	66-125			Separation section
MTO				-2.7	Compressor

First step is to cover the heating required by the processes by extraction of steam from the central utility plant to the process. The surplus heat is then investigated for power production. The heat required in the MTO unit (2.1 MW for the background process and 5.2 MW for the separation process) will be covered by steam produced in the gasifier. The heat needed in the WGS can be covered by the combustion of off-gases (methanol or MTO), steam from the MTO water jackets or by extracting steam from the steam turbine used for power production. The approach chosen is to use steam available from the MTO water jacket.

Production of power is done in a multistage steam turbine, with superheat and reheat of the steam. Power production has been maximized with the available heat for power, superheat and reheat, giving a net electricity production of 14.1 MW.

The summary of the utilities needed by use of the *second approach* is given in Table 6.5. To recapture the second approach briefly; first heat available by cooling of process streams are used to maximize the internal heat recovery within each unit (process to process heat recovery), next surplus steam and off-gases are sent to the common utility plant where steam is extracted for heating of cold process streams in the MTO unit and the WGS, and finally the surplus heat is used for power production.

Table 6.5: Summary of the utilities needed in the *second approach* (use of a common utility plant)

Process [MW]	Surplus heat >200°C	Surplus heat Total	Heat deficit (cold streams)	Power (required)	Surplus heat (steam/ off-gases)
Gasification	0	116.2	0	4.9[1]	0
WGS	0	0	0	0	0
Methanol	0	15.1	0	0	0
MTO	0	12.7	0	0	0
Utility plant	0	48.8	0	0	0

[1]ASU not included

The *first* and *second approaches* are summarized in Table 6.3 and Table 6.5, respectively. For both process integration approaches, the heating required within all processes are covered. The main difference between the two approaches is the power produced. The second approach is able to cover a larger amount of the required power, leaving a need for 4.9 MW in the gasifier, compared to the first approach which requires 10 MW of power in the gasifier. However, the higher power production in the second approach comes with the cost that the processes are now more dependent of each other. In addition the first approach does not require the entire process train to be co-localized, which opens up for the possibility that intermediate products can be transported.

In summary, co-localization of the process train can be beneficial, as process integration between the units decrease the need for utilities. By including all available steam and combustion of off-gases in a central utility plant, it is possible to decrease the need for utilities, however, this approach makes the processes more dependent on each other. From the LCA in Section 6.2, it is known that production of electricity is a large contributor to greenhouse gas emissions. The possibility of process integration through a central utility system should consequently be evaluated as part of the LCA. This is further outlined in Chapter 7. It is, however, important to note that the use of a central utility plant requires more piping and potentially more heat exchangers. This will have an impact on both investment costs and emissions from production of equipment.

There is a large surplus of low quality energy (heat below 200°C) in the system, and there are very few processes that can utilize this. The main source for the low-temperature heat is the quench in the gasification section. A configuration without the quench, which still avoids the formation of dioxins, would be thermodynamically favourable. The low temperature water can otherwise e.g. be used as a heat source for district heating. The next section compares the PtP concept with alternative concepts for production of plastics and treatment of plastic waste given in the literature.

6.4 Comparison with alternative concepts

Comparison of results from various LCA studies should be done with care, since different goal and scope of the studies result in differences in system boundaries, functional units and uncertainty of the data used. Results from various studies are, however, presented below in order to compare the PtP concept with other available options. The comparison is not a thorough benchmarking of the PtP concept, but rather a survey of available options with their approximate numbers. First, a comparison with virgin production of plastic materials is done, followed by recovery options for plastic waste and finally production of plastic materials from biomass by use of the same process train as in the PtP concept.

It is important to note that most published numbers include a benefit for avoided burden when waste treatment is studied. For instance both landfill of the waste and production of virgin material are avoided when the waste plastic is recycled, which is taken credit for in the total emissions from the scenario. In addition, the avoided production of virgin plastic material in recycling scenarios, as well as the avoided production of energy (electricity or heat) in incineration of plastic material with energy recovery is taken credit for. In the evaluation of the PtP concept, benefits from avoided burden are not included, and the comparison with the published results is done with this in mind. The reason for not including the avoided burden in the evaluation is the scope of the study, which is to compare various process configurations within the system. Whether or not the avoided burden is included does not influence the choice between the different configurations. In addition, from a process design point of view, the total amount of emissions from the system is important in order to cope with process improvements.

6.4.1 Production of plastic from virgin sources

Hunt (1995) reported that a typical plastic product life cycle shows that 1.5-2.0 kg of CO_2 is formed per 1.0 kg of plastic material produced. The numbers include extraction of raw materials and production process. In the SimaPro software, various databases are available, that include data for different production processes and waste scenarios. For plastic production, APME has contributed with industrial data, represented as average numbers over the years 1992-1993. CO_2-eqvivalents for some selected plastic materials include; HDPE: 1.88 kg CO_2-eqv, LDPE: 2.07 kg CO_2-eqv, PP: 1.99 kg CO_2-eqv and PVC: 1.9 kg CO_2-eqv, all given per kg of plastic material produced and with the IPCC 2001 GWP method with a time frame of 100 years (described in Section 2.5.3). The database Ecoinvent (2004) is the most extensive database in SimaPro. The numbers they give for plastic production are the same as the ones given by the industrial data provided by APME.

6.4.2 Treatment of plastic waste

Plastic waste can be treated by a range of methods, as described in Section 4.2. The various treatments involve different processes and different end-products, and correspondingly different emissions. In a study of municipal solid waste, Beigl and Salhofer (2004) conclude that material recycling of plastic packaging leads to clearly lower global warming emissions but to very high costs, compared to landfilling and incineration.

Finnveden et al. (2000) have published numbers for incineration, landfill and recycling of PE, PP, PS, PET and PVC. Mechanical recycling of the waste results in the lowest impact for all plastic types, ranging from 0.3 kg CO_2-eqv per kilo of PE to 2 kg CO_2-

eqv per kg of PP. The study is based on the available databases in SimaPro 4.0, and all avoided burdens have been accounted for. The Ecoinvent database (2004) provides CO_2-equivalents for mechanical recycling of PP, PE, PVC and mixed plastics, all numbers given for treatment of 1 kg waste and credit is taken for the avoided production of 1kg of the same plastic material from virgin resources. Negative numbers indicate a net positive effect.

Recycling of PE: -1.6 kg CO_2-eqv
Recycling of PP: -1.7 kg CO_2-eqv
Recycling of PVC: -1.9 kg CO_2-eqv
Recycling of mixed plastics: -2.0 kg CO_2-eqv

Without taking credit for avoided products, all the plastics will have a value of about 0.3 kg CO_2-eqv per kg of treated plastic material.

For incineration of plastic materials Baumann and Tillman, 2004 have reported that 2.8 kg CO_2-eqv are formed per kg of treated waste. This is supported by the findings of Finnveden et al. (2000), giving a GHG potential of commodity plastics like PE, PP and PS of approximately 3 CO_2-eqv/kg plastic material, and Hunt (1995) reporting that CO_2 from combustion of commodity plastics is in the range of 3.1-3.4 kg CO_2 / kg of plastics (Hunt, 1995). The Ecoinvent database (2004) gives the CO_2-eqv without taking credit for the avoided production of electricity from the incineration of the plastic waste:

Incineration of PE: 3.0 kg CO_2-eqv
Incineration of PP: 2.6 kg CO_2-eqv
Incineration of PVC: 2.2 kg CO_2-eqv

Landfilling, which is the final option for treatment of the plastic waste, is reported by Finnveden et al. (2000) to be slightly higher with 3.2-3.5 CO_2-eqv/kg plastic material. The Ecoinvent (2004) gives a much lower value of 0.0854 kg CO_2-eqv, varying from 0.11 for PE to 0.063 PVC.

As a reference, Ross and Evans (2003) have given the greenhouse gas emissions from the entire life span of the plastic material, including production, use and disposal of PE film to be 4.66 kg CO_2-eqv.

6.4.3 Comparison with biomass

A comparison of the plastic waste to plastic concept, PtP, and biomass to plastic, BtP, by use of the same process route has been done based on the LCA approach described in Section 6.2. The processes taken into account are given in Figure 6.20, together with the system boundary. The same definitions of system boundary, allocation, functional units and data sources as those given for evaluation of the PtP concept in Section 6.2 are valid.

The comparison is not done in order to eliminate one of the candidates, biomass or plastic waste, but rather to look at the different possibilities of the available options.

More details are given in Nouri and Kaggerud (2006) and Nouri et al. (2007). The composition of the waste is given in Appendix 1.

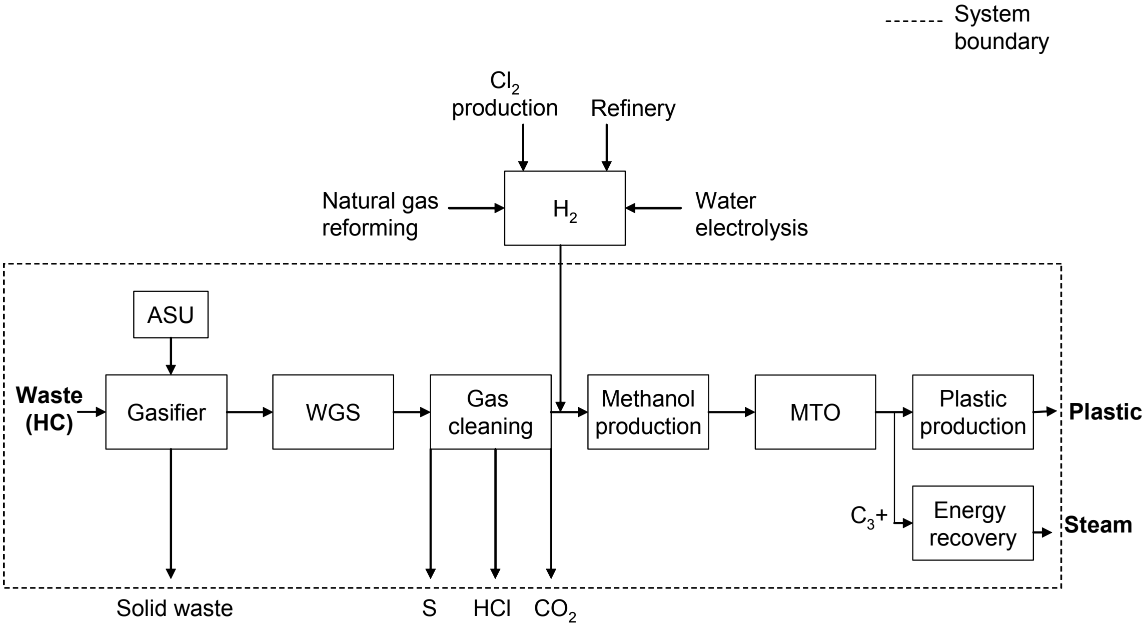

Figure 6.20: Block diagram for production of plastic from biomass (wood waste) or plastic waste, with the system boundary shown as the dotted line.

The results presented here include the entire system producing new plastic from wood waste and plastic waste, respectively, and are based on the combined Hysys, Excel and LCA-iT models described in Section 6.2. All numbers are given per functional unit, 0.68 kg HDPE and 0.32 kg PP. The CO_2-equivalents are divided into renewable and non-renewable. Non-renewable comes from combustion of fossil fuels, e.g. electricity production and fuels, whereas CO_2 formed by carbon in the waste material is renewable. It can be argued that CO_2 from oxidation of plastic waste is not renewable, and should have been given a different name. Whether this CO_2 is renewable or not is not considered here, as the idea is the division of the CO_2 into categories showing whether it comes from the treated material or not. The reason for keeping renewable and non-renewable CO_2 separate is the added knowledge that can be achieved by this method.

A base case scenario for both wood and plastic waste has been considered, and the results are then compared with results from alternative configurations. The alternative configurations are technological improvement of the gasifier and additional H_2 to the system. In addition, the system is tested for sensitivity with respect to change in transport system and variation of electricity mix. The focus is on global warming potential, given as CO_2-equivalents. Results covering other impact categories are given in Nouri and Kaggerud (2006).

The different scenarios have the following characteristics:

1) **Base case:**
   The base case scenario is the core PtP concept introduced in Section 5.1.
2) **Improved gasifier:**
   The water slurry gasifier in the plastic waste case is replaced by an oil slurry gasifier. This improves the heating value of the waste in the gasifier and result in a higher quality syngas. Production of the oil is not included in the assessment as the oil used is assumed to be waste oil that needs treatment.
3) **Added hydrogen:**
   By-product hydrogen from chlorine production or an oil refinery is added to the synthesis gas in order to avoid the need for a WGS. Production of hydrogen is not included in the assessment since the hydrogen is a byproduct from another process.

The results from the various scenarios are summarized in Table 6.6 and Table 6.7 for plastic waste and biomass, respectively.

Table 6.6: Summary of CO_2-eqv for *plastic waste* in the various scenarios

	Base case		**Improved gasifier**		**Adding pure H_2**	
[kg CO_2 eqv]	Renewable CO_2	Non-renewable CO_2	Renewable CO_2	Non-renewable CO_2	Renewable CO_2	Non-renewable CO_2
Gasifier	3.23	0.50	1.0	0.17	2.43	0.37
ASU	0	1.15	0	0.66	0	0.86
WGS	1.58	0	1.77	0	0	0
Gas cleaning	0	0.07	0	0.04	0	0.05
Methanol	0	0.17	0	0.16	0	0.13
Steam island	0.50	0	0.43	0	0.48	0
MTO	0.35	0.01	0.35	0.01	0.35	0.01
Plastic prod.	0	0.25	0	0.25	0	0.25
Transport	0	0.03	0	0.01	0	0.03
Total	**5.66**	**2.18**	**3.55**	**1.30**[1]	**3.26**	**1.82**

[1] 50% oil slurry in the treated material; 1.4 kg of waste plastics per functional unit and 1.4 kg of oil per functional unit.

Table 6.7: Summary of CO_2-eqv for *wood waste* in the various scenarios

[kg CO_2 eqv]	**Base case**		**Hydrogen added**	
	Renewable CO_2	Non-renewable CO_2	Renewable CO_2	Non-renewable CO_2
Gasifier	3.51	0.20	2.50	0.14
ASU	0	0.49	0	0.35
WGS	1.15	0	0	0
Sulferox	0	0	0	0
CO_2 removal	0	0.08	0	0.06
Methanol	0	0.31	0	0.22
Steam island	0.61	0	0.52	0
MTO	0.35	0.01	0.35	0.01
Plastic prod.	0	0.25	0	0.25
Transport	0	0.05	0	0.03
Total	**5.62**	**1.39**	**3.37**	**1.06**

The BtP and PtP processes are more complementary than competitors. The BtP process is a way to produce plastic from biomass, thus being an alternative to other plastic production processes. The PtP is an alternative to waste management of plastic wastes and recycling systems and could therefore be used to handle the plastics produced by the BtP at their end of life. It is, however, interesting to look at the results in relation to each other, and that is done in the following.

Production of plastic waste from biomass and plastic waste is possible by use of the BtP and PtP processes, respectively. The base case scenarios show an advantage for the biomass case, with respect to the non-renewable CO_2-equivivalents. The main reason for the lower CO_2 emissions in the biomass process, is the lower oxygen use in that case due to the oxygen content in the biomass itself (typical biomass composition, dry basis: 50wt% C, 6wt% H, 40wt% O, 2wt% ash and 2wt% others). The main source for non-renewable CO_2-equivivalents in both base case scenarios is the oxygen production (ASU) for the gasifier. The gasifier is the main contributor in the renewable category, and this is due to formation of CO_2 in the gasification process (Section 5.2.2). WGS does also contribute to renewable CO_2 emissions as a result of the formation of equal amounts of CO_2 when H_2 is required (Equation 5-3). The higher hydrogen content is desirable in the methanol production. Various improvements for both the PtP and the BtP are investigated. Improvement of the plastic waste gasifier by use of oil slurry in stead of water slurry reduces the total CO_2 emissions for the system by almost 40%.

If hydrogen is available as a by-product close to the PtP/BtP plant, addition of hydrogen is beneficial for the CO_2 emissions to avoid the need for a water gas shift reactor to increase the H_2/CO-ratio prior to the methanol production unit. Note that the emissions from production of hydrogen are not included in the calculations as hydrogen is only looked at when it is available as a by-product. When this approach was taken, the reduction in renewable CO_2 was 40% and non-renewable CO_2 was 22% for both plastic and wood waste. When production of hydrogen is included in the assessment, this conclusion is not valid.

Sensitivity analyses are carried out with respect to transport systems and the electricity mix. The electricity mix used in the calculations is the EU electricity mix (Appendix 5). If coal based electricity is used in the calculations, the total non-renewable CO_2 emissions increases with 75%, whereas calculations with hydropower results in a decrease of 90%. The transport distance included in the scenarios is transport of the waste for 200 km by truck. For increased transport distances, the total emissions are of course increasing. However, since transport has a low contribution to the total non-renewable CO_2, the increase in total non-renewable CO_2 is lower than for electricity. By increasing the transport distance to transport by ship from Norway to Poland (600 km) and truck in Norway (200 km) and Poland (200 km), the total non-renewable CO_2 increases with 10%. By including ship transport from Asia to Europe (10 000 km) for the intermediate product methanol, the total non-renewable CO_2 increases with 30%.

Both BtP and PtP show interesting possibilities compared to virgin production and to other recovery options. Moreover, the use of sources of excess hydrogen for other purposes than fuel-cell dedicated programs leads to great improvement of biomass and waste based processes. The PtP process is closing the loop of plastic materials by a flexible recycling concept with a minimum need for pre-treatment like sorting and washing. The mass flows in the BtP and PtP are given in Figure 6.21. More wood waste is needed than plastic waste, due to the high water content in the wood waste. On the other hand, the plastic waste requires more than the double amount of oxygen than the wood case. Loss from the “Waste to MeOH” and “MTO” boxes is CO_2, hydrocarbons, ash, water and other inorganic compounds.

The method used for evaluation of the concepts combine process modeling and life cycle assessment. This gives a good understanding of the bottlenecks in the process with regard to both the environmental impact and process performance. The method enables an effective early-design phase evaluation.

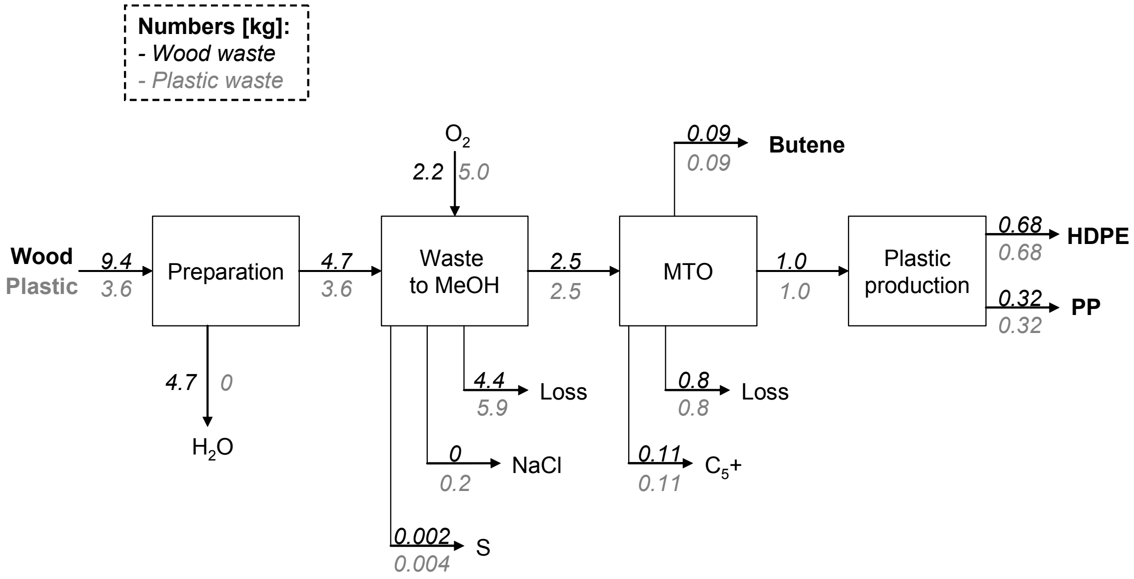

Figure 6.21: Mass flow distribution of wood waste and plastic waste in the waste to plastic system

6.5 Summary of the system evaluation

Section 6.3 has identified possibilities for energy savings through process integration within and between the units, whereas Section 6.1 gave ideas on how to increase the atom utilization (chemical integration) within the system by use of the extended PtP concept. In Section 6.2 the greenhouse gas emissions from the life cycle of the system have been evaluated by use of life cycle assessment.

In the life cycle assessment, steam needed in the WGS is assumed to be provided by combustion of off-gases in the methanol unit. From the process integration study it is known that it is possible to utilize steam and other utilities in a common utility system for the total system, which also can reduce the utility power required in the gasifier. Unfortunately the model employed in the LCA does not have the needed level of details in order to include the identified potential for process integration. The model used in the LCA uses aggregated numbers for the units, whereas process integration requires information on all process streams within the units. Chapter 7 combines PI and LCA through a more detailed modeling and assessment, by use of the proposed LCA-PI algorithm. The process integration findings are included in the inventory analysis.

The two approaches with improved gasifier and added hydrogen show best performance compared with the other alternatives in Section 6.2. These configurations are, however, not developed further in Chapter 7. The main reason is that hydrogen and oil are not easily available, meaning that the large amounts needed in this system will be difficult to obtain. Those configurations are consequently not seen as likely alternatives. Chapter 7 is primarily used to show the method of how to combine LCA and process integration, and the reference case is extended with two methane reformers.

7 Combining LCA and Process Integration

Purpose of the chapter:

1. *Process integration to improve LCA*
2. *LCA to improve process integration*
3. *LCA and process integration in process design*
4. *Case study to quantify findings*

Increased environmental awareness has led to more environmentally friendly products and processes. Over the last decades, however, a new aspect has been increasingly important; the life cycle perspective. The life cycle perspective means that all activities related to a product should be included, from cradle to grave, in order to decrease the overall environmental impact with respect to the given product. The life cycle perspective is included in the macro scale of process synthesis as it is presented in Chapter 2.

The life cycle perspective has been quantified in the environmental performance tool called life cycle assessment (LCA). This chapter shows how process integration can improve the quality of the LCA and vice versa. Process integration introduces a more consistent and improved data set to the LCA, which results in a more fair comparison of the alternatives. On the other hand LCA can help identifying the areas with the largest potential for process integration. In order to quantify these benefits, combined process integration and LCA is applied to a case study. The case study is a chemical recycling concept for plastic waste, which yields a variety of products and includes a range of processes.

Smith et al. (1990) suggested an approach for applying pinch technology to environmental problems. Zhelev and Ridolfi (2006) have introduced the combined emergy-pinch analysis which addresses both energy recovery and environmental concerns. Emergy analysis was proposed by Odum (1996) and is a thermodynamic method that evaluates complex systems by use of one single criterion – the quantity of solar energy necessary to make them available. Traditionally, the pinch concept deals with different resources on a one by one basis (energy, water, hydrogen, etc.), and the idea behind he combined emergy-pinch analysis is to unite different resources and to highlight the future of generated waste.

Emergy analysis has also been proposed to help overcome the inadequacy of single-criterion approaches to life cycle assessment (Ulgiati, 2006) and for the joint analysis of industrial and ecological systems (Bakshi, 2000 and 2002), again in combination with LCA. Emergy has, like LCA, been characterized as simplistic, contradictory, misleading and inaccurate (Hau and Bakshi, 2004). Further, a main challenge is the lack of complete databases with standardized emergy input for various activities. The combination of LCA and process integration as proposed in this chapter can be another way to quantify the environmental burdens of a system.

Compared to the approaches on total site and reduction of emissions by process integration by Dhole and Linnhoff (1993), Klemeš et al. (1997) Axelsson et al. (1999 and 2003) and Ådahl et al. (2004) given in Section 2.3, the LCA-PI algorithm suggested in this chapter differs, first and foremost in the way the that the LCA play a more prominent role, among others since it is carried out as the first step in the approach.

7.1 LCA and process integration

LCA is often criticized because it is difficult to compare different studies. The most prevailing reasons are the choice of system boundaries for the assessment, data quality, allocation of impacts to products and the fact that the methodology is still under development. Especially when large process systems are evaluated, integration of chemicals and energy within and between the units has a great potential for improving the system. Unfortunately LCA does not take this into account. By including process integration within the LCA, the results generated are more robust and the data quality is improved.

The main reasons for combining LCA and process integration (PI) are stated below:

1) Process integration requires mass and energy balances within the concept, thus providing essential and high quality data for the LCA.
2) Process integration identifies the potential and possibilities for heat recovery between and within the units.
3) Life cycle assessment quantifies the environmental impact of the various process alternatives (including design alternatives proposed by process integration).
4) Information is established on both environmental burdens and energy use.
5) An iterative method which combines process integration and life cycle assessment will give a process design closer to the optimum, with respect to environmental performance.

By combining the two methodologies, the environmental evaluation of the system will benefit from the strong points of both. Where PI can provide a guide towards efficient use of heat sinks and sources, LCA summarizes the environmental burdens within a "cradle to grave" perspective and identifies the areas with largest potential for improvement. In order to provide useful information for the process integration part of the study, the emissions quantified in the LCA are divided into process and utility waste. This is in agreement with the definition given by Smith and Petela (1991) for waste minimization in the process industry, and used in Section 6.2.5.

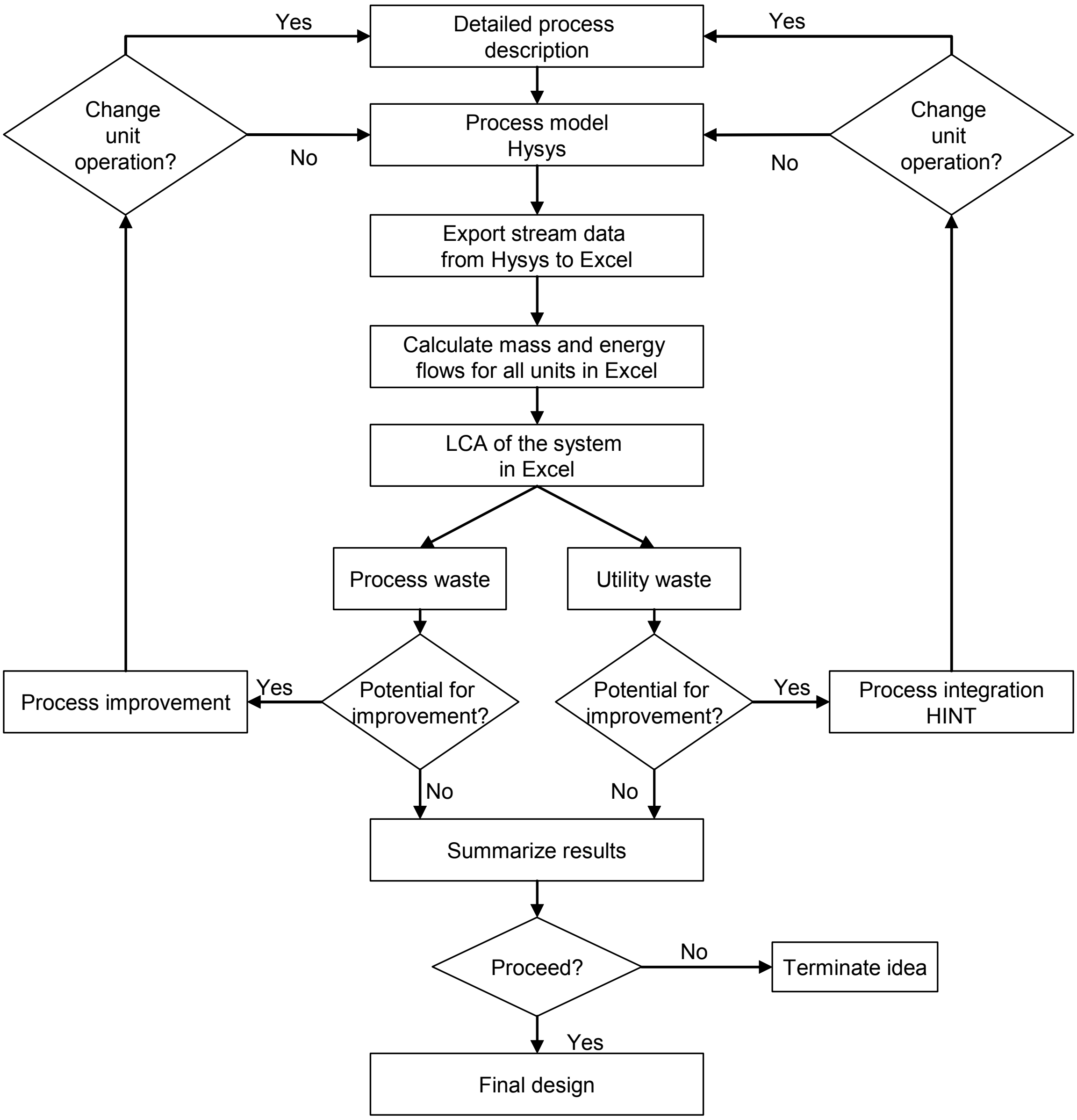

Figure 7.1: The LCA-PI algorithm

7.1.1 The algorithm

An algorithm is developed in order to combine the two tools, LCA and PI, efficiently. The proposed algorithm is given in Figure 7.1. The LCA-PI algorithm described here shows how LCA and PI can be combined successfully in environmental process design. The algorithm starts with a set of possible process routes, for instance developed by the methods in Chapter 6.

A detailed process description is carried out with the level of detail that is available at the current level of design. Based on the description, a process model is built in a simulation tool. The mass and energy balances are summarized, and form the basis for an LCA. The results from the LCA identify the sources of the various emissions, and based on this the potential for improvement is established. The LCA results are divided into process and utility waste in order to give a good basis for evaluation of the improvement potential with respect to process integration and more general process changes. If the LCA identifies large potential for improvements, an adjusted process description with a corresponding process model is established. A new LCA is then carried out in order to evaluate the changes. This iterative process is continued until all potential improvements have been evaluated. The details of the best designs are then summarized, and a more detailed design can be carried out if the process shows promising results. If not, the idea is terminated. The algorithm can be expanded to include other evaluation criteria such as economics; this is briefly discussed in Chapter 8.

7.1.2 Tools

The iterative procedure described above will of course be more efficient if it is built into a model rather than handling the iteration manually. A model has been developed in Excel in order to carry out the case study in Section 7.2. The choice of software in the LCA-PI algorithm is also given in Figure 7.1.

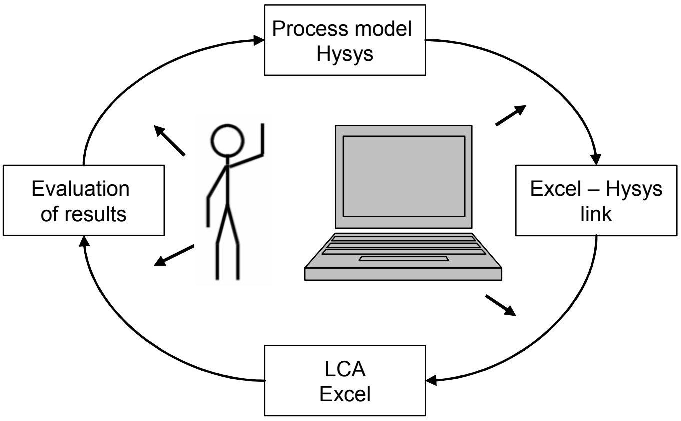

Figure 7.2: User interface for the LCA-PI; computer and process designer

Figure 7.2 shows the interface between the different software tools used in the evaluation. A process model is built in Hysys. The Hysys-Excel link exports stream data from the Hysys flowsheet to the Excel model. The stream data is then used to calculate mass and energy flows for all units in Excel. More details on the Hysys and Excel models are given in Appendix 6 and 7, respectively.

The process integration study is carried out in HINT. The results are given for each unit, divided into process and utility waste. The utility waste is further categorized with respect to the origin (electricity, production of natural gas, etc.) Alexander et al. (2000)

have used a similar approach in their proposal for an optimization tool for environmental design; combining a Hysys process model through a Hysys-Excel link and then doing an LCA in Excel. In this thesis, however, process integration is included in addition to the LCA.

7.2 Case study

The concept for recycling of plastic waste is used as an example to quantify the benefits from combined use of process integration and life cycle assessment. Details of the concept are given in Chapter 5. Compared to the model in Chapter 6, where steam was calculated as available within the system, production of steam is now done by use of utilities. The units requiring steam are the WGS, the gas cleaning section, the SMR and the ATR. The emissions from production of utility steam are calculated by use of the data given for utility steam in the Ecoinvent database (2004).

The total emissions are in focus when it comes to the overall rating of one system compared to another. However, in order to identify possible improvements within the system, the partition into utility and process emissions are beneficial. Only emissions contributing to GWP (CO_2 equivalents) are included in this study. In general, the use of utilities should be minimized for a system. The more inefficient the use of energy is within a system, the more fuel is burned resulting in larger flue gas emissions. In this case, where CO_2 emissions occur from both the utilities and the process itself, the general rule of minimizing the use of utilities is not enough. It is necessary to include CO_2 emissions from both the utilities and the process in the evaluation.

7.2.1 Assumptions and premises

The case study is based on the following set of premises and assumptions.

Premises:
1) More than 50 wt% of the feedstock (plastic waste and natural gas) should be plastic waste in order to be classified as “recycling”.
2) The introduction of a reformer unit should avoid the need for a water gas shift reactor.
3) The H_2/CO-ratio of the syngas fed to the methanol reactor should be close to 2.
4) Economic evaluations are not included.
5) Only emissions that contribute to the category greenhouse gas emissions are included in the LCA (this can easily be expanded to other impact categories).

Assumptions:

1) The following reactors are modelled as Gibbs reactors in Hysys: SMR, ATR, WGS and combustion of off-gases to provide heat.
2) The methanol reactor is modelled as a conversion reactor in Hysys.
3) The plastic waste gasifier, MTO unit and plastic production are modelled as conversion reactors in Excel.
4) Energy use and component splits are modelled linearly with respect to change in capacity.
5) All unconverted syngas is combusted to provide heat for the process, an exception is the unreacted methane from the reformer unit.
6) Natural gas is modelled as methane.
7) Steam for the SMR is available from combustion of off-gases.
8) The fluid package used in the Hysys models is Peng-Robinson.
9) The calculation of emissions from electricity production is taken from the EU mix.

7.2.2 Step 1: Establish and perform LCA of the system

The case starts with the reference case as given in Figure 7.3. All unconverted materials from the methanol and MTO units are combusted in the utility systems in order to produce steam for those units. All emissions from the utility system are included in the utility waste category. In the reference case, plastic waste is gasified with pure oxygen, shifted in the WGS to adjust the H_2/CO-ratio, sulfur and CO_2 are removed before the syngas is converted into methanol, followed by the MTO process and finally production of the plastic products PE and PP (polyethylene and polypropylene). All steam needed in the methanol unit and the MTO is provided by combustion of off-gases (utility system). Emissions from production of steam needed in the WGS, gas cleaning and plastic production are calculated by use of the Ecoinvent database (2004). Use of electricity is not included in the figure, but the ASU, gasifier, gas cleaning system, methanol production, MTO process and plastic production all require electricity. The process integration study is limited to utilization of heat within each unit (hot and cold streams) and use of off-gases to produce steam in the methanol unit and MTO. No process integration takes place between the units, and there is no utilization of steam to power the compressors.

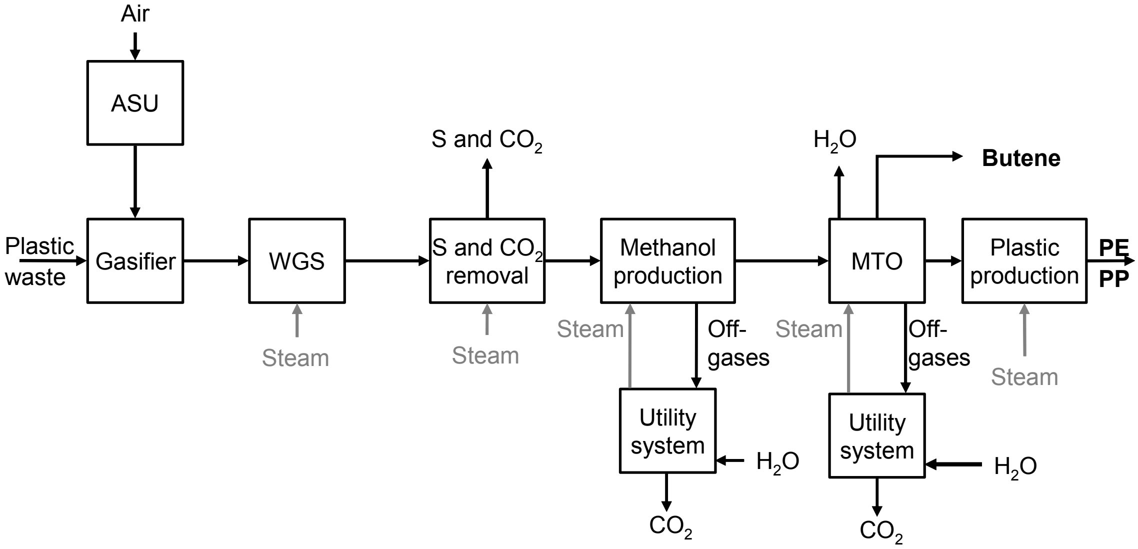

Figure 7.3: Superstructure of the Plastic waste to Plastic (PtP) concept, the grey arrows represent steam

The result from the LCA of this system is given in Figure 7.4. The calculation of CO_2 equivalents is given by Equation (6-3) and the functional unit is defined in Section 6.2.2. From Figure 7.4 it can be seen that the process waste contribute more than the utility waste to the total emissions, 4.8 kg CO_2-eqv and 3.4 kg CO_2-eqv per functional unit, respectively. In addition, there are only two contributors in the process waste category, gasifier and WGS, whereas in the utility waste category there are 8 contributing activities. As it is easiest to decrease the total emissions by reducing the largest contributors, process waste will be the first category for improvement.

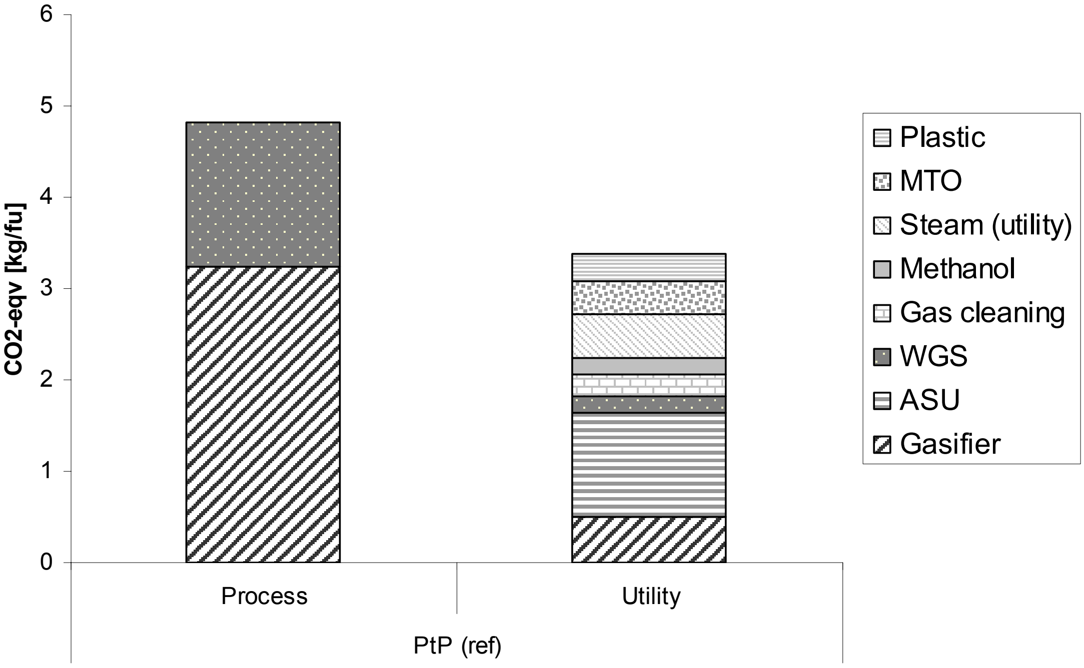

Figure 7.4: Process and utility waste in the reference case of PtP

In the process waste category, the gasifier is the largest contributor. Improvement of the gasifier was introduced in Section 6.2. In order to improve the gasifier, oil was used as the slurry material instead of water. As discussed in Section 6.5, it is expected to be difficult to obtain large quantities of oil, and improvement of the gasifier will not be further discussed here. It is worth noting, however, that improvement of the gasifier is a powerful way of improving the system as it is the largest contributor to CO_2 emissions. The WGS is the other contributor in the process waste category. CO_2 formed in this process step is a result of the desire for higher hydrogen content of the syngas before it enters the methanol production. This CO_2 can be said to come from system restrictions. In order to reduce the CO_2 emissions from the WGS alternative ways of increasing the hydrogen content in the syngas should be investigated. In Section 6.1, addition of pure hydrogen and the use of a methane reformer unit were proposed. The use of a steam reformer unit was identified to have a high potential in the SFA of the configuration, and the introduction of a reformer unit is the next step in order to look for ways to decrease the process waste.

7.2.3 Step 2: Decrease the process waste

The plastic waste to plastic concept with the introduction of a reformer unit is shown in Figure 7.5. The reformer unit can either be a steam methane reformer (SMR) or an autothermal reformer (ATR). The various unit operations are described in Section 5.2 and 5.3. The dotted lines represent alternative process routes, whereas the solid-drawn lines/arrows represent mandatory unit operations/material streams. The numbers in brackets correspond to the various alternatives evaluated in this step. The base line in

Figure 7.5, from plastic waste to new plastic materials, represents the core strategy in the concept.

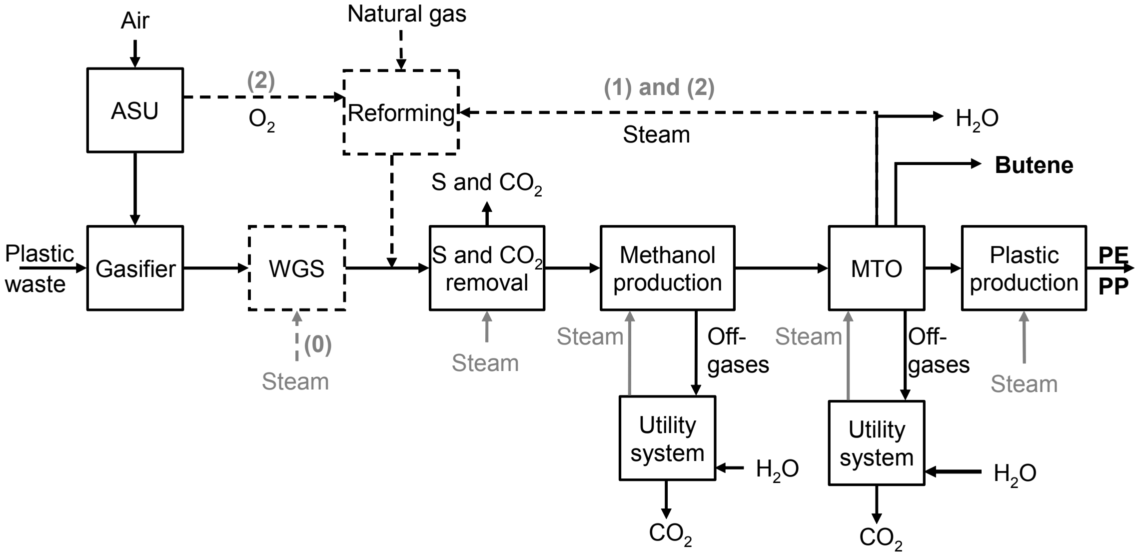

Figure 7.5: Superstructure of the extended Plastic waste to Plastic (PtP) concept, the grey arrows represent steam

Kaggerud and Gundersen (2006a) have identified some promising process routes within the PtP concept. The process routes that are evaluated are the following, where the numbers correspond to the numbers in Figure 7.5:

(0) **The reference case:**
Plastic waste is gasified with pure oxygen, shifted in the WGS to adjust the H_2/CO-ratio, sulfur and CO_2 are removed before the syngas is converted into methanol, followed by the MTO process and finally production of the plastic products PE and PP (polyethylene and polypropylene)

(1) **Steam reformer added:**
The water released in the MTO reactor is recycled to the steam reformer. The higher H_2/CO-ratio in syngas from the steam reformer avoids the need for the WGS. The endothermic steam reformer reaction is supported by heat from external combustion of natural gas.

(2) **Autothermal reformer added:**
The water released in the MTO reactor is recycled to the autothermal reformer. The higher H_2/CO-ratio in the syngas from the reformer avoids the need for the WGS. The endothermic steam reformer reaction is combined with the exothermic partial oxidation of natural gas. Oxygen is provided by the ASU.

The first step is to build the process model which includes the ATR and SMR. The process model could have been built as an optimization task, however, a case based simulation have been used in order to identify the best operating conditions. The results from the various simulations in the SMR case are summarized in Table 7.1. The target values that have been set for each test are the temperature out of the SMR and the H_2/CO-ratio in the syngas after mixing with the syngas from the gasifier. The input value, the steam/carbon ratio, has also been set for each test. Heating of the reactor and methane for the reaction have then been supplied in order to meet the required target values. All ratios are given on molar basis. Again, steam for the methanol and MTO units is produced by combustion of the off-gases in those units, whereas steam needed in the reformer unit, gas cleaning section and plastic production are calculated by use of the Ecoinvent database (2004). The process integration study in this step is limited to utilization of heat within each unit (heating of the reactants in the reformer unit with the product gas) and use of off-gases to produce steam in the methanol unit and MTO. There is no process integration between the units and no utilization of steam to power the compressors.

Table 7.1: Summary of tests with SMR included in the PtP concept

Test	**S/C¹⁾**	**T out of SMR [°C]**	**Heat [MW]**	**H_2/CO²⁾**	**$CH_4$³⁾ [kmol/h]**	**CO_2 eqv from unconverted $CH_4$⁴⁾**	**Total CO_2 eqv⁵⁾**
SMR1	*2*	1000	91	2.02	1000	1.8	*6.8*
SMR2	*2.5*	1000	86	2.03	900	1.0	*6.4*
SMR3	*3*	1000	81	2.01	800	0.6	*6.1*
SMR4	*3.5*	1000	79	2.02	750	0.4	*6.1*
SMR5	*2*	800	61	2.00	1050	18.4	*24.1*
SMR6	*3*	800	72	2.00	1000	12.3	*18.5*

1)Steam/carbon-ratio fed to the reactor; 2)H_2/CO-ratio in the syngas fed to the methanol reactor; 3)Methane fed to the reformer; 4)With decreasing temperature, increasing amount of CH_4 is left unconverted in the reformer; 5)Overall emissions (in CO_2 equivalents) for the PtP concept.

The most important trends for the system with an SMR are the following:

1) Increase in temperature out of the SMR results in a decrease in total CO_2 for the system
2) Increase in S/C-ratio decreases the CH_4 needed for the reactor
3) Increase in S/C-ratio decreases total CO_2 emissions
4) Unconverted CH_4 is the largest contributor to overall emissions at low temperatures

SMR1 to SMR4 all operate at high temperature and have low CO_2 emissions, which is in agreement with the findings in Section 5.3.

The results from the ATR case are summarized in Table 7.2. The inputs that have been varied are the steam/carbon-ratio and the O_2/carbon-ratio fed to the reformer. The H_2/CO-ratio in the syngas after mixing with the syngas from the gasifier has been set to 2. Methane has then been supplied in order to meet the required target values.

Table 7.2: Summary of tests with ATR included in the PtP concept

Test	S/C1)	T out of ATR [°C]	O_2/C2)	H_2/CO3)	$CH_4$4) [kmol/h]	CO_2 eqv from unconverted $CH_4$5)	Total CO_2 eqv6)
ATR1	2	776	*0.5*	2.0	1300	12.7	*18.6*
ATR2	2	849	*0.6*	2.06	1500	4.5	*10.6*
ATR3	2	996	*0.7*	2.02	1900	0.3	*5.9*
ATR4	2.5	747	*0.5*	2.0	1150	13.0	*20.0*
ATR5	2.5	815	*0.6*	2.0	1150	4.7	*11.2*
ATR6	2.5	938	*0.7*	2.02	1450	0.5	*6.7*
ATR7	3	721	*0.5*	2.05	1100	13.8	*21.2*
ATR8	3	786	*0.6*	2.06	1100	5.5	*12.5*
ATR9	3	891	*0.7*	2.02	1200	0.8	*7.4*
ATR10	3	1065	*0.8*	2.0	1700	0.03	*6.5*

1)Steam/carbon-ratio fed to the reactor; 2)O_2/carbon-ratio fed to the reactor; 3)H_2/CO-ratio in the syngas fed to the methanol reactor; 4)Methane fed to the reformer; 5)With decreasing temperature, increasing amount of CH_4 is not converted in the reformer; 6)Overall emissions (in CO_2 equivalents) for the PtP concept.

The most important trends for the system with an ATR are the following:

1) Increase in temperature out of the ATR results in a decrease in total CO_2 for the system
2) Increase in S/C-ratio decreases the CH_4 needed in the system
3) Unconverted CH_4 is the largest contributor to overall emissions at low temperatures
4) Emissions increase with increasing S/C-ratio

ATR3, ATR6 and ATR10 have the lowest total CO_2 emissions, these tests correspond to the highest temperature for each S/C-ratio. The findings are in agreement with the results presented for ATR in Section 5.3.

For both the SMR and the ATR, a high temperature is preferable. Tests ATR3 and SMR3 seem to be the most promising in each of the cases. The overall CO_2 emissions in these two configurations are in the same range. A higher consumption of natural gas in the ATR is due to the lower H_2/CO-ratio in the syngas from the ATR which requires more syngas to meet the target value of 2 in the syngas to the methanol process.

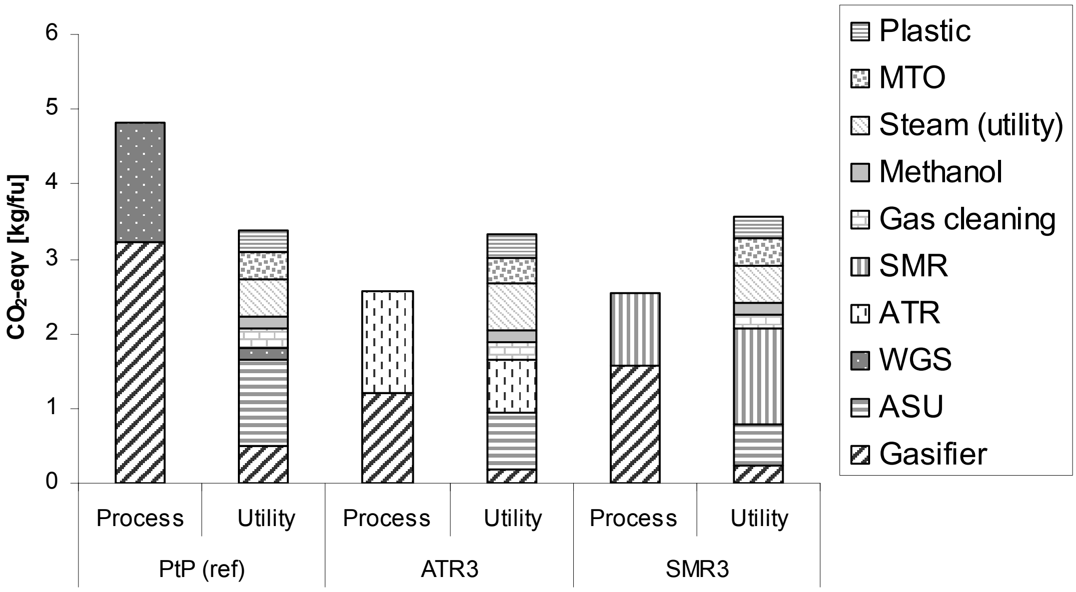

Figure 7.6: CO_2 emissions from process and utilities in the reference case and the two alternative configurations

In Figure 7.6 the most promising configurations with ATR and SMR, respectively, are compared with the reference case. ATR3 and SMR3 correspond to the tests in Table 7.2 and Table 7.1.

The utility emissions are the largest contributor in the ATR case. The process emissions are dominated by the CO_2 produced in the gasifier and the ATR. The ASU, and the production of steam by combustion of off-gases as well as utility steam, are the most important contributors to the utility emissions. Among the units, the ATR and the gasifier dominate the picture with slightly above 50% of the total emissions, utility and process emissions in total.

The utility emissions are the largest contributor to the overall emissions in the SMR case as well. The utility emissions are dominated by the combustion of natural gas for heating of the SMR, but the production of steam by combustion of off-gases and utility steam also contribute with large shares. The process emissions are again dominated by the CO_2 produced in the gasifier and the SMR. The gasifier and SMR are also the most important unit operations with regard to overall emissions.

The reason why the absolute numbers for the gasifier decreases from the reference case to the ATR and SMR case is the increase in production volume when a reformer is added. The CO_2 emissions are given per functional unit and when the amount of product is increased the gasifier has a smaller contribution. This is also the reason why absolute number for the ASU decreases from the reference case to the ATR3 case.

Compared with the reference case, both ATR3 and SMR3 look promising. Both give a considerable decrease in process waste emissions, whereas the utility waste emissions are still high. Use of an ATR which requires oxygen increases the emissions from the ASU, whereas the SMR have large emissions from combustion of natural gas to provide heat for the endothermic reaction. The next step is to look into the utility waste category to identify process integration opportunities, and how to decrease the overall emissions.

7.2.4 Step 3: Decrease the utility waste

The various contributions to utility waste are given in Figure 7.7. Not surprisingly, the emissions from use of electricity is higher for ATR than SMR, this is of course due to the additional O_2 needed in the ATR. The off-gases from the methanol plant have a higher CO_2 content in the ATR-case, which result in higher CO_2 emissions in steam production for the ATR3 than SMR3.

The emissions from production of steam are calculated by use of the Ecoinvent database (2004), and the process unit, "Production of steam for chemical process at plant". Steam is required in the ATR, SMR, gas cleaning and plastic production. The methanol and MTO units are self-sufficient with respect to steam, by combustion of off-gasses.

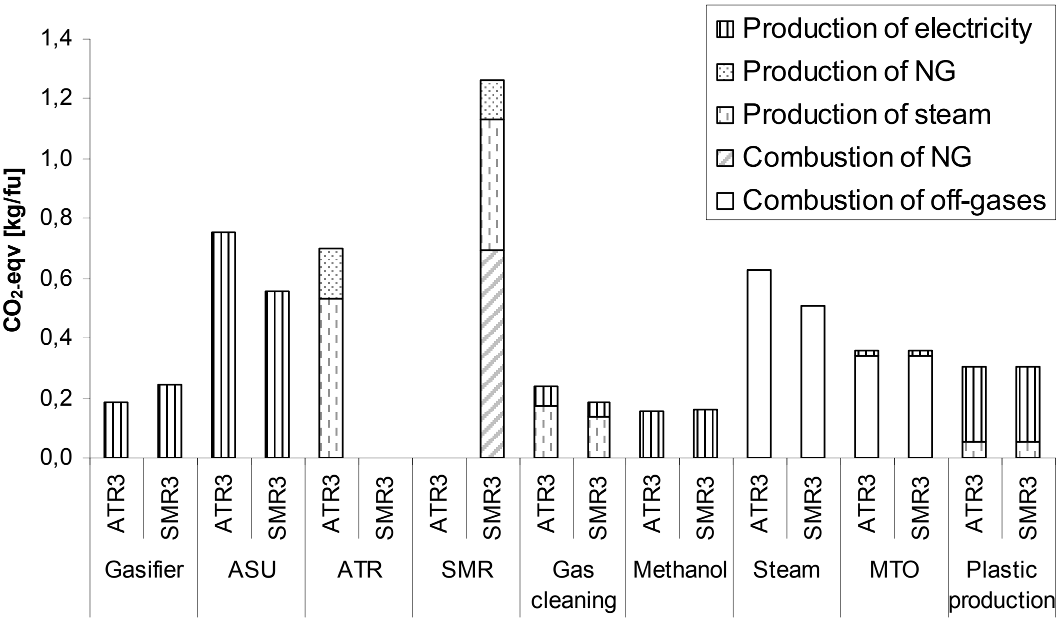

Figure 7.7: Comparison of CO_2 equivalents related to utility waste for PtP with ATR and SMR.

Of the utilities, electricity, combustion of off-gases and production of steam are the largest overall contributors, whereas heat for the SMR and electricity for the ASU are the largest single contributors. Reduction of electricity demand in the system through process integration can be done by utilization of steam for power production, or use of heat as a substitute for electricity if applicable. The latter is only possible if electricity is used for heating, and this is not the case in this system. Consequently, the only possibility for reduction of electricity use, is to utilize surplus heat to produce steam, which is then used to power turbines for electricity production (as done in Section 6.3, process integration). Combustion of off-gases in the methanol unit (labelled “Steam”) and the MTO (labelled “MTO”) is done to produce heat and steam for the units. In the methanol unit, unconverted syngas is burned in a combustion chamber to produce steam. In the MTO unit, tail gas is combusted for production of steam. Heat for the SMR is provided by combustion of natural gas.

The largest contributors to the utility waste are heating of SMR, electricity, and steam production from combustion of off-gases as well as utility steam. The process integration study in Section 6.3 showed that large amounts of heat is available in the system as steam, hot process streams and combustible off-gases. The surplus heat can provide heat for cold process streams, power by expansion of steam, or steam used directly as the reactant in the ATR or SMR. As pointed out above, heating of the SMR has the largest potential for reduction of emissions by process integration together with the various productions of steam in the system. Electricity does also contribute heavily to the green house gas emissions, and from the process integration study (Section 6.3) it is known that the demand for utility electricity within the system was heavily reduced by process integration within and between the units. There will, of course, be a trade-off whether to use the available heat (steam) for power production, heating or a feedstock to the process.

In order to identify the possibilities for improvement by use of process integration within the system, the process integration tool, HINT, has been used. The same premises as in Section 6.3 is used here; only steam and off-gases are fed to the central utility plant, whereas process to process heat exchange has been maximized within each unit. Again the plastic production unit, ASU and gas cleaning are not included in the detailed process integration study. The heat and power requirements of those units are, however, included in the total assessment of the process integration potential. The details of the process integration study are given in Appendix 8.

The process integration study in Section 6.3 showed that the largest saving potential is process integration between the methanol unit, gasifier and the WGS. The MTO unit can also be integrated, but with proper process integration within the unit (as given in Section 6.3.4) all heating and power required is provided within the unit and there is no surplus heat.

The product mix in the MTO unit used in the process integration study (Section 6.3) differs slightly from the MTO process used in the LCA (Section 6.2 and Chapter 7). Since a detailed Hysys process model of the MTO unit has not been constructed, a process integration study for the MTO unit with the LCA product composition will not be undertaken. The heat and power required varies with product composition due to different loads in the distillation columns and the reactors. The difference in product composition is relatively small, ethene/propene ratio of 61/39 (PI) compared to 68/32 (LCA), however, it is not possible to use the existing process integration study for the product composition used in the LCA. From Section 6.3 it is known that the MTO is self sufficient with respect to generation of power and heat for the process. That fact, in addition to the large potential for process integration within and between the other units has led to the conclusion that the MTO is not included in the detailed process integration study in this chapter. The MTO is said to be self sufficient with heat and power by proper process integration within the unit. In addition, the possibility to compare the results from Chapter 7 with the results in Chapter 6, has been preferred.

The process integration study for the SMR3 and ATR3 cases is given in Appendix 8. Only the gasifier, ATR/SMR and methanol plant are included in the detailed process integration study. The MTO is, however, regarded self sufficient with power and heat, as discussed above. Gas cleaning, ASU and plastic production are included only if there is a surplus of power in the system. For both cases, the process to process integration is maximized within each unit, whereas all steam and off-gases are sent to the central utility plant. The central utility plant can produce power by expansion of steam in steam turbines and distribute steam for heating of process streams.

In the ATR case, only power is produced in the central utility plant as there is a surplus of heat in the system. In the SMR case, however, both heat and power is needed from the central utility plant. The trade-off between production of steam and power is evaluated by combined analysis of process integration possibilities and LCA.

In addition to the difficulties experienced in Section 6.2, with assignment of CO_2-eqv to the units and allocation of emissions to the products, a new question is raised when it comes to processes where process integration has been done between the units. In the ATR3 case, steam and off-gases are taken from the gasifier, methanol unit and ATR, and fed to the central utility plant which produces power for all units. The utility plant will then be both an emitter of greenhouse gas (combustion of off-gases) and a producer of power. Here it is chosen to assign the combustion of the off-gases (purge gas from the methanol unit) to the central utility plant. As all the units contribute with heat and off-gases to the central utility system, all units will be provided with power from the utility system, and the remaining power demand is spread evenly among the units. Alternative assignment methods are of course possible, and it is important to keep in mind which assignment method that is used.

Starting with the ATR case, the following benefits have been found by process integration within the units:

1) There is enough heat for steam production and heating of the reactants in the ATR unit
2) Surplus heat is available for power production from the gasifier, methanol and ATR
3) The MTO unit is self sufficient with heat and power by process integration and combustion of tail gas

The heat and off-gases available in the system as well as the power required after process integration within the units are summarized in Table 7.3. In addition, there is a power demand in the ASU, gas cleaning and plastic production.

Table 7.3: Summary of the ATR3 case; after process integration within the units

Process [MW]	Surplus heat >200°C	Surplus heat Total	Heat deficit (cold streams)	Power (required)	Surplus heat (steam/ off-gases)
Gasification	0	134.7	0	10	0
ATR	20.5	20.5	0	17.5 1)	0
Methanol	16.3	44.3	0	19.8	65.4 + 41.5

1) Power needed in the ASU for production of O_2 for the ATR

The heat and off-gases available in the system were then sent to the central utility plant, and by production of power in a steam turbine, a total of 43.1 MW of power could be produced. The utilities that are needed *after* process integration within and between the units are given in Table 7.4.

Table 7.4: Summary of the utilities needed in the ATR3 case when a central utility plant is used

Process [MW]	Surplus heat >200°C	Surplus heat Total	Heat deficit (cold streams)	Power (required)	Surplus heat (steam/ off-gases)
Gasification	0	105.7	0	1.4	0
ATR	0	0	0	1.4	0
Methanol	13.7	41.7	0	1.4	0
Utility plant	0	123	0	0	0

In addition, there is still need for power in the gas cleaning section, as well as power in the ASU (gasifier) and plastic production. The change in CO_2-eqv from the utility system of the ATR is shown in Figure 7.8.

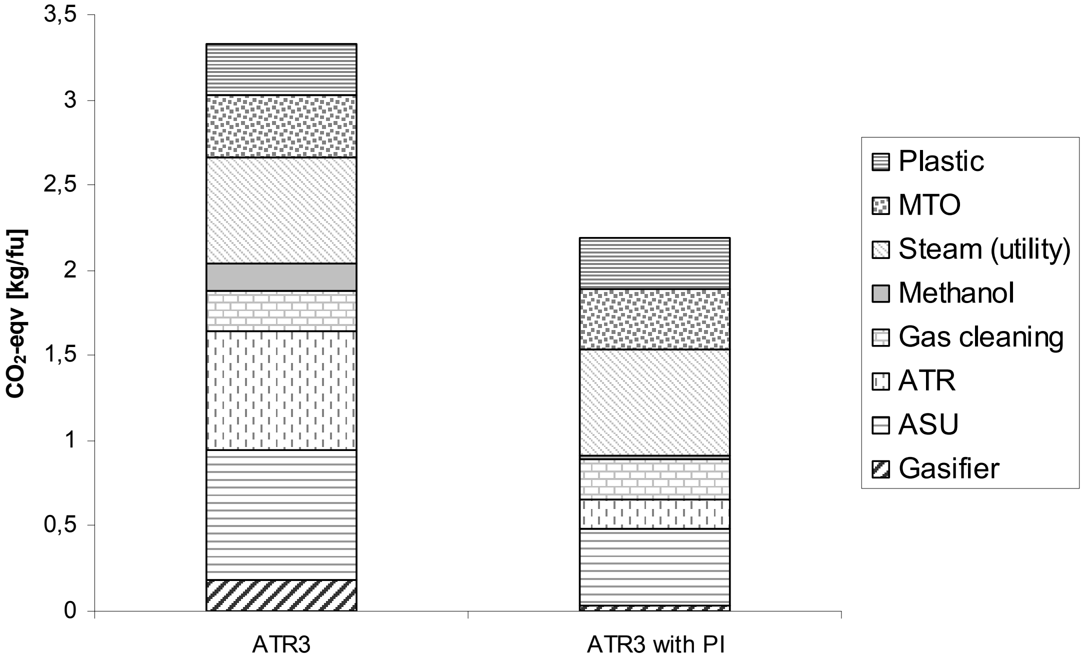

Figure 7.8: Utility waste in the ATR3 case, before and after process integration

Next, process integration possibilities in the SMR3 case are evaluated, and the following benefits are found by integration within the units:

1) Steam required in the SMR can be produced by cooling of the product gas.
2) Heating needed in the SMR, whereas the gasifier and the methanol unit have a heat surplus
3) The MTO unit is self sufficient with heat and power by process integration and combustion of tail gas

The heat and off-gases available in the system as well as the power required after process integration within the unit are summarized in Table 7.5. In addition there is a power demand in the ASU, gas cleaning and plastic production.

Table 7.5: Summary of the SMR3 case, after process integration within the units

Process [MW]	**Surplus heat >200^{o}C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	76.9	0	0
Methanol	14.6	34.8	0	15.9	50.7 + 31.0

In this case, there is a trade-off between production of power and use of the steam as heat. Four different approaches have been evaluated with respect to process integration and total CO_2 emissions, and the details are given in Appendix 8. The approaches range from only heating of the SMR to only power production, via a combination of both, and the results are given here.

Only the 31 MW of heat available from combustion of off-gases is warm enough to heat the SMR reactor, the off-gases will therefore be sent to the SMR unit and are combusted together with the methane. If all the high temperature heat available from the off-gases is used for heating the SMR, no heat is available for superheat and reheat of the steam in the power production. Without superheat of the steam, only small amounts of power can be produced. The utilities needed, heat available and total CO_2 emissions from this approach are given in Table 7.6.

Table 7.6: Summary of the SMR3 case, with heating of the SMR reactor

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	45.9	0	0
Methanol	14.6	34.8	0	15.9	50.7
Total CO_2-eqv emitted from the SMR3 with this approach					**5.35**

An alternative configuration is to use part of the heat available for preheat of the steam and methane which are the reactants in the SMR. The product gas of the SMR unit can then be used for heating of the streams at high temperatures. As the product gas of the SMR unit has a temperature of 1000°C, the reactants can be heated to 990°C by the product gas. If the reactants (steam and methane) are heated to 990°C, 48.1 MW of heat is needed to cover the heat of reaction within the reactor. The heat from combustion of off-gases is then used to heat the SMR reactor, which reduces the need for methane in the combustion. The approach is summarized in Table 7.7. It is, however, not possible with today's technology to carry out process to process heat exchange at such high temperatures (up to 1000°C), and the following two configurations (results given in Table 7.7 and Table 7.8) are to be seen as a purely theoretical approach. The high temperatures can give metal dusting when operating with CO/H_2-mixtures.

Table 7.7: Summary of the SMR3 case, with heating of reactants and the SMR reactor (theoretical)

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	17.1	0	0
Methanol	6.0	26.2	0	15.9	30.6
Total CO_2-eqv emitted from the SMR3 with this approach					**5.08**

An alternative approach is to utilize the remaining heat, after heating for the reactants, for power production. Power production is done in a central utility plant by expansion of steam in a three stage steam turbine. A total of 18.7 MW of electricity is produced, leaving 8.5 MW of the heat from the combustion of off-gases available, after the power generation. The heat will be used for heating of the SMR reactor. There is not enough power to cover the demand in the gasifier and the methanol unit, and the remaining 7.2

MW of power is divided evenly among the two units. The findings are summarized in Table 7.8.

Table 7.8: Summary of the SMR3 case, with heating of reactants and SMR, and power production (theoretical)

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	125.5	0	3.6	0
SMR	0	0	39.6	0	0
Methanol	6.0	26.2	0	3.6	0
Utility	0	42.5	0	0	0
Total CO_2-eqv emitted from the SMR3 with this approach					**5.06**

The last approach is production of power from all the available steam and off-gases, heating of the SMR is then done by combustion of methane only. A total of 28.6 MW of electricity is produced in the three stage steam turbine, giving a surplus of power of 2.7 MW from the system. The power can be utilized in the gas cleaning section, ASU or plastic production. The power has been utilized in the ASU prior to the calculation of total CO_2-eqv in this approach. The findings are summarized in Table 7.9.

Table 7.9: Summary of the SMR3 case, with power production

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	119.4	0	0	0
SMR	0	0	76.9	0	0
Methanol	14.6	33.5	0	0	0
Utility	0	67.2	0	0	0
Total CO_2-eqv emitted from the SMR3 with this approach					**5.24**

From the results presented above, it is clear that process integration reduces the overall CO_2 emissions in all approaches. The two approaches with heating of the process reactants (Table 7.7 and Table 7.8) are the most promising approaches, they are, however only theoretically available. Among the other two configurations (Table 7.6 and Table 7.9), the case with power production from all the available steam and off-gases are the most promising. A discussion of the different pros and cons of these two configurations are given in the following.

The first of the two approaches utilizes the heat available from combustion of the off-gases in the methanol unit to cover heating of the SMR reactor. This approach requires piping from the methanol unit to the SMR unit, whereas power for the methanol unit and the gasifier is provided by utility power. In the second approach, steam and off-gases from the methanol unit and the gasifier is sent to the common utility plant and used in power production. This approach is more complex than the previous since it, in addition to piping, requires a central utility plant. A central utility system is required for back-up in both configurations, but this does not make the various processes dependent on each other. Emissions from the construction of piping and equipment are not included in the assessment, but the minimization of equipment is used as a rule of thumb. On the other hand, the use of off-gases in combination with methane in the SMR reactor might require a more complex burner. The second approach is the preferred configuration, with respect to greenhouse gas emissions. With respect to complexity, the first approach might be the preferred one. In addition to the complexity and emissions from the system, both costs and operational issues like flexibility and control has to be taken into consideration. These aspects are, however, not included here.

The change in utility emissions in the SMR3 case, by use of the process integration approach with power production, is given in Figure 7.9.

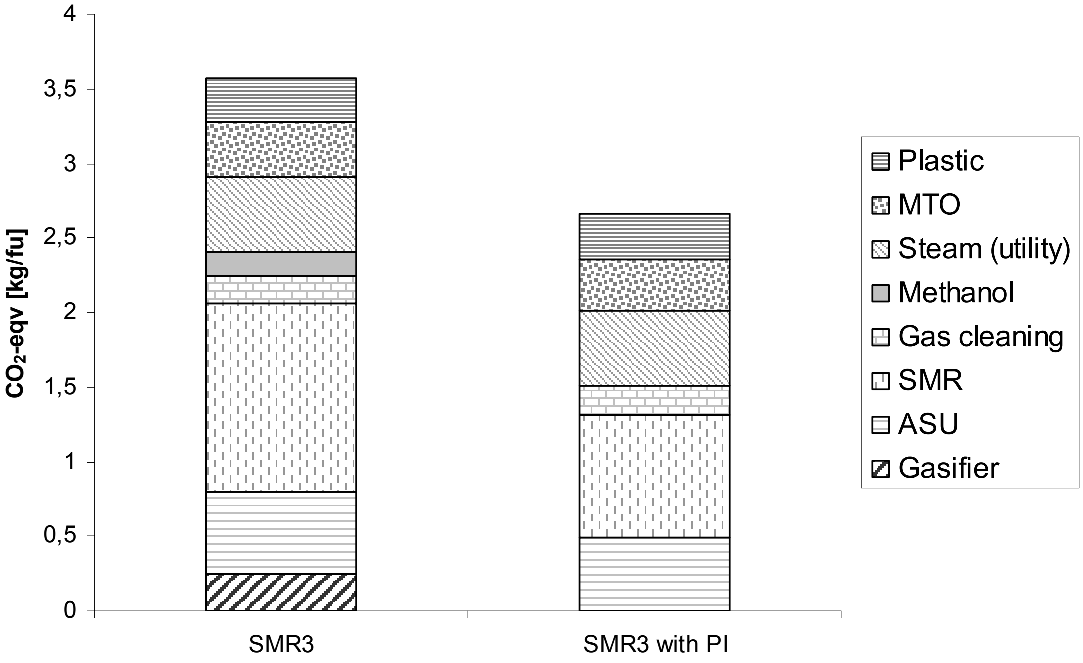

Figure 7.9: Utility waste in the SMR3 case, before and after process integration

As for the ATR3 case, the utility waste is reduced significantly by proper process integration. The emissions from the SMR unit are reduced due to the heat supplied by the methanol unit and the steam production in the utility plant, labelled Steam (utility) in the figure. All other units remain unchanged in this case, as the units that contribute with heat are not credited for avoided burden.

7.2.5 Step 4: Summarize the findings

The last step in the procedure is to summarize the findings. From step 2 it is known that the process waste can be reduced by including a reformer unit in the value chain from plastic waste to plastic, whereas step 3 has shown how process integration can reduce the utility waste.

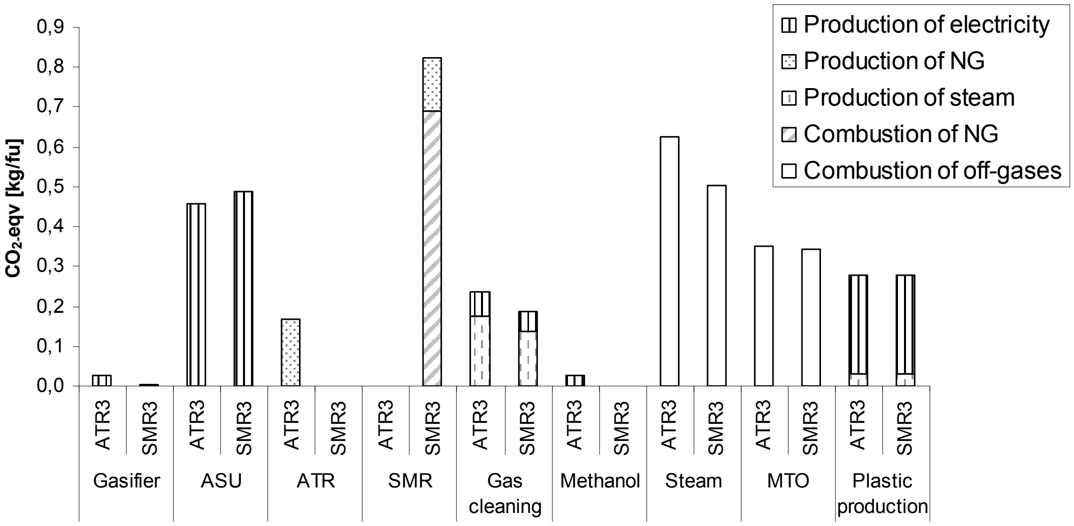

Figure 7.10: Utility emissions in ATR3 and SMR3 after process integration

The utility waste for each unit in the ATR3 and SMR3 case is summarized in Figure 7.10. The utility emissions given in Figure 7.10 differ from the original utility emissions in Figure 7.7 in several ways. After process integration, the production of steam in the ATR and SMR cases is realized by heat available from the processes. In the ATR3 case the heat available from the methanol unit, ATR and gasifier is used for production of power. The power produced covers most of the need in the gasifier, methanol unit and oxygen production of the ATR. In the SMR3 case, power is produced from the heat and off-gases available in the methanol unit as well as the gasifier. The power produced covers the needs in the gasifier and the methanol unit and part of the demand in the ASU. The power production has led to lower utility emissions from the ASU in the ATR3 case than in the SMR3 case. The reason why it is reduced to a lower level, and not the same level, is the use of a functional unit and the fact that more plastic material is produced in the ATR3 case compared to the SMR3. Combustion of natural gas and off-gases, and production of electricity are the dominant sources of emissions after process integration.

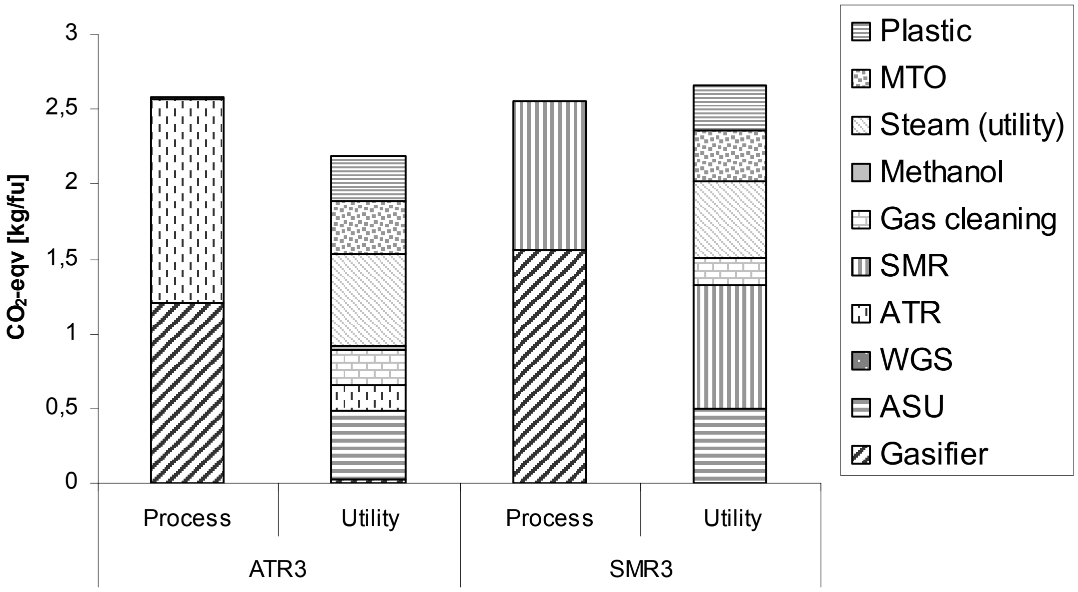

Figure 7.11: Process and utility emissions in the ATR3 and SMR3 cases after process integration

The overall emissions in the two cases are summarized in Figure 7.11, divided into process and utility waste. The overall CO_2 emissions show a small advantage of the ATR3 case. The largest difference is found in the utility waste category, which is discussed above. In the process waste category, the overall emissions are more or less the same, but with a larger share for the gasifier in the SMR case. The reason for this difference is, again, the larger production of plastic material in the ATR case. In other words, more methane based material is contained in the final product in the ATR3 case.

Both the SMR3 and the ATR3 use a common utility plant for production of power. Since the use of a common utility plant increase the dependency of the processes as well as the investment costs for constructing the plant, a brief look at the alternative process integration configurations are taken. In the ATR3 case the alternative to the common utility plant is power production as well process to process integration within each unit. This will avoid the interdependency of the units, but equipment for power production is still needed. In the SMR3 case, one alternative is of course to do only internal process integration within each unit, but in addition the possibility of utilizing the off-gases from the methanol unit in heating of the SMR reactor is investigated. The greenhouse gas emissions are slightly higher than in the case with power production in a common utility plant, but the complexity and interdependency decreases. This heat exchange configuration in the SMR3 case is simple as only the SMR unit and the methanol unit are integrated through pipes. As discussed in Section 7.2.4, the co-firing of methane and off-gases might require a more complex burner.

Both cases have pros and cons, and the choice between them will be determined by economic and operability considerations. By looking at emissions only, preference is, however, given to the ATR3 case.

Finally, a discussion about process integration between the units and co-localizing of the entire process train is given. Step 3 has shown that the overall emissions are significantly decreased by process integration within and between the units. Process integration between the units requires, however, that the units are located at the same site, and as discussed above, increases the dependency between the units. An alternative to process integration between the units would be process integration within each unit only. From Section 6.3, it is known that the process integration between the units decreases the need for utilities compared to the alternatives with process integration within each unit only. The approach with process integration both between and within the units is used here. Smith and Petela (1991) concluded that even though the process waste is usually more harmful than utility waste, utility waste tends to be produced in larger quantities than process waste, and this sheer volume can have a great environmental impact. This also shows the importance of utilizing the full potential for process integration.

In addition to the approaches described above, the system has additional degrees of freedom. The temperature and pressure in the reformer can be changed, the unconverted CH_4 in the reformer product can be combusted to provide heat, gas cleaning can be done with distillation or membrane separation, etc. The detailed information provided by the LCA-PI algorithm can help the designer to identify areas with large potentials for improvement.

The oxygen production in the ASU, is a large contributor to overall CO_2 emissions, hence ways to decrease this impact should be investigated. The ASU is energy intensive, and alternative methods for production of oxygen might be considered in the future. Alternative production schemes are use of membranes, and water electrolysis. The former has the advantage of potentially lower energy requirements. The technology exists, but full scale experience is limited. The latter has the advantage of simultaneous production of hydrogen, but water electrolysis also requires large amounts of energy. The cryogenic process route (ASU) is the preferred one today, whereas advanced concepts for heat integration can favour the use of membranes or chemical separation in the future (Smith and Klosek, 2001).

It is important to note, however, that the use of an alternative electricity mix can change the results, since power production is compared to methane combustion. This is discussed in the next section, which looks at the sensitivity of the results presented in Chapter 7.

7.3 Sensitivity analysis

Uncertainty and sensitivity analysis offer valid tools for characterizing the uncertainty associated with a model. Here, the factors that contribute the most to the output variability and the quality of the model are in focus. The results have been tested with respect to sensitivity of various inputs. The inputs tested are:

1) Electricity consumption in the ASU ("El-consumption")

2) Oxygen consumption in the gasifier ("O_2 use")
3) Transport distance ("Transport distance")
4) Methane potential in GWP calculations ("CH4 GHG-potential")
5) Heat requirement in the SMR ("Heat in SMR")

The results of the sensitivity analysis are shown for the cases studied in Section 7.2, ATR3 and SMR3, before process integration (after step 2). In addition, general trends are discussed together with the influence on the other tests in Table 7.1 and Table 7.2. The section starts with a comparison of the influence of the various inputs to the model, and the results are shown in Figure 7.12 and Figure 7.13.

In both Figure 7.12 and Figure 7.13, the various input variables are varied between 50 % and 200% of the original input (0.5 to 2 in the x-axis). Consequently, x = 1 is the value used in the original model. From Figure 7.12 it can be seen that a change in the GHG potential chosen for unconverted methane is the input value with the largest potential to change the total CO_2 equivalents from the PtP system, followed by the heat requirement of the SMR. The CH_4 GHG potential is discussed later in this section. The electricity consumed in the ASU and the need for oxygen in the gasifier are linearly dependent and consequently they have the same potential in changing the total CO_2 equivalents. A doubling of the transport distance for the waste has negligible effect on the total CO_2 equivalents of the system. The original transport distance is short, however, and a test of the sensitivity of much longer distances has been carried out, see Figure 7.14.

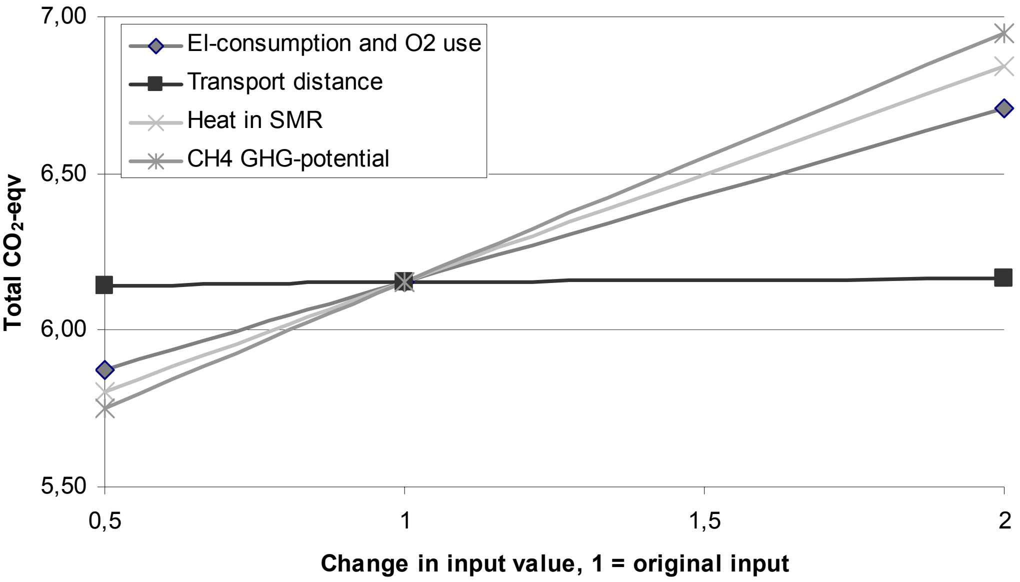

Figure 7.12: Sensitivity of the various input variables in the SMR3 case

In Figure 7.13, the sensitivity of the ATR3 case is shown. For this case, the electricity consumption in the ASU has the highest potential, followed by the GHG-potential for methane and oxygen needed in the gasifier. Again the transport distance shows no impact on the total CO_2 equivalents within this scale of change. For the ATR, el-consumption in the ASU and oxygen used in the gasifier is decoupled as the ASU is used for production of oxygen both for the gasifier and the reformer.

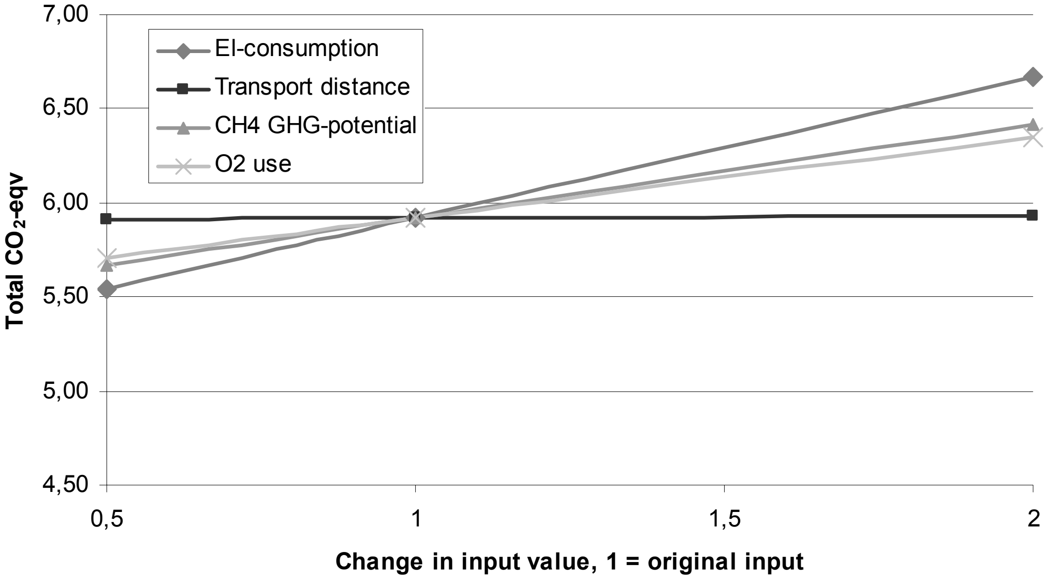

Figure 7.13: : Sensitivity of the various input variables in the ATR3 case

A doubling of the transport distance shows no change in the total CO_2 equivalents for neither of the cases. As mentioned, the original transport distance is short (200km) and much longer distances can be expected. The results from the sensitivity analysis, where the transport distance is varied from 100 km to 3000 km, are given in Figure 7.14. As can be seen, even with an increase of 15 times the original transport distance, the total CO_2 equivalents increase with only 3-4 % for the two cases. A transport distance of 3000 km is the equivalent of travelling from Oslo to southern Spain.

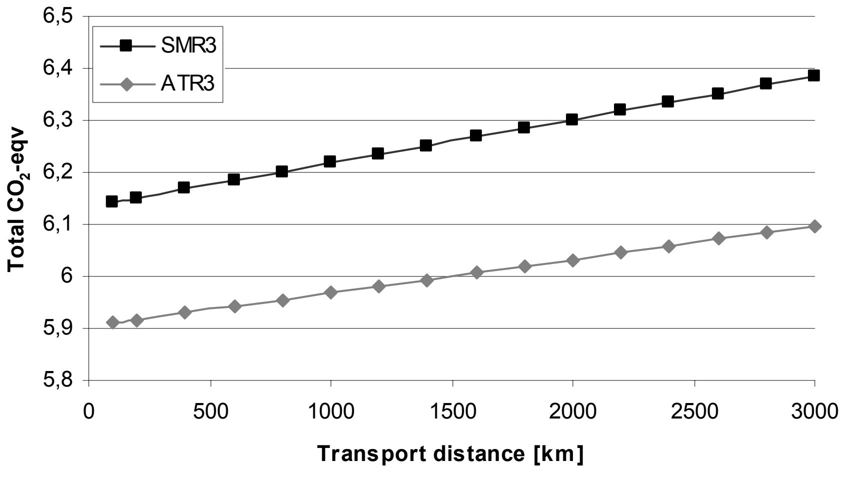

Figure 7.14: Sensitivity of changes in transport distance for SMR3 and ATR3

The choice of the correct level of GHG-potential for the methane is under debate. In this thesis the potential has been set to 56 (see Equation 6-3), which is the level set for a 20 year timeframe by the Intergovernmental Panel for Climate Change (IPCC). For long-term projects, IPCC suggest to use a 100 year timeframe where CH_4 has a radiative forcing potential of approximately 21.5 (± 35 %) times grater than 1 kg of carbon dioxide (Ross and Evans, 2003). The 100 year time frame is also the one used to calculate emissions in the Kyoto protocol. In order to look at the influence of the choice of GHG-potential for methane, a sensitivity analysis has been undertaken. The results of the sensitivity analysis are given in Figure 7.15. A reduction of the GHG-potential to the level given by IPCC for a 100 year time frame reduces the total CO_2 emissions 4-6%. It is important to note that the difference between the two cases decreases with decreasing CH_4 potential.

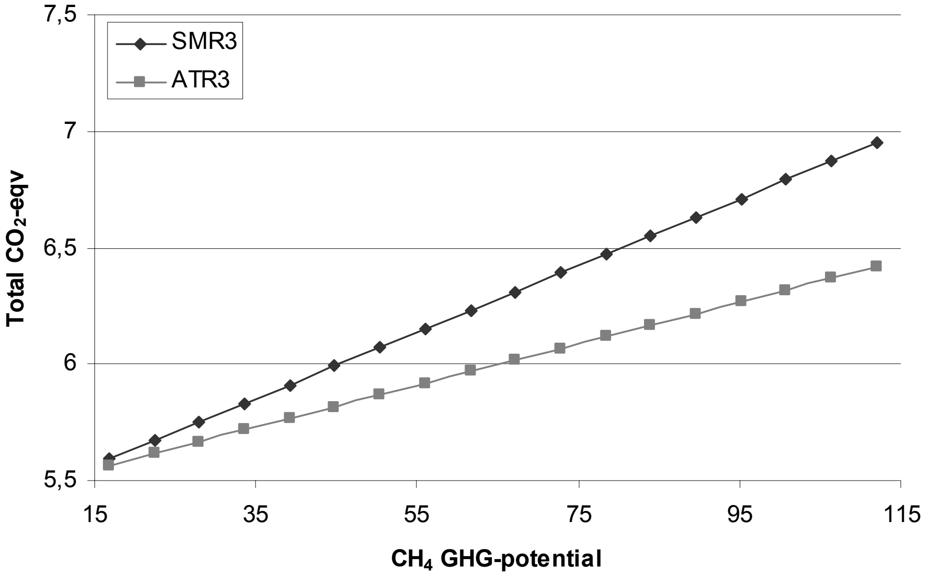

Figure 7.15: Sensitivity of changes in methane GHG-potential for SMR3 and ATR3

When comparing the two cases, ATR3 and SMR3, it is important to look at the interval the sensitivity analysis gives for each of the cases. For the original best guess for the two cases, ATR3 has a lower impact than SMR3, but for all impact categories except from transport, the interval given by the sensitivity analysis shows an overlap between the two cases. As both cases have a low amount of unconverted methane, the simultaneous change in CH_4 GHG-potential will not affect the mutual relation between the two cases. It will, however, be important when compared with other studies (see Section 6.4). The oxygen consumption in the gasifier will also change with the same amount for both cases, hence no change in the mutual relation. The relative strength between the two cases will, however, be affected by a change in electricity consumption in the ASU and heat required in the SMR3. The change in electricity consumption of the ASU will have a larger impact on the ATR3 than the SMR3 as more oxygen is needed due to the oxygen demand of the ATR3. A change in heat demand of the SMR3 will of course change only the total CO_2 equivalents of the SMR3, leaving the ATR3 unchanged. A reduction to 70 % of the original heat requirement of the SMR3 will decrease the total CO_2 equivalents of the SMR3 to the original score of the ATR3 (5.96 compared to 5.92). When the electricity use increases in the ASU, the advantage of the ATR3 case is decreasing with increasing electricity consumption, and intercepts at two times the original electricity consumption.

The impacts discussed above include internal differences between the various inputs for the most promising cases, ATR3 and SMR3. Next follows a discussion about the impact of the various inputs for the other cases given in Table 7.1 and Table 7.2.

Both ATR3 and SMR3 have low values of unconverted methane, while for the cases ATR7 and SMR5 the amount of unconverted methane is high, and the sensitivity with regard to GHG-potential for the methane is consequently high. By reducing the CH_4 potential to the IPCC level for a 100 year timeframe, the overall GHG-potential is reduced with 33-38%. The reason is that unconverted methane constitutes a larger amount of the overall CO_2 equivalents than for ATR3 and SMR3. When the GHG-potential of methane has an increasing influence on the cases with large unconverted methane, changes in both electricity consumption/oxygen use and transport have less impact on the total numbers. The reason is that as unconverted methane increases, the total CO_2 equivalents are dominated completely by the unconverted methane, and changes in the other inputs are negligible.

It is important to note, however, that large amounts of unconverted methane from the gasifier or reformer will not be acceptable in the process design. Unconverted methane lead to increased costs due to higher raw material requirements, need for larger equipment and need to separate the unconverted methane from the product stream. Unconverted methane can, to a certain extent, be recycled within the system, but the cases with high amount of unconverted methane will be avoided.

The cases with low amounts of unconverted methane, like SMR3 and ATR3, can be compared with the given model. For cases with higher methane slip, the results have to be treated with care as large amounts of unconverted methane are not acceptable from an economic point of view.

In Appendix 9, the LCA results for the PtP reference case, ATR3 and SMR3 are compared to results from the SimaPro 7.0 Educational software. Each of the three scenarios has been modeled in SimaPro, using the mass flows calculated in the Excel spreadsheet. For all numbers, the SimaPro software gives slightly lower total CO_2 equivalents than the LCA model built in Excel. The largest deviations among the units are found for the SMR, ATR and ASU. All these units require input from the techno sphere; electricity and natural gas. For the SMR and ATR the reason for the lower contribution from the SimaPro software is the lower CO_2 potential used for methane in SimaPro, compared to the LCA model in Excel – the IPCC 100 years compared to 20 years. For the ASU the reason is a difference in the electricity mix used in the SimaPro software compared to the Excel model. The different composition of the electricity mix is given in Appendix 5, which lead to different CO_2 emissions. A change in the electricity mix will highly influencing the results of the analysis (see Section 6.4.3), and it is important to reflect on the correct electricity mix before going into the analysis. In Table 7.10 the total CO_2-eqv from the ATR3 and SMR3 case (with and without process integration) are given with different composition of the electricity mix. The EU mix in the second column is the base case electricity mix used for all calculations in chapter 7. The emissions from hydropower and coal based power are taken from the Ecoinvent database (2004).

Table 7.10: Total CO_2-eqv from the ATR3 and SMR3 by various composition of the electricity mix

Total CO_2-eqv [kg/fu]	EU mix (base case)	Hydropower	Coal based power
ATR3 without PI	5.92	4.51	7.85
ATR3 with PI	4.78	3.96	5.91
SMR3 without PI	6.14	4.89	7.87
SMR3 with PI – Power[1]	5.24	4.46	6.31
SMR3 with PI – Heat[2]	5.35	4.10	7.04

[1] Detailed results given in Table 7.9, [2] Detailed results given in Table 7.6

From Table 7.10 several observations can be made, the most important is the one that the choice of electricity mix heavily influence the overall CO_2-eqv calculated from the system. The change from one electricity mix to another will, however, not change the mutual relation between the various cases studied, with one exception. The exception is the SMR3 case with process integration for heating of the SMR reactor or power production. In the base case (EU mix) the configuration where the available heat is used for power production has a small advantage over the case where available heat is used for heating of the reactor, the same is the case with the coal based power. By use of hydropower, the heating of the reactor will, however, be the most beneficial. The reason for this is of course that the more pollution that is emitted in the external power production, the more incentives exists for avoiding a high external electricity use. This is in agreement with the findings by Ådahl et al. (2004) who report that the when considering a combined heat and power (CHP) unit at process plant site, the changes in electricity are far more important than individual differences between processes.

The reason for using the EU mix in this assessment is the fact that the emissions from this case lies between the two extremes; hydropower and coal based power production. The total results are then tested for other electricity mixtures in the sensitivity analysis.

7.4 Discussion

The emissions from the system are divided into utility and process waste, as suggested by Smith and Petela (1991). Process waste is the emissions that are a created within the process itself, like CO_2 in the product from a gasifier. Utility waste is the indirect emissions that result from production of utilities for the system, like CO_2 in production of electricity or combustion of off-gases to provide heat.

The division into process and utility waste provides additional knowledge about the system which can be used in process design. The definition of the process waste means that all emissions included in this category can be decreased by changes in unit operations or the system of unit operations. Emissions in the utility category can be decreased either by improved process integration, or change in utilities.

The categorization of utility and process waste opens up for the iterative coupling of LCA and PI. In addition it helps the designer to concentrate on the largest sources of emissions. Large utility emissions means that there is a large potential for process integration, whereas large process emissions means that the focus should be on the process in general and the specific unit in particular. LCA was used to calculate the overall emissions from the system, when different configurations for process integration were applied. The LCA provided valuable information in deciding which of the configurations to chose, based on environmental considerations.

The main benefit in combining PI and LCA, however, is that it enables the engineer to consider the overall changes in the system. Changes made in the operation of one unit might also change the basis for process integration within the system. An example is the increase in temperature for the ATR in order to decrease the unconverted methane. The development of a tool which combines PI and LCA in process design will provide this overall information to the designer. This could preferably be combined with a simulation tool like Hysys.

It has been shown that LCA and process integration can be successfully combined in order to optimize the system with respect to emissions. The case study has used CO_2 emissions as an example, however, all other impact categories can be included. The LCA-PI algorithm with accompanying models in Excel and Hysys has proven beneficial as changes made in Hysys will be summed up in the Excel LCA. This avoids the need for manual iteration between Hysys and Excel. The models have the possibility to assign the corresponding emissions to the units in the process, in addition to distinguishing emissions from the process and the utilities. Further, process integration introduces the focus on utility and energy use in the system evaluated by the LCA.

Although the case study is an example of LCA applied to a process, the framework presented also applies to the traditional LCA; the one used to evaluate products. Traditional LCA also includes processes, where process optimization in general and process integration in particular can be introduced.

8 Optimization of environmental and economic performance

This chapter gives an introduction to evaluation/optimization, which is the last stage in process design as it is defined by Hendry et al. (1973). LCA alone, or in combination with process integration, will not determine which product and process is the most cost effective. Therefore the information from an LCA study should be used as one component of a more comprehensive decision process.

Yang and Shi (2000) have given a review of the integration of environmental impact minimization into conceptual chemical process design. They conclude that combined approaches are needed to solve the complex problems faced when large process systems are subject to multiobjective optimization. This chapter indicates how LCA and economic evaluation can be combined in multiobjective optimization of environmental and economic performance. Some ideas on how it can be applied to the PtP case are given towards the end of the chapter.

The main purpose of this chapter is to indicate how optimization can be built on top of a design procedure where LCA and process integration have been used to explore options for improved environmental performance and increased thermodynamic efficiency. Multiple trade-offs *always* exists in process design and pose no problem the optimization stage as long as the different impact factors can be quantified in economic terms. This is of course the case when considering raw material utilization, energy utilization and equipment minimization. A considerable more challenging problem is the case when the impact factors can not easily be measured in economic terms. Examples of such situations include process flexibility, process operability and controllability, safety and environmental impact. The main focus of this chapter is the simultaneous optimization of economic factors such as investment cost and operating cost with the environmental performance of the plant.

8.1 LCA and system optimization

Historically, optimization of processes has been done with respect to economic assessment only. During the last decade, environmental criteria have been introduced and combined with the economic criteria in optimization tasks. However, the focus of these studies has often been on emissions and waste in the process itself, i.e. a process analysis approach. As stated in Section 2.5.7, a system perspective is needed to optimize all the processes within the system boundaries. LCA in combination with traditional optimization tools can be used to fulfil this need. When one process within a larger system is optimized, the system can be sub-optimized as the burden is shifted to operations outside the process studied. When an LCA approach is used, the system is in focus, and the *system* is optimized rather than a single process. In other words; the impact of the entire system is minimized.

In order to combine the outcome of the LCA and the economic criteria, a multiobjective model is set up. A multiobjective problem (MOP) is any decision problem that involves a set of objectives instead of a single one. MOP methods are generally divided into preference-based methods and generating methods (Diwekar, 2003). Preference-based methods attempt to quantify the solution that best suits the decision maker's preference. Generating methods, like the constraint method, have been developed to find a set of preferred solutions or the trade-off surface, also known as a Pareto set. The latter approach is used here.

The MOP model can have several objectives, however, in this work only two objectives have been included; profit and environmental burden or impact. Mass and energy balances are the equality constraints, while material availability, heat requirements, production capacity etc. are the inequality constraints. The optimum solutions are those given by Pareto-optimum curves. In Figure 8.1 an illustration of the Pareto optimum solutions is given. By definition, the Pareto optimum solutions are optimal in the sense that none of the objective functions can be improved without worsening the value of some other objective function (Azapagic and Clift, 1999b). All solutions along the line are possible optimum solutions, and the choice between them is done by trade-off between the various categories.

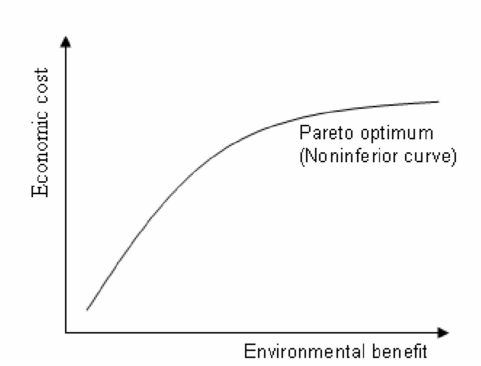

Figure 8.1: Pareto optimum solutions, and the trade-off between economic and environmental benefit (Azapagic and Clift, 1999b).

Mathematical programming was introduced in Chapter 2 as one of the approaches within process synthesis. The solutions produced by the solvers are normally referred to as "optimal". It is important to note, however, that in the majority of cases this only means that the solver has found a solution which satisfies the mathematical conditions for local optimality. Except for so-called convex problems and a few special classes of other problems, there is no guarantee for finding the global optimum, however, a local optimum nevertheless constitutes a design which is feasible.

As discussed in Section 2.2.1, most process synthesis problems are mixed integer nonlinear problems, MINLP. However, many problems can be simplified. The general formulation of mathematical programming problems typically encountered in process synthesis is given by Equations (8-1) to (8-3), see for example Biegler et al. (1997).

Minimize/maximize

$$f(\vec{x},\vec{y}) \tag{8-1}$$

subject to

$$\vec{g}(\vec{x},\vec{y}) \le \vec{0} \tag{8-2}$$

and

$$\vec{h}(\vec{x}) = \vec{0} \tag{8-3}$$

Where $\vec{x}$ and $\vec{y}$ (matrixes) continues and discrete (i.e. binary; 0, 1) decision variables. The objective function, Equation (8-1), can be profit (maximize) or cost (minimize) or some environmental performance indicator. The inequality constraints, Equation (8-2), can be product quality specifications, limits on operating conditions, environmental regulations or pure logical constraints related to the discrete variables. Finally, the equality constraints, Equation (8-3), are typically material and energy balances, equilibrium relations, etc.

When discrete variables are present and at least one of the functions in Equations (8-1) to (8-3) is nonlinear, the formulation above is a mixed integer nonlinear programming problem (MINLP problem). Without discrete decision variables present, the problem simplifies to a nonlinear programming problem (NLP problem). The simplest possible case is when all the functions f, $\vec{g}$ and $\vec{h}$ are linear. The problem then reduces to a linear programming (LP) type which can be solved fairly easily to global optimality. It is a problem of this kind that will be briefly discussed here.

LP problems are often formulated in an alternative manner to take advantage of the fact that all the reactions are linear:

Minimize

$$f = \vec{c}^{\,T} \cdot \vec{x} \tag{8-4}$$

subject to

$$A\vec{x} = \vec{b} \tag{8-5}$$

In Equation (8-5), inequality constraints are transformed into equality constraints by the introduction of slack variables.

For an optimization problem with LCA as the basis, the LP model has the same general form as any design problem, but the constraints include all the activities from cradle to grave. In addition, the functional output of the system is treated as one of the constraints and the objective functions include both environmental *and* economic functions.

It is necessary to distinguish between optimization of the environmental burden and the environmental impact. The *Environmental burden* is represented by the following objective function (Azapagic and Clift, 1999b):

Minimize

$$B_m = \sum_{i=1}^{I} bc_{m,i} x_i \qquad (8\text{-}6)$$

where $bc_{m,i}$ is burden *m* from process or activity x_i. Whereas the *environmental impact* is given by Equation (8-7) (Azapagic and Clift, 1999b):

Minimize

$$E_k = \sum_{m=1}^{M} ec_{k,m} B_m \qquad (8\text{-}7)$$

where $ec_{k,m}$ is the relative contribution of burden B_m to impact E_k. An example of a burden is CO_2, whereas the impact category greenhouse gas emissions is an example of environmental impact.

Systems where economy and various environmental burdens or impacts are taken into account, yield multiobjective optimization problems. MOP identifies stages in the life cycle of a system where improvements can be made. Optimization can be performed either at the inventory or the impact assessment level, in each case the environmental objectives are defined as either burdens or impacts, respectively (Azapagic and Clift, 1999b). Optimization of the full set of equations defined by Equations (8-1) through (8-3) and (8-6) or (8-7) yields the Pareto optimum solution, which represent the compromize between the objectives of economic and environmental performance. The equations within the MOP might not be linear, if they are non-linear, a similar methodology is used, but the system is more difficult to solve. Azapagic and Clift (1999a) have applied the method successfully to a case study on production of various boron products.

Several papers on how LCA and optimization can be combined have been published. Azapagic (1999) gives an overview of the field in his review article. A presentation of relevant contributions is given in the following. Kniel et al. (1996) have combined LCA and multiobjective optimization to process design of a nitric acid plant. The methodology is initiated with an existing design, which is then the basis for the plant model. Material and energy flows, together with economic parameters, are then used to develop environmental and economic models, which is combined in the multiobjective optimization. They have used a valuation of the environmental burdens based on the marginal changes in each of the effect scores due to a marginal change in mass of product output from the process. Based on the environmental index and the discount rate of return, a Pareto plot was constructed. Bretz and Fankhauser (1997) have also used LCA in optimization of chemical processes. Their approach was to build a LCA software (ECOSYS) based on in-house manufacturing process data. Two synthesis paths for production of the intermediate chemical product DNS were compared, one of them existing, the other one under development. Data from the one in operation where taken from the in-house databases, whereas the one under development where modelled in a simulation tool (Aspen®).

Tan (2005) has proposed an alternative optimization technique, called symmetric fuzzy linear programming (SFLP) for combination of LCA and optimization. The SFLP is a formulation where constraints are made flexible by introducing the concept of degree of feasibility. SFLP was developed by Zimmermann (1992). Compared to an ordinary LP, only one additional variable and objective function is needed. According to Tan (2005) the MOP used by Azapagic and his co-workers is a time-consuming approach, and gives a set of optimum solutions in the Pareto-surface. The SFLP provides a single optimum solution by use of linear equations, a weighting is hence included in the equations.

Khan et al. (2001) developed a methodology, called GreenPro, which is a systematic approach for process design. The methodology is close to the approach by Azapagic and Clift (1999a), combining LCA and economic criteria in a MOP. Based on the tool GreenPro, Khan et al. (2002) also developed a tool called *GreenPro-I*, which is a risk based life cycle assessment and decision making methodology for process plant design. The procedure combines LCA and risk assessment in a cradle-to-gate approach for design of processes. When the environmental impact for the production system is established, the process is optimized by use of multi-criteria decision-making methods, including environmental, economic and technological inputs. The optimization problem is solved by use of fuzzy programming. Included in the programming is a valuation step, where all the impacts are given various weights. Björk and Rasmuson (2002), Song et al. (2002) and Baratto et al. (2005) have also published case studies of LCA applied on processes and used in a multiobjective optimization of the system. Alexander et al. (2000) has undertaken a case study on LCA and optimization of a nitric acid plant simulated in Hysys. They emphasize the need for transparent elicitation methods of preferences by the decision maker and other stakeholders.

The different approaches for optimization of processes given above, all include the life cycle perspective of the processes. However, it is an important difference between the approach by Azapagic and Clift (1999a) and Baratto et al. (2005) compared to Khan et al. (2002) and Tan (2005). The two former uses a generating method, which leaves the trade-off between various optimum solutions to the expert evaluating the results, whereas the other approaches include the trade-off within the model, referred to as preference-based methods.

Graphical presentation of the results

The results from the optimization are often presented graphically. When the number of criteria to be optimized exceeds three, a graphical presentation is no longer possible. In an LCA there are often 10-15 different criteria, according to the impact categories given in Table 2.1 in addition to the economic criteria. One way to solve this is by use of the constraint method (Azapagic and Clift, 1999b). In the constraint method, the system is first optimized for each objective to identify the feasible region and other functions are ignored. One of the functions is then arbitrarily chosen as an objective function and all other objectives are converted to constraints.

8.2 Optimization within the plastic waste to plastic concept

In this section the possible application of multiobjective optimization on the PtP concept is discussed.

8.2.1 Method

Azapagic and Clift (1999a) have outlined a method to combine these tools, called "Optimum LCA Performance" (OLCAP). The procedure is as follows:

1) Completion of the LCA study
2) Formulation of the optimization problem in the context of LCA
3) Multiobjective optimization (MO) on environmental and economic criteria
4) Multicriteria decision analysis and choice of the best compromise solution.

The suggested algorithm for the PtP case is based on the OLCAP method, and includes the following steps:

1) Formulate linear equations for each impact category, based on the algorithm given in Figure 7.1.
2) Formulate economic/profit equations
3) Formulate the constraints in the system
4) MO optimization
5) Pareto plot and evaluation

8.2.2 Benefits

The multiobjective optimization method does not need to aggregate the various impacts (objectives) in a valuation stage. Valuation is controversial, so the possibility to look at all the objective functions in a MO and choosing by trade-off is acknowledged. By providing a graphical presentation of the feasible region, the decision makers can do the complete valuation by use of the optimum area. This approach has been used successfully in large projects, including the project "Sustainable mobility", lead by World Business Council for Sustainable Development, with participants from the major oil producers, car manufacturers and suppliers of material and components to the car industry (WBCSD, 2004). In addition, most of the studies referred to in Section 8.1 acknowledge the benefit of Pareto plots.

LCA used on processes takes into account the function of the system. In the PtP concept the function of the system is to treat 300 000 tonnes of plastic waste per year. By applying LCA to the PtP concept it is possible to evaluate the system and it's true footprint. When LCA is used alone (without optimization), information about the weak points in the concept is identified, which can be used to develop the concept further. If then the results from the LCA are used together with economic criteria, it is possible to use the information to create the optimum process with respect to both economic and environmental performance. If only the production routes within the PtP concept are included in the study, the optimum product mix of the PtP is identified. When other processes for production of the products are taken into account, it is possible to answer the question whether PtP should be used at all. If production of all the products in question can be produced in a more beneficial way than by use of the PtP concept, then PtP should not be used at all. The most comprehensive of the scopes are the most interesting, but also the most time consuming of the possible approaches. To include the alternative production routes, substitution of the processes can be used to avoid allocation.

8.3 Conclusion

The focus of LCA has been on products, however, more recently methods and case studies for application of LCA on processes have emerged. The same framework as used for products is used, but now the functional unit is a function of the process rather than the product. The results from LCA used on processes have found various applications, among them is the use in optimization of processes and systems. The results from the LCA are used as environmental input to a multiobjective optimization, where it is optimized together with the economical characteristics of the system. Several case studies have been published, showing that optimization can be done by this combination. In this chapter it is indicated how this can be used on a large system for plastic recycling, yielding a variety of products. When LCA is applied on a process, the true footprint is identified. Consequently, combined LCA and optimization seems to be a suitable tool to answer the question regarding what to do with the plastic waste within the PtP concept.

9 Discussion, conclusions and contributions

This chapter sums up the work presented in this thesis. It starts with discussions of the two main areas of contributions; the recycling concept (Section 9.1) and methodology development (Section 9.2). In Section 9.3 the main contributions are summarized, whereas Section 9.4 gives some suggestions for further work within the field.

9.1 PtP challenges and opportunities

Western Europe generates around 20 million tonnes of plastic waste annually. In 2003, 16% was recycled and 22% incinerated with energy recovery while the major part was landfilled (APME, 2003). The EU post-consumer waste directives will force more plastic waste to be recycled. These directives include; The Packaging and Packaging Waste (94/62/EC), End-of-life Vehicles, ELV, (2000/53/EC), Waste Electrical and Electronic Equipment, WEEE, (2002/96/EC) and the Landfill directive (1999/31/EC). All these directives require increased recycling of plastic waste back to plastic as well as increased total recovery. As a result of these post-consumer waste directives, it has been estimated that an additional recycling capacity in the order of 2 million tonnes per year is requested in 2008 (Kaggerud et al., 2004b). It is envisaged that only a limited part of this could be achieved by mechanical recycling. This is due to lack of end-markets for the recycled material and the presence of large quantities of mixed plastic waste (APME, 1998). In addition the ban on landfilling of carbonaceous waste, like in Sweden and Germany, requires even larger fractions of plastic waste to be treated.

Household waste accounts for 80% of the total amount of plastic waste. This waste stream is often contaminated with food, detergents, metals, paper, etc. Only 8% of the plastic waste from households is recycled at present (Delavelle and Shaw, 2002). This source is an excellent feedstock for the PtP concept.

The plastic waste available for treatment increases, and according to Patel et al. (2000) the reason for this is the increased use of plastic material as well as the long life time of many plastic products. Furthermore, consumer choice increases the variety of polymers and additives. This can sometimes be for good reasons such as longer shelf-life of food in packaging or merely for aesthetic purposes. These changes create a major challenge for mechanical recycling, since everything that goes into such recycling is bound to come out in the recyclate. This also applies to additives that may have been phased out or become obsolete. Mechanical recycling hence often implies down-cycling. APME has raised a concern that the availability of end-markets for plastic waste recyclate may be a limiting factor for the long term sustainability of high rates of mechanical plastic waste recycling (APME, 1998). In the PtP concept, plastic waste is broken down to the chemical components CO and H_2, which can be purified and used to produce a variety of products. As the market requires high quality plastic material, the plastic waste can be used as a feedstock to meet this requirement.

In addition to the increased amount of plastic waste available for treatment, the fact that fossil fuels are non-renewable makes concepts that can utilize alternative raw materials attractive. When the supply of fossil fuels becomes limited, waste materials will still be present. This makes it attractive and important to develop concepts and processes that can convert waste into valuable products. To become sustainable, energy and materials will have to be produced from renewable resources. In addition, one will have to take care of the waste that is generated. As the waste is at a high energy level, it should be kept at this high energy level by recycling it back to new materials, rather than recovery of the energy only. This is in accordance with the EU waste hierarchy (Section 4.2.2), but will of course only work as a rule of thumb.

Before going into the evaluation of the concept, it is necessary to remind the reader that the unit operations have been modeled with a limited level of details, for example with respect to number of chemical components and complexity of the reactor models. The reason for not doing a more rigorous process modeling is the scope of the study. The focus is on system analysis at a superior level, looking at the theoretical maximum. If the theoretical maximum shows promising results, more detailed modeling and assessment should be undertaken. Rather than spending large resources on complex models in the early design phase, the potential of the system is screened by use of simplified models.

Evaluation of the concept

The plastic recycling system can be extended by use of alternative feedstocks and product extractions at various stages in the process chain. This will offer an increased flexibility of the concept. As the plastic waste or an alternative carbonaceous feedstock is converted to synthesis gas in the process, it opens up for a variety of products. Bulk chemicals like methanol and ammonia are produced from synthesis gas. In addition, H_2, various fuels, heat and electricity can be produced from synthesis gas. The various options were presented in Chapter 5.

The main obstacles in the PtP concept, converting plastic waste to new plastics, are the low H_2/CO-ratio in the syngas compared to what is required in the methanol production and the water produced in the MTO unit. In order to increase the amount of hydrogen, three options have been evaluated: 1) Use of WGS, 2) Add pure hydrogen, and 3) Add a reformer unit. In order to overcome the loss of material with water produced in the MTO, water can be recycled to the WGS or a reformer unit.

The use of a WGS increases the H_2/CO-ratio by reacting steam with CO to produce H_2 and CO_2. The main drawback with this approach is the production of CO_2, which results in both a low material efficiency in the concept as well as greenhouse gas emissions. The second approach, adding pure hydrogen, avoids the need for a WGS, and consequently less CO_2 is created. Less CO_2 means higher carbon efficiency in the system, but unfortunately the hydrogen efficiency is still low due to the water produced in the MTO reaction. An additional aspect is the availability of pure hydrogen streams, as production of H_2 is not included in the assessment. In general, addition of a hydrogen stream is beneficial if a surplus of hydrogen is available nearby, for instance from a chlorine plant or an oil refinery.

The third approach, adding a natural gas reformer, either an ATR or an SMR, improves both the H_2/CO-ratio and the water released in the MTO. The syngas from the reformer unit has a higher H_2/CO-ratio than required in the methanol production, and by combining the syngas from the reformer and the gasifier, the WGS can be avoided. An additional benefit is the possibility to recycle the water from the MTO to the reformer in order to increase the hydrogen efficiency. The use of a natural gas based reformer introduces non-renewable fossil fuels into the products, but increases both the carbon and hydrogen efficiency of the concept. The last option for improving the hydrogen efficiency is to recycle water from the MTO to the WGS. This leaves the carbon efficiency unchanged from the base case, whereas the hydrogen efficiency is increased.

The various options discussed above are all aimed at increasing the atom utilization. From Section 2.4 it is known that the term chemical integration is used for approaches which focus on high atom utilization. The chemical integration possibilities discussed above, show that there are several benefits through co-localization of the process train. In addition to the chemical integration possibilities, the potential for process integration has been investigated. Again, the results show a potential for significant savings by integration between and within the various units. In summary, both chemical and process integration will benefit from co-localization of the process train.

The LCA of the core PtP concept in Chapter 6 showed that the overall greenhouse gas emissions from the system are high, and the main contributor was identified to be the gasifier. The system was improved by use of a better gasifier or the addition of pure hydrogen. Both the process and utility emissions did, however, still have a large potential for improvement. Motivated by the findings from the chemical and process integration study, additional measures for reduction of the emissions were taken in Chapter 7 by combining the LCA and PI.

In Chapter 7 the LCA of the PtP concept identified the main contributors to greenhouse gas emissions. The results show that in the reference case, the process waste dominates. The process waste can be reduced by the introduction of a reformer unit (ATR or SMR). In the two improved cases, ATR3 and SMR3, utility waste is the largest contributor to greenhouse gas emissions. Among the units, the gasifier is a large contributor to process waste in all three cases, whereas the WGS, ATR and SMR, respectively, are responsible for the remaining process waste. Within the utility waste category the diversity is higher, but a common result is that the production of oxygen from the ASU is a large contributor. For the SMR case the heating of the SMR reactor is the largest source of utility emissions before proper process integration has been undertaken. Other utility emissions come from production of steam (by combustion of off-gases and utility steam by combustion of fossil fuels) and consumption of electricity.

The next step showed how the utility waste could be decreased by proper process integration within and between the units. In both the ATR3 and SMR3 cases, process to process integration is maximized within each unit, whereas all steam and off-gases are sent to a central utility plant. The central utility plant can produce power by expansion of steam in turbines and/or distribute steam for heating of process streams.

In the ATR3 case, there is a surplus of heat available in the ATR after steam is produced and the reactants heated. Surplus heat is also available from the gasifier and methanol unit. The MTO is self sufficient with heat and power by process to process heat integration and combustion of off-gases for production of power and heat. In addition, the central utility plant produces power from the available surplus heat, which covers most of the power required in the gasifier, methanol unit and the ATR.

In the SMR3 case, steam required in the SMR is covered by cooling of the SMR product gas, however, external heating of the SMR is still necessary. Heat is available from the methanol unit and the gasifier, whereas the MTO unit is again self sufficient with power and heat. Various process integration configurations were evaluated for the SMR3 case. The most promising configuration was found to be the one which produces power from the heat and off-gases in the common utility plant. In this configuration, no heat is used for heating of the SMR reactor, hence all heating has to be required by external firing of methane.

The summary of the two cases is given in Figure 7.11, showing a small advantage for the ATR3 case with respect to greenhouse gas emissions. The results are, however, in the same range and the choice between them will be determined by economic and operability considerations.

An overview of alternative treatment methods for the plastic waste is given in Section 6.4. All numbers are given per kg of plastic treated, whereas the PtP results are given per material produced (which is the functional unit). The corresponding numbers for the PtP case is in the range of 2.3 kg CO_2-eqv in the reference case to 2.0 kg CO_2-eqv in the ATR3 case. This means that the PtP cases have lower overall CO_2-eqv than incineration, but still higher than mechanical recycling. The main reason for the lower CO_2 emissions in the mechanical recycling case is the low energy demand of that process. Mechanical recycling is, however, still limited to relatively pure process streams. The use of biomass as an alternative source of carbonaceous waste was investigated in Section 6.4.3, showing that the overall GHG emissions are slightly lower for the biomass case. The main reason for this difference is the lower oxygen demand in the biomass case as the biomass contains oxygen in the molecular structure.

Possible improvements
Two interesting improvements within the system, which has not been tested, are:

1) Improved MTO by adding an olefin cracking process (OCP)
2) C_4 and C_{5+} from the MTO can be fed to the gasifier (recycle)

The adding of an olefin cracking process was introduced in Section 5.2.5, and converts the heavier olefins to the desired products, propene and ethene. This improvement of the MTO unit can lead to better performance of the overall system. The second approach, feeding higher olefins in the MTO back to the gasifier is another way of improving the systems performance. Recycling of these olefins is not possible in a reformer unit, and is an alternative to the OCP, if the entire process train is located at the same place.

Loops

Mechanical recycling is the preferred recycling option for plastic waste today. Holmgren and Henning (2004) reported that mechanical recycling can decrease the energy use for production of new HDPE from a total of 80 MJ/kg (8.2 MJ/kg of electricity, 49.4 MJ/kg of oil and 22.3 MJ/kg of natural gas) to 2.9 MJ/kg (electricity) for recycled material. The challenge for mechanical recycling is the mixed and contaminated waste streams, which require extensive pre-treatment. One possibility is to recycle as much as possible by mechanical recycling, whereas large and mixed waste streams should be treated chemically or incinerated to recover its energy content. Chemical recycling can be used to increase the flexibility and utilize plastic waste as an important source for various chemicals and a valuable source when fossil fuels become more expensive (extinction). Patel et al. (2000) stated that as the amount of recycled material will increase, there is a need to develop methods to treat second and third cycles. Open loop recycling might be interesting. He suggested establishing a cascade of mechanical recycling and, finally, applying feedstock recycling or extracting energy. The PtP concept or similar concepts can be the last step in such a cascade.

Economic considerations

Economic considerations have not been part of the study, however, some general thoughts will be given briefly. The long process train with large units will require large investments as well as considerable operating costs. An interesting observation on the raw material (plastic waste) is that it might be assigned with a gatefee. This means that instead of paying for the raw material, the waste owner might pay a fee to get the waste treated. The gatefee of plastic material is not a fixed number, but numbers from 50-400€/ton have been suggested. The gatefee will of course be dependent on the market for plastic waste, and is characterized by a large uncertainty. For comparison, the current contract prices of methanol and HDPE are ~285€/ton and ~1050€/t (ICIS Pricing, 2006), respectively. This shows that the income from a gatefee might be significant.

Conclusion

The core PtP concept is able to convert plastic waste into new plastic materials, with a potential carbon efficiency of 63%. By expansion of the concept with reformer units or additional hydrogen, the carbon efficiency can be increased significantly. Adding a reformer unit or a pure hydrogen stream means that materials other than the plastic waste are introduced, and the complexity is of course increased. Other carbonaceous materials, like biomass, can be treated in the same process train, and other products than plastic material can be produced. Despite the fact that it seams to be technically feasible to produce new plastic material from plastic waste by use of the PtP concept, it is the belief of the author that a standalone plant using the PtP concept is not a wise idea. The main reasons for this are the long process train and the difference in H_2/CO-ratio in the syngas compared to what is required in the methanol process. It is shown that the overall greenhouse gas emissions decrease with the introduction of a reformer unit. One way to implement the PtP concept could be to build it as an add-on in a larger system. This can be done by the combined use of a small scale gasifier for treatment of plastic waste, and a large scale facility for reforming of natural gas.

9.2 Systems oriented methodologies

The system oriented methods applied to the case study have provided valuable information at different levels, starting with chemical integration, SFA and superstructures, via LCA and process integration, to the combined approach of LCA and process integration. All methods focus on environmental assessment, where CO_2 emissions have been emphasized in particular through the use of greenhouse gas emissions as an example of impact categories.

In Chapter 3 it is suggested to combine process integration with chemical integration in co-production of power and chemicals. The standalone power plants show an efficiency reduction for the various power production technologies when CO_2 capture is introduced, compared with a standard high efficiency gas turbine combined cycle plant without CO_2 capture, in the range of 9-13%-points. The decrease in efficiency results in increased fuel consumption and the need for CO_2 capture increases the size of the process trains. Fundamental changes seem to be needed to decrease this efficiency loss. In Chapter 3, process and chemical integration is proposed as one option to increase the overall efficiency as co-production of power and chemicals is utilized. It is expected that chemical and process integration will give economy of scale savings, better utilization of the raw materials, improved energy efficiency and savings in investment costs. The captured carbon can be stored or alternatively used as part of chemical products, like methanol or urea.

A new definition of chemical integration is proposed that makes it strongly related to process integration. The proposed definition of chemical integration can even be part of a broader definition of process integration. Chemical integration has been introduced as a systematic method for designing systems with special emphasis on high atom utilization.

SFA for processes and construction of superstructures at the block diagram level have been used in that respect. The superstructure was first applied to the natural gas case in Chapter 3, showing how various chemicals and energy carriers can be co-produced in an industrial cluster. The same idea was then applied to the chemical recycling concept, PtP, giving an overview of the various products and add-ons that can be included in the concept (Figure 5.11). In order to evaluate the various possibilities, SFA was used to calculate the theoretical carbon and hydrogen efficiencies in the core PtP concept (Figures 6.2 and 6.3). The efficiencies were calculated from stoichiometric equations for each unit operation, giving the overall efficiency as well as the bottlenecks of the system.

The SFA identified the low H_2/CO-ratio in the produced syngas as a main obstacle in the concept. This knowledge was used to identify various ways of increasing the

H_2/CO-ratio in the syngas. Based on this, a new and more complex superstructure could be established (Figure 6.4). The new superstructure was subsequently evaluated by SFA, showing a large potential for the configuration with a reformer unit.

The SFA and superstructure approach gives an overview of the potential of various options. In order to choose among the various options, however, more thorough analysis is required. The focus of this thesis is environmental assessment, hence emissions and energy use are central aspects. Life cycle assessment has been used to evaluate the emissions, whereas process integration has been used to look at energy use. Process integration identifies the potential and possibilities for heat recovery within a system, whereas LCA is an environmental assessment tool which quantifies the environmental impact of a system. The energy use will of course also be reflected in the overall greenhouse gas emissions.

LCA has been applied to the PtP case study in order to quantify the greenhouse gas emissions from the various process configurations. The traditional LCA studies alternative ways of fulfilling a functional unit, usually a product or a service. The approach applied here is different as it focuses on process configurations and improvements to produce the *desired product*, and even further to treat the same amount of waste material to produce *another product*. This means that the fundamental difference between LCA applied to processes and products is that rather than evaluating the various products that can fulfil a defined function, various process configurations that can produce the defined product are evaluated.

In order to do process oriented LCA, detailed knowledge of the unit operations is needed. Depending on the level of detail that is required for the evaluation, one can either use the process units provided in LCA tools like SimaPro (e.g. Ecoinvent database), or build a process model in a process simulation tool and calculate emissions and waste based on the model. The second approach is chosen here, as this approach allows the process designer to change the process configuration on a more detailed level, gain more knowledge of the origin of the various emissions as well as the ability to include methods like process integration. The results have, however, been compared with results from building the same process train in SimaPro (see Appendix 9).

Two main issues on how to assign the emissions within the system have been identified:

1) Assignment of the emissions to the various units
2) How to differentiate between the emissions that originate from the material treated compared to emissions from utilities and other additives.

The assignment of emissions is discussed in Appendix 4, and the challenge is to assign the emissions to the unit where they are formed rather than where they are emitted. For the core PtP case this can be exemplified by looking at the gasifier, WGS and the gas cleaning section. All CO_2 is emitted in the gas cleaning section, but it is created in either the gasifier or the WGS. In order to do a proper analysis of the system, the emissions need to be assigned to the unit where they are formed, which in this case is either the gasifier or the WGS. The gas cleaning unit should only be assigned with the emissions that are formed within that unit.

The second issue, which deals with types of emissions, has been solved in two ways depending on the purpose of the study. The first approach is used in the comparison with biomass (Section 6.4.3), where the emissions are divided into renewable and non-renewable. All emissions that come from the waste material or biomass is categorized as renewable, whereas everything else (production of electricity and natural gas, etc.) are termed non-renewable. The motivation for using this categorization is that it allows for easy evaluation of the efficiency of the plant with respect to loss of treated material. As mentioned in Section 6.4.3, it can easily be argued that emissions from plastic waste should not be termed renewable. The name is, however, not the crucial part, more important is the fact that the division into separate categories provides information that can be used in system improvements. One example is the identification of the gasifier as the main contributor to renewable emissions. Improvement of the gasifier has consequently been evaluated.

The second approach to deal with the type of emissions is discussed in Section 6.2.5, where it is suggested to divide the emissions into process based and utility based emissions. The approach is similar to the previous categorization, but this time all emissions that come from production of utilities are in one category, even for the utilities produced by combustion of unconverted material or by-products. The intention is to help identify areas for improvement both within the process and the utilities, and of course to allow for a closer link to process integration. The information on whether the emissions come from the waste material or background processes is, however, still kept in the Excel model (see Appendix 7).

The LCA can be used as a stand alone assessment of the concept, but by dividing the emissions into utility and process waste, LCA can be used to identify the process integration potential within the concept. On the other hand, the process integration analysis of the core PtP concept shows that significant amounts of energy might be saved through heat integration between and within the processes. Heat integration alone, is, however, not sufficient to minimize the environmental burden within the system, hence the combination of the two tools has been proposed. The algorithm suggested in Section 7.1, which combine the two tools, utilizes the strengths from both tools and makes them both act as process synthesis tools as well as process analysis tools (referred to the definition given by Hendry et al., 1973).

Integration of chemicals and energy within and between the units has a great potential for improving the system. Unfortunately, LCA does not take this into account. By including process integration within the LCA, the results generated are more robust and the data quality is improved. By combining the two methodologies, the environmental evaluation of the system will benefit from the strong points of both. Where PI can provide a guide towards efficient use of heat sinks and sources, LCA summarizes the environmental burdens within a "cradle to grave" perspective and identifies the areas with largest potential for improvement.

The categorization of utility and process waste opens up for the iterative coupling of LCA and PI. In addition, it helps the designer to concentrate on the largest sources of emissions. Large utility emissions means that there is a large potential for process integration, whereas large process emissions means that the focus should be on the process in general and the specific unit in particular. The main benefit in combining PI and LCA, however, is that it enables the engineer to consider the overall changes in the system. Changes made in the operation of one unit might also change the basis for process integration within the system.

It has been shown that LCA and process integration can be successfully combined in order to optimize the system with respect to emissions. The case study have used greenhouse gas emissions as an example, however, all other impact categories can be included. The LCA-PI algorithm with accompanying models in Excel and Hysys has proven beneficial as changes made in Hysys will be summed up in the Excel LCA. This avoids the need for manual iteration between Hysys and Excel. The models have the possibility to assign the emissions to the corresponding units in the process, in addition to distinguish emissions from the process and the utilities. In the case study in Chapter 7, LCA and PI were also combined in order to identify whether the heat and off-gasses available should be used for power production or heating of process streams.

Chapter 8 briefly introduces the combination of environmental and economic evaluation of a system through use of multiobjective optimization. This part has not been studied in detail, and is intended as a guide on how the environmental assessment carried out in this thesis can be combined with economic assessment in order to have a more thorough process evaluation. The method suggested is the use of a multiobjective optimization with use of Pareto plots, rather than a weighted single criterion evaluation. The use of Pareto plots enables the decision maker to get a better picture of the different trade-offs that are needed in order to reach a conclusion.

Baumann and Tillman (2004) define studies which only include a gate-to-gate perspective as environmental flow models of industrial plants rather than complete life cycle assessment. As transport of waste material is taken into account as well as electricity production, the term LCA is used in this thesis for evaluation of the system even though it is close to a gate-to-gate perspective. However, the approach with combined PI and LCA can be used also for a normal LCA.

9.3 Contributions

Two main areas of contributions have been identified; methodology development and the recycling concept. An overview of the main contributions within both areas is given in this section.

Several methods have been combined for environmental evaluation of large systems. The first approach was to use a **superstructure on block diagram level** in order to identify possible co-production options. The superstructure is used as an aid in chemical recycling which aim at designing integrated production systems with special emphasis on high atom utilization (best combination of raw materials, process steps, intermediates and final products, both materials and energy). Further, **substance flow analysis was used on processes** to calculate the overall atom efficiency and identify the bottlenecks by looking at the flow of atoms in the system.

A **new definition of chemical integration** is proposed that makes it strongly related to process integration. The proposed definition of chemical integration can even be part of a broader definition of process integration.

LCA has been applied to the Plastic waste to plastic concept (PtP) both alone and **in combination with process integration**. In Chapter 6, LCA is applied in process evaluation and development of alternative process routes. Traditionally, LCA has been used for comparison of various *products* that can fulfill the same function. In this work, an alternative approach has been used; **LCA used for evaluation of various process configurations**. The LCA helps identify the main contributors to the overall emissions, making it possible to focus the improvement of the system at the bottlenecks. The emissions in the system have been divided into utility and process waste (based on the suggestion by Smith and Petela, 1991) in order to increase the knowledge of the origin of the waste. The division into utility and process waste has proven helpful in the standalone LCA in order to identify the areas with largest potential for improvement, but is most of all beneficial in the last approach where LCA is combined with process integration.

LCA and process integration have been combined in Chapter 7, and an **algorithm have been developed** as a tool for improved process design. By **dividing the emissions into utility and process waste**, LCA can be used to identify the process integration potential within the concept. Large amounts of utility waste means that the overall emissions can be considerably reduced if there is an unused potential for process integration. On the other hand, a large fraction of process waste means that in order to reduce the overall emissions from the system, improvement of the various units or the system should be investigated. The LCA-PI algorithm shows how LCA and process integration can be combined in order to reduce the overall emissions, step by step.

The above mentioned **methods have been applied** in development and evaluation of the chemical recycling concept throughout the thesis. A **new recycling concept for chemical treatment of plastic waste has been developed and evaluated**. All sorts of carbonaceous material can be treated in the recycling concept, yielding a variety of products ranging from energy, via chemicals like methanol and ammonia to new plastic materials. The environmental assessment of a stand alone PtP process has shown that the overall greenhouse gas emissions do not favor the construction of such a plant, compared to other treatment options. The main reasons are the long process train and the difference in H_2/CO-ratio in the syngas compared to what is required in the intermediate methanol process. It is shown that the overall greenhouse gas emissions decrease with the introduction of a reformer unit in the extended PtP concept. Even though the core PtP concept does not seem to meet the requirements as a stand alone plant, one way to **implement the PtP** concept could be to build it as an **add-on in a larger system**. This can be done by the combined use of a small scale gasifier for treatment of plastic waste, and a large scale facility for reforming of natural gas.

The main focus of this thesis has been **environmental assessment.** Through the use of greenhouse gas emissions as the example of an impact category, special emphasis has been given to CO_2 emissions. However, in order to evaluate a system, the economics can never be omitted. The combined assessment of environmental impact and cost is indicated in Chapter 8.

9.4 Suggestion for further work

In line with the rest of this chapter, the suggestions for further work are divided into the recycling concept and development methodology, starting with the recycling concept.

The main obstacle in the recycling concept is the low hydrogen content in the synthesis gas compared to what is required in the methanol production. Alternative process routes for chemical recycling of plastic waste should be investigated in order to overcome this problem. Alternatives that could be interesting include going directly from syngas to olefins (requires new catalysts) or pyrolysis of the waste material with subsequent steam cracking to olefins. Ren et al. (2006) give an overview of possible process routes from hydrocarbons to olefins.

Possible improvements are available for the existing PtP concept as well; including an OCP unit (olefin cracking process) in the MTO unit and recycling of heavy hydrocarbons produced in the MTO to the gasifier. Neither of these options have been investigated in the thesis, but are expected to improve the overall efficiency of the system. The gasifier unit was identified as the main contributor to the total CO_2 emissions, hence various ways to improve the gasifier should be investigated. In addition, the cryogenic grinding used as the pretreatment method for the entrained flow gasifier should be evaluated, and if possible other pretreatment options should be identified.

When it comes to further development of the methodologies, there is still room for improvement. First of all an optimization of the PtP concept can be undertaken, in addition to the case based approach used in this thesis. The environmental optimization of the concept can then be combined with an economic assessment yielding a multiobjective optimization. The trade-off between the various objectives can be done by use of Pareto plots.

The LCA-PI algorithm should be further developed in order to include more impact categories as well as being used in a more traditional LCA approach. Finally, there is still a potential for developing the synergy when LCA and process integration is combined. In addition to the findings reported in Chapter 7 on environmental assessment of the concept, LCA and process integration might be used in targeting and optimizing the number of units. LCA provides a method to assess environmental burden from construction of equipment, whereas process integration can identify minimum number of heat exchangers. The combination of these two tools might be able to identify the environmental optimum number of heat exchangers.

A last suggestion is to include an LCA-button in simulation software, such as Hysys. The simulation model includes all energy and mass balances, which is the basis for carrying out an LCA. Further, all changes made in the simulation model will be summed up in the LCA. According to the findings in this thesis, it is important to be able to assign the emissions to the right unit, and distinguish between process and utility emissions.

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Nomenclature

All numbers in the thesis are given by use of the metric system.

Abbreviations:
aq: Solved in water
AI: Artificial intelligence
APME: Association of plastic manufacturers in Europe
ASU: Air separation unit
ATR: Autothermal reformer
BFW: Boiler feed water
BtP: Biomass to polymer
C-eff: Carbon efficiency
CHP: Combined heat and power
CO_2-eqv: Carbon dioxide equivalent
CSTR: Continues stirred tank reactor
DME: Dimethyl ether
ECVM: European council of vinyl manufacturers
ELV: End of life vehicles
eqv: Equivalents
F-T synthetic fuels: Fischer-Tropsch synthetic fuels
fu: Functional unit
GCC: Grand composite curve
GHG: Green house gases
GTL: Gas to liquid
GWP: Global warming potential
H-eff: Hydrogen efficiency
HCFC: Hydrochlorofluorcarbon (a class of refrigerants)
HDPE: High density polyethylene
HHV: Higher heating value
HRSG: Heat recovery steam generator
IEA: International Energy Agency
I/O-analysis: Input/output analysis
IPCC: Intergovernmental panel for climate change
ISO: International organization for standardization
ITM-O_2:
LCA: Life cycle assessment
LCA-iT: Name of LCA software
LCA-PI: Suggested algorithm for combining LCA and PI
LCI: Life cycle inventory
LDPE: Low density polyethylene
LNG: liquefied natural gas
LP: Linear programming
LP steam: Low pressure steam
MeOH: Methanol

MEA: Monoethanolamine
MFA: Material flow accounting (b-MFA: Bulk MFA)
MINLP: Mixed integer non-linear programming
MJ: Mega joule [10^6 J]
MOP: Multiobjective optimization problem
MTBE: Methyl tertiary butyl ether
MTO: Methanol to olefins
MW: Mega watt [10^6 W]
NLP: Nonlinear problem
PE: Polyethylene
PET: Polyethylene terepthalate
P-graphs: Process graphs
PI: Process integration
PP: Polypropylene
PS: Polystyrene
PSE: Process systems engineering
PtP: Plastic waste to plastic
PVC: Polyvinyl chloride
ref: Reference case
SETAC: Society for Environmental Toxicology and Chemistry
SFA: Substance flow analysis
SFLP: Symmetric fuzzy linear programming
SMR: Steam methane reformer
VCM: Vinyl chloride monomer
WGS: Water gas shift
WGS-CO_2: Water gas shift reactor with CO_2 permeable membrane
WGS-H_2: Water gas shift reactor with H_2 permeable membrane

Definitions
Biomass: Biological material, such as grass, trees, etc.
Recovery: Treatment of waste by utilizing the material or energy
Recycling: Treatment of waste by utilizing the material
Syngas: Synthesis gas (CO, H_2, CO_2, CH_4, H_2O)

Symbols

A: Matrix of known coefficients in LP constraints
$\vec{b}$: Matrix of known numbers in LP constraints
B_m : Environmental burden
$bc_{m,i}x_i$: Burden m from process or activity x_i
C_p: Heat capacity [kJ/kgK]
C_{n+}: Hydrocarbons with n or more carbon atoms
$\overrightarrow{c^T}$: Real numbers in the LP objective function, transposed matrix
E_k : Environmental impact

$ec_{k,m}B_m$: Relative contribution of burden B_m to impact E_k
$\vec{g}$: Matrix g, inequality constraints
$\vec{h}$: Matrix h, equality constraints
H/C: Hydrogen/carbon ratio
m: Mass flow [kg/h]
N: Molar flow [kmol/h]
O_2/C: Oxygen/carbon ratio
P: pressure [bar]
Q: Heat [kW]
S/C: Steam/carbon ratio
T: Temperature [K or ^{o}C]
T': Reduced temperature [K]
$\vec{x}$: Matrix x, decision variable
$\vec{y}$: Matrix y, decision variable
ΔH_{rx}: Heat of reaction [kJ/kg]
ΔT_{min}: Smallest temperature difference [K]
η: Efficiency

Subscript/superscript:
End: End point
Start: Start point
In: Condition at start
Out: Condition at end
i: Atom
x: Number of carbon atoms
y: Number of hydrogen atoms
n: Number of monomers in a polymer
z: step

List of appendices

A1 Composition of waste material
A2 Gasification and pre-treatment of plastic waste
A3 Process integration in the core PtP concept
A4 Assignment of CO_2 emissions in the process train
A5 Electricity mix
A6 Hysys models
A7 Excel models
A8 LCA and process integration
A9 Comparison of LCA results with SimaPro results

A1 Composition of waste material

The composition of the waste that is treated in the gasifier is given in this appendix. In the PtP concept, only plastic waste is treated. In Section 6.4.3, plastic waste is compared with use of biomass in the same process train. Wood contains more oxygen than plastic waste. The H/C-ratio is higher for plastic waste, on weight basis it is 0.11 and 0.15 for wood and plastic, respectively.

Mixed plastic waste with a maximum chlorine content of 3.5% can be treated in the gasifier by Future Energy (2003). The composition used for the plastic waste calculations is given in Table A1.1.

Table A1.1: Composition of plastic waste

Component	Waste composition [wt%]	Waste composition, dry basis [wt%]
C	66.4	73.7
H	9.8	10.9
O	6.4	7.1
N	0.5	0.6
S	0.08	0.09
Cl	3.2	3.6
F	0	0
Ash	3.6	4.0
H_2O	10	0

The composition of the wood waste used is the one given for sawdust (Ekbom et al., 2003). The composition is given in Table A1.2.

Table A1.2: Composition of wood waste

Component	Waste composition [wt%]	Waste composition, dry basis [wt%]
C	24.2	51.1
H	2.8	5.9
O	18.3	38.6
N	0.2	0.4
S	0.02	0.04
Cl	0	0
Ash	2.0	4.2
H_2O	52.6	0

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A2 Gasification and pretreatment of plastic waste

Three different gasification technologies are available for partial oxydation of plastic waste; fixed bed, fluidized bed and entrained flow. The main differences with regard to operation are given in Table A2.1.

Table A2.1: Characteristics of the various gasification technologies

Gasification technology	Particle size [mm]	Product gas [main components]	Operating temperature
Fixed bed	50-150	H_2, CO, CO_2, H_2O, Hydrocarbons	~1100°C
Fluidized bed	10-100	H_2, CO, Hydrocarbons	~900°C
Entrained flow	< 1	H_2, CO	~1200-1500°C

In general, entrained flow requires extensive pretreatment in order to produce the micro particles needed, whereas the high quality of the syngas means that most of the carbon and hydrogen in the treated waste is recovered as syngas. For the fixed and fluidized bed, less pre-treatment is needed, but due to more CO_2 and unconverted hydrocarbons either an upgrading of the syngas is needed or less of the hydrogen and carbon is recovered.

The pretreatment options will of course vary with the required particle size. For the fixed bed and most of the fluidized beds, mechanical grinding is sufficient. For production of particles to the entrained flow this is not the case. In order to produce the micro particles required, the waste can either be heated in a pyrolysis reactor or cooled to cryogenic temperatures by use of liquid nitrogen. In a pyrolysis reactor plastic waste is heated to ~600°C without addition of oxygen. The pyrolysis product is a mix of hydrocarbons, solid, liquid and gas, which can then be grinded mechanically. The cryogenic grinding has the same purpose; produce porous and brittle material that can be grinded mechanically. The cryogenic grinding with liquid nitrogen operates at -196°C. Due to the available liquid nitrogen from the air separation unit, the cryogenic grinding is the approach chosen here.

The composition of the syngas from different gasification technologies are given in Table A2.2 below. Nippon steel is a fixed bed gasifier, Na et al. (2003) has used a fixed bed technology, Future Energy is an entrained flow gasifier, whereas the Ebara gasifier is a two-stage gasification where the first reactor is a fixed bed and the second a fluidized bed.

Table A2.2: Plastic waste composition with corresponding synthesis gas for various technologies

Nippon steel[1]		**Na et al, 2003**		**Future Energy[2]**		**Ebara[3]**	
Predicted for commercial scale		*Laboratory tests, mixed waste*		*Predicted for commercial scale*		*Commercial scale*	
In [wt%]	**Out [mol%]**	**In [wt%]**	**Out [mol%]**	**In [wt%]**	**Out [mol%]**	**In (N.A.)**	**Out [mol%]**
C 49.19	H_2 33.2	C 51.6	H_2 16	C 65.7	H_2 38.7	C	H_2 35-43
H 6.79	CO 45.3	H 8.2	CO 43	H 9.7	CO 37.4	H	CO 30-35
N 0.09	CO_2 6.7	N 0.8	CO_2 29	N 0.5	CO_2 22.1	N	CO_2 20-25
S 0.16	H_2O 2.3	S 0.12	H_2O -	S 0.79	H_2O	S	H_2O -
O 12.09	N_2 1.5	O 25.0	CH_4 12	O 6.3	CH_4	O	CH_4 <0.1
Cl 30.96		Cl 0		Cl 3.2	N_2 1.4	Cl <3mol%	N_2 5-10
Ash 0.71		Ash		Ash 3.5		Ash	
$H_2/CO = 0.9$		$H_2/CO = 0.4$		$H_2/CO = 1$		$H_2/CO = 1$	

[1] Buehl *(2002) and plant visit*

[2] *Future Energy (2003)*

[3] *Heermann et al. (2001), Kameda et al. (2002) and plant visit.*

Upscale from laboratory or pilot plant to commercial plant increase the CO yield and decrease the amount of CO_2 formed. The main reason for that is the homogenous composition in the large scale gasifier compared to the smaller one with more local variations. The results given by Na et al. (2003) is based on laboratory tests on mixed waste, and despite the high hydrogen content in the waste, a very low H_2/CO-ratio is given. One reason for this might be the difference between laboratory and commercial scale, second the different gasification technologies used. The various technologies summarized in the table, yield different syngas quality, however, the Future Energy data are seen as representative.

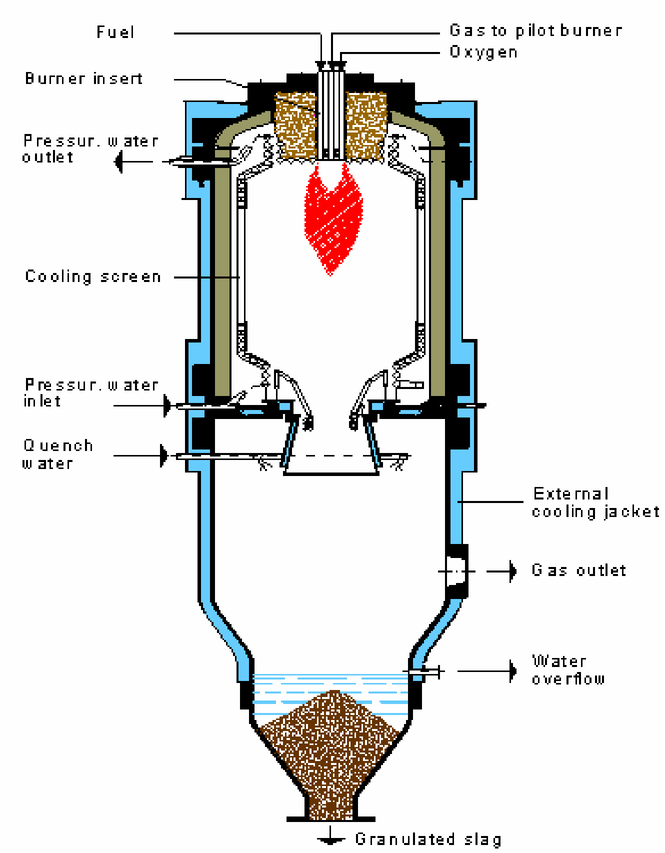

Figure A2.1: Gasification reactor with cooling screen

The technology chosen for gasification of plastic waste is the gasifier provided by Future Energy. The gasifier is based on Noell technology and a pilot plant has been operated in Freiberg since 1979. The reactor is an entrained flow gasifier with a cooling screen and direct quench to avoid dioxin formation, the reactor is given in Figure A2.1.

The reactor operates with slurry, consisting of the plastic waste in either oil or water. The numbers used here are taken from a feasibility study performed by Future Energy for Hydro Polymers in 2003. The gasification technology is chosen mainly because of the good data availability of this technology compared to the other technologies.

Calculation of heat released in gasification of plastic waste

The heat of formation for plastic materials is not given in literature, but can be calculated from the lower heating value (LHV) for the plastic material. The lower heating value is the heat released in complete combustion of the material to CO_2 and H_2O, where the product is in gas phase.

The general reaction for combustion of hydrocarbons is given as, Equation (A2-1):

$$(C_xH_y)_n + n(x+\frac{y}{2})O_2(g) \rightarrow nxCO_2(g) + \frac{yn}{2}H_2O(g) \quad \text{(A2-1)}$$

Where the lower heating value and heat of reaction can be given as, Equation (A2-2):

$$-LHV(C_xH_y)_n = \Delta H_{rx} = nxH_f(CO_2) + \frac{yn}{2}H_f(H_2O) - H_f((C_xH_y)_n) \quad \text{(A2-2)}$$

Solved for heat of formation of the plastic material, Equation (A2-3):

$$H_f((C_xH_y)_n) = LHV(C_xH_y)_n + nxH_f(CO_2) + \frac{yn}{2}H_f(H_2) \quad \text{(A2-3)}$$

Heat of reaction in the gasifier can then be calculated from the gasification reaction, Equation (A2-4):

$$(C_xH_y)_n + \frac{nx}{2}O_2(g) \rightarrow nxCO(g) + \frac{yn}{2}H_2(g) \quad \text{(A2-4)}$$

Where the heat of reaction is, , Equation (A2-5):

$$\Delta H_{rx} = nxH_f(CO) - H_f((C_xH_y)_n) \quad \text{(A2-5)}$$

Calculation of the heat released in the reaction, using HDPE as an example

For HDPE the LHV = 45000 kJ/kg (Basel, 2000), n = 4851, x = 2, y = 4 and M_m = 136300 kg/kmol (Gerharts et al., 1985-1996)

The other molecules have the following heat of formation:
$H_f(CO_2)$ = -394 kJ/mol; $H_f(H_2O)$ = -242 kJ/mol and $H_f(CO)$ = -111 kJ/mol

LHV on mole basis:

$$LHV = 45000kJ/kg \cdot 136300kg/kmol = 6133500000kJ/kmol = \underline{6133500kJ/mol}$$

From Equation (A2-3), the heat of formation is then calculated for HDPE at 25°C:

$$H_f(HDPE) = \underline{-36972kJ/mol}$$

Next, the heat of reaction in the gasification reaction can then be calculated from Equation (A2-5), again at 25°C:

$$\Delta H_{rx} = \underline{-1039950kJ/mol}$$

The reaction takes place at 1400°C. As the enthalpy is a function of state, the total heat balance can be calculated by the heat of reaction at 25°C and then heating of the products to 1400°C. Heating of CO and H_2 is calculated in Hysys, due to the change in heat capacity with temperature.

Heating of $nxCO \quad and \quad \frac{yn}{2}H_2$ from 25°C to 1400°C requires <u>844000 kJ/mol HDPE</u>

Total heat released in the gasification reactor is then:
$\underline{Q} = \Delta H_{rx} - \text{heating of products} = \underline{195950 kJ/mol \text{ HDPE}}$

<u>For the gasifier used in the calculations</u>

Input = 40 000 kg/h mixed plastic, calculated as HDPE
M_m(HDPE) = 136300 kg/kmol

$$Input = \frac{40000 kg/h}{136300 kg/kmol} = 0.2935 kmol/h = 293.5 mol/h$$

Total heat released in the reactor:
$\underline{\underline{Q}} = \underline{195950 kJ/mol \text{ HDPE}} \cdot 293.5 mol \text{ HDPE}/h = 46930000 kJ/h = 13036 kJ/s \simeq \underline{\underline{13MW}}$

In order to keep a temperature of 1400°C in the gasification reactor, 13 MW of heat has to be removed. This means that if the plastic waste was pure HDPE, 13 MW of heat is released in the gasification reaction, without adjusting for heat loss, humidity or other impurities.

The heat that can be recovered from the hot product gas, if the CO and H_2 gas is cooled from 1400°C to 35°C, is 68.4 MW. This means that the cooling duty in the cooling screen is 16% of the total heat available.

The calculations done here are based on ideal reactors, where only CO and H_2 are produced, and only HDPE to be reacted. In the process integration study of the gasifier, 130 MW is available for cooling in the product gas. The reason for the higher number is the non-ideal reactor where water and CO_2 are produced in addition to CO and H_2. As combustion of plastic is a more exothermic reaction than the gasification, and the present water has a high heat capacity, more heat will be available both for the reactor cooling and the cooling of the product gas.

The gasifier is equipped with a cooling screen which allows the ash and other inorganics to become liquid and flow downward to exit the reactor through the quench. The cooling screen consists of tubes where pressurized water is circulated in a closed loop. The temperature of the cooling screen is not given, but it is assumed that the water is too cold for a profitable production of steam. No details are given for steam production or heat released in the gasifier, hence this has not been included in the calculations. From the calculations above it can be seen that the majority of the available heat is included as the cooling of the product gas constitute 84% of the available heat in the ideal case.

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A3 Process integration in the core PtP concept

The mass flows, pressures and temperatures used in the process integration study are given in Figure A3.1. Only the carbon and hydrogen-containing compounds are included in the given mass flows, whereas the main additional components are indicated with the grey arrows. The mass flows details of the CO_2-stream from the gas cleaning section is not given, but can be calculated from the other input and output from that unit.

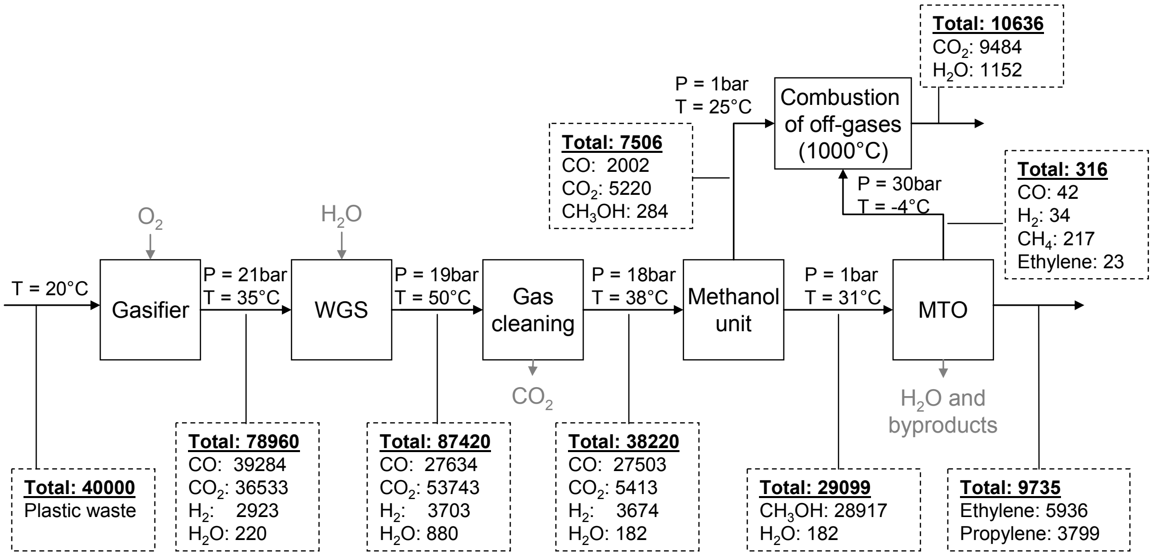


Figure A3.1: Carbon and hydrogen containing mass flows [kg/h] in the plastic waste to plastic concept

All mass flows are given in kg/h. Mass flow, temperature and pressure are given at the entry and exit of the unit. Details on mass flows, temperature and pressure inside each unit are given in the following. The fluid package used in the Hysys models is PRSV (Modified Peng-Robinson model for non-ideal systems). The $\Delta T_{min} = 10°C$ used in all calculations.

The power production by expansion of steam has a high degree of freedom. The *pressure levels* chosen in the expansion of steam comes from a trade off between steam levels available, number of steps in the expansion and the rule of thumb which says that the pressure levels should be halved in each step. The *level of superheat and reheat* is determined by the temperature and amount of heat available for heating in the system. The *number of stages in the expansion* is set to two when power production is done internally in each process, and three in the central utility plant. The *steam mass flow* used in power production is set from the assumption that all steam available is utilized. The choice of pressure, temperature and number of stages are given for each unit. Since the power production has a high degree of freedom, alternative configurations to what is chosen here can of course be constructed.

Gasifier

The Hysys models for cooling of the syngas with and without quench are given in Figure A3.2 and A3.3, respectively. The streams for the two alternative configurations are given in Table A3.1 and A3.2. All temperatures are in Celsius and heat transferred is given in MW.

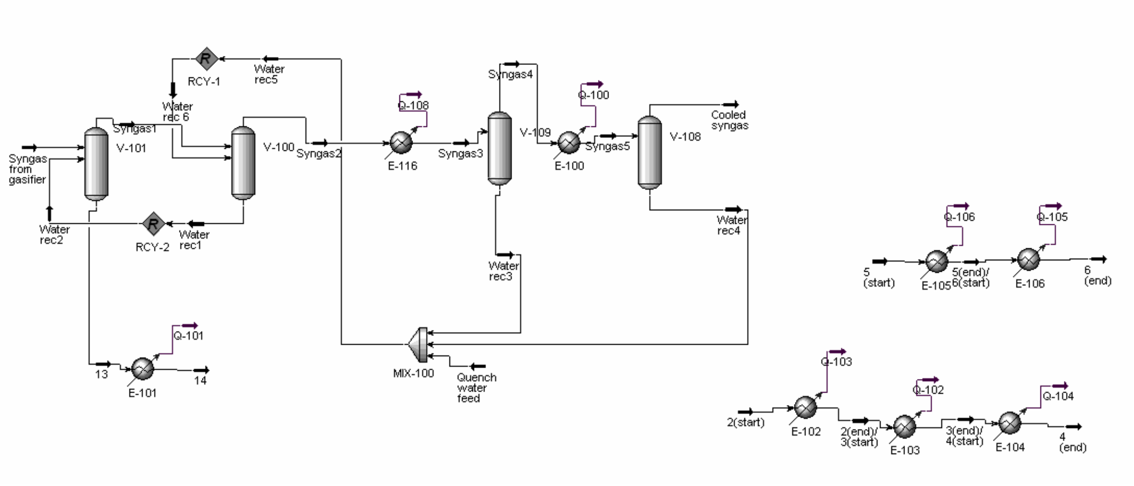


Figure A3.2: Hysys model for cooling of the syngas with quench

The cooling of the syngas by use of a quench is modelled in Hysys, and given in Figure A3.2. Input to the model is the hot syngas leaving the gasifier, whereas the cooled syngas is fed to the WGS and gas cleaning section. Heat is available in E-116, E-100 and E-101. Due to change in heat capacity with decrease in temperature, E-100 and E-116 are divided into smaller steps given as streams 2-3-4 (E-116) and 5-6 (E-100). The numbered streams correspond to the numbers given in Table A3.1. Quench water is removed from the syngas in a series of vessels (V-101, V-100, V-109 and V-108).

Table A3.1: Streams within the gasification unit with quench

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Water	Hot	Sensible	200.4	35	11.1
2	Syngas	Hot	Sensible	198.8	190	46.7
3	Syngas	Hot	Sensible	190	175	33.9
4	Syngas	Hot	Sensible	175	158.7	18.1
5	Syngas	Hot	Sensible	158.7	110	16.8
6	Syngas	Hot	Sensible	110	35	8.1

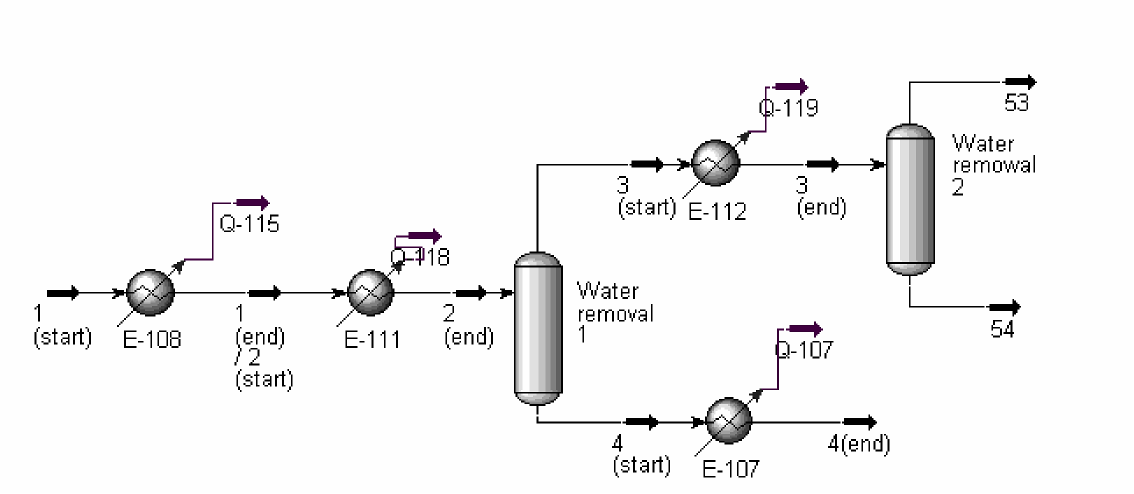


Figure A3.3: Hysys model for cooling of the syngas without quench

In Figure A3.3 the Hysys model for the case without the use of a quench is given. Again the input is the hot syngas from the gasifier, whereas the output (53) is the input to the WGS. The numbers given on the streams correspond to the numbers in Table A3.2. Water in the syngas is removed in two vessels.

Table A3.2: Streams within the gasification unit without quench

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Syngas	Hot	Sensible	1400	178	89.9
2	Syngas	Hot	Sensible	178	100	36.1
3	Syngas	Hot	Sensible	100	35	4.6
4	Water	Hot	Sensible	100	35	3.7

WGS and gas cleaning

The Hysys model for heat exchange within the WGS and gas cleaning section is given in Figure A3.4. Only the heating and cooling requirements within the WGS is included in the process integration study, total energy use in the gas cleaning section is, however, included in later energy calculations.

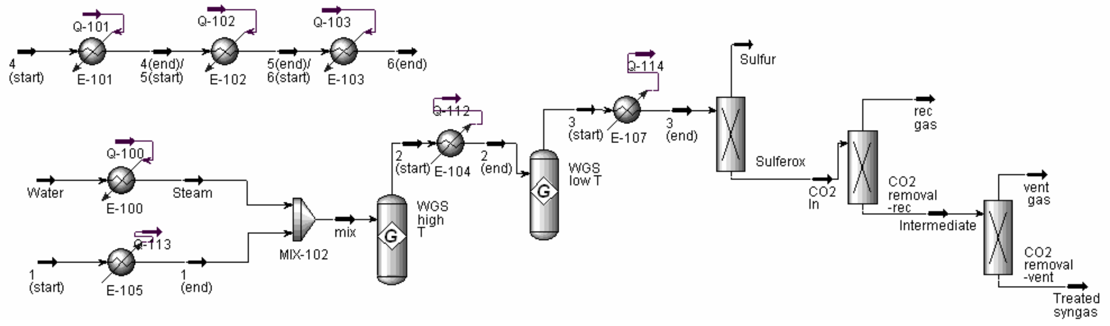


Figure A3.4: Hysys model for cooling in the WGS and gas cleaning

Cooled syngas from the gasifier and water enters the model (stream 1). The water is then evaporated to steam in E-100, divided into stream 4, 5 and 6 to cover preheating, boiling and superheating. Syngas are heated to the desired temperature in E-105. Heat is available in E-104 and E-107, cooling of stream 2 and 3, respectively. Temperatures and heat available in the streams are given in Table A3.3, where the stream numbers correspond to the numbers given in Figure A3.4.

Table A3.3: Streams within the WGS unit

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Syngas	Cold	Sensible	35	350	10.6
2	Syngas	Hot	Sensible	425	260	6.6
3	Syngas	Hot	Sensible	294	50	9.6
4	Water	Cold	Sensible	25	224	1.9
5	Water	Cold	Latent	224	224	4.3
6	Water	Cold	Sensible	224	350	0.6

Methanol

The Hysys model of the methanol unit is given in Figure A3.5. Treated syngas from the gas cleaning section is compressed in K-100 and then cooled in E-100. Latent heat is available in the water jacket surrounding the conversion reactor (stream 5). After the reactor, the product is cooled in E-102, prior to separation of gas and liquid in V-100. Unconverted syngas is compressed in K-101 and recycled to the reactor. Due to change in heat capacity as the product condenses, E-102 is divided into E-107 to E-109, given as stream 2 to 4.

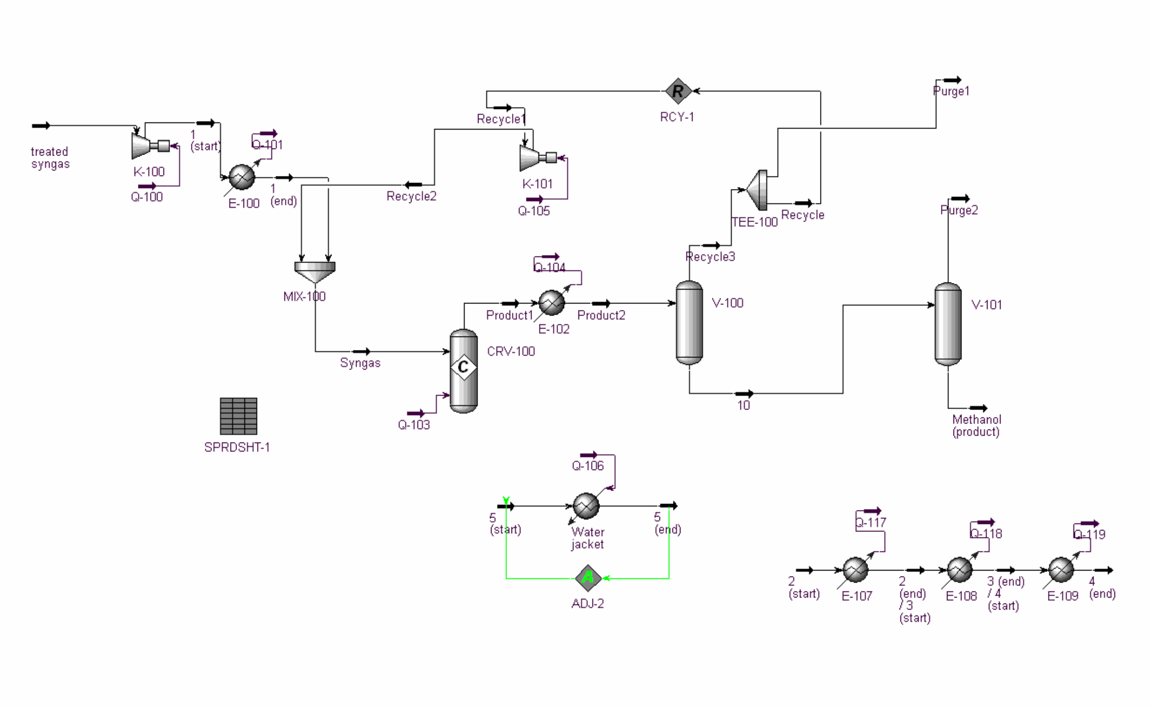


Figure A3.5: Hysys model for cooling in the methanol unit

Stream data for heating and cooling demands in the methanol unit is given in Table A3.4.

Table A3.4: Streams within the methanol unit

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Syngas	Hot	Sensible	253	204	1.3
2	Methanol	Hot	Sensible	250	125	9.5
3	Methanol	Hot	Sensible	125	80	3.1
4	Methanol	Hot	Sensible	80	40	2.3
5	Steam	Hot	Latent	250	250	26

In addition to heating and cooling, the methanol plant includes two compressors, which have the following duties:

K-100: 5.33 MW
K-101: 0.93 MW

<u>Production of power in the methanol unit</u>
The latent heat (steam) in stream 5 can be used in power production in order to power the compressors. Some superheat of the steam may be required. In Figure A3.6, a configuration for utilization of the steam is given. The saturated steam from the water jacket is superheated in E-110, and then expanded from 25.5 bar to 12.5 bar in K-102, the steam is then heated in E-104, before further expansion to 0.15 bar in K-103. In order to condense the steam, the stream is cooled in E-105 before it is pumped to the desired pressure of 25.5 bar and finally heated in E-106 to the boiling temperature (225°C).

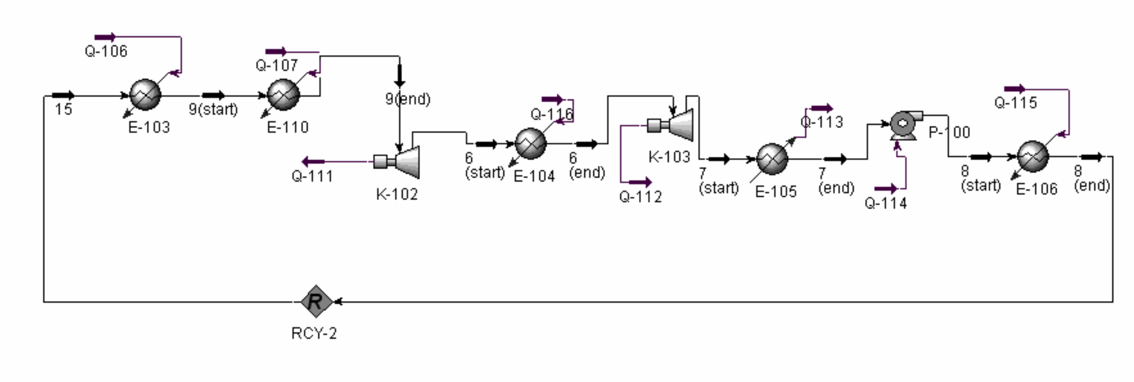


Figure A3.6: Power production from the steam produced in the water jacket

In addition to the streams given in Table A3.4, heat is available from combustion of the purge streams, Purge 1 and 2 in Figure A3.5. This heat can for example be used for superheating of the steam before the turbines (in Figure A3.6) or in steam production, either for power production or heating purposes.

For combustion at 1000°C, the heating value of the purge gas is 6.98 MW. The heating value is used as an approximation for the heat available from the purge gas for steam production or heating of process streams. The temperature used for the available heat is 1000°C. It is important to note, however, that in practice the heat will be available from cooling of the product gas from an adiabatic reactor. Rather than heat available at 1000°C, heat will be available from cooling of the product gas from the adiabatic flame temperature to a chosen end temperature. This means that the heat calculated by use of the heating value is higher than the "real" heat available.

In order to utilize the steam produced in the water jacket of the methanol reactor (stream 5), various levels of superheat and reheat can be chosen. The configurations investigated here are set to cover the power demand, but not produce excess power, and heat used should be available in the process.

With a two-stage expansion with superheating and intermediate heating as given in Table A3.5, a total of 6.33 MW of power is produced in the two stage steam turbine. The streams in Table A3.5 are included in the GCC in Figure A3.7, together with streams 1 to 4 in Table A3.4.

Table A3.5: Stream data for the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
6	Cold	Sensible	195	200	9.6
7	Hot	Sensible	53.66	53.65	32.1
8	Cold	Sensible	53.93	225	10.0
9	Cold	Sensible	223.5	300	2.3

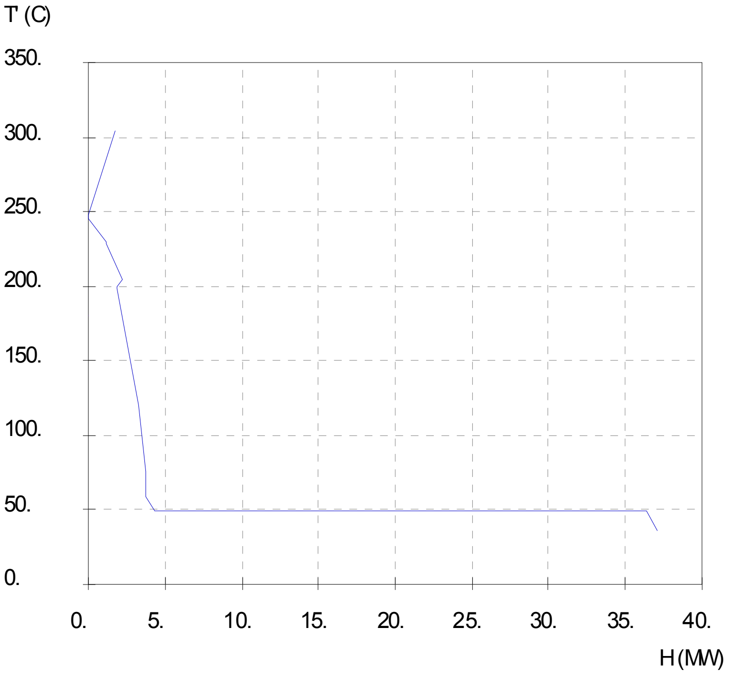


Figure A3.7: Methanol unit with power production

The introduction of heating in the power production gives a pinch point at 250°C /240°C, and there is now a need for utility heating and cooling. The 2.27 MW of heat needed above pinch (superheat of the steam) can be provided by the combustion of purge gas. Heating of stream 6 and 8 is possible by use of the hot streams in the methanol process.

By integrating the methanol background process with the power production, utility cooling required is 37.2 MW, whereas no utility power is required in the compressors. In addition, 4.71 MW of the heat available in the reactor where the purge gasses are combusted can be utilized in other processes.

MTO

The flowsheet of the MTO process is given in Figure A3.8. The refrigeration cycle for the separation columns is given in Figure A3.10.

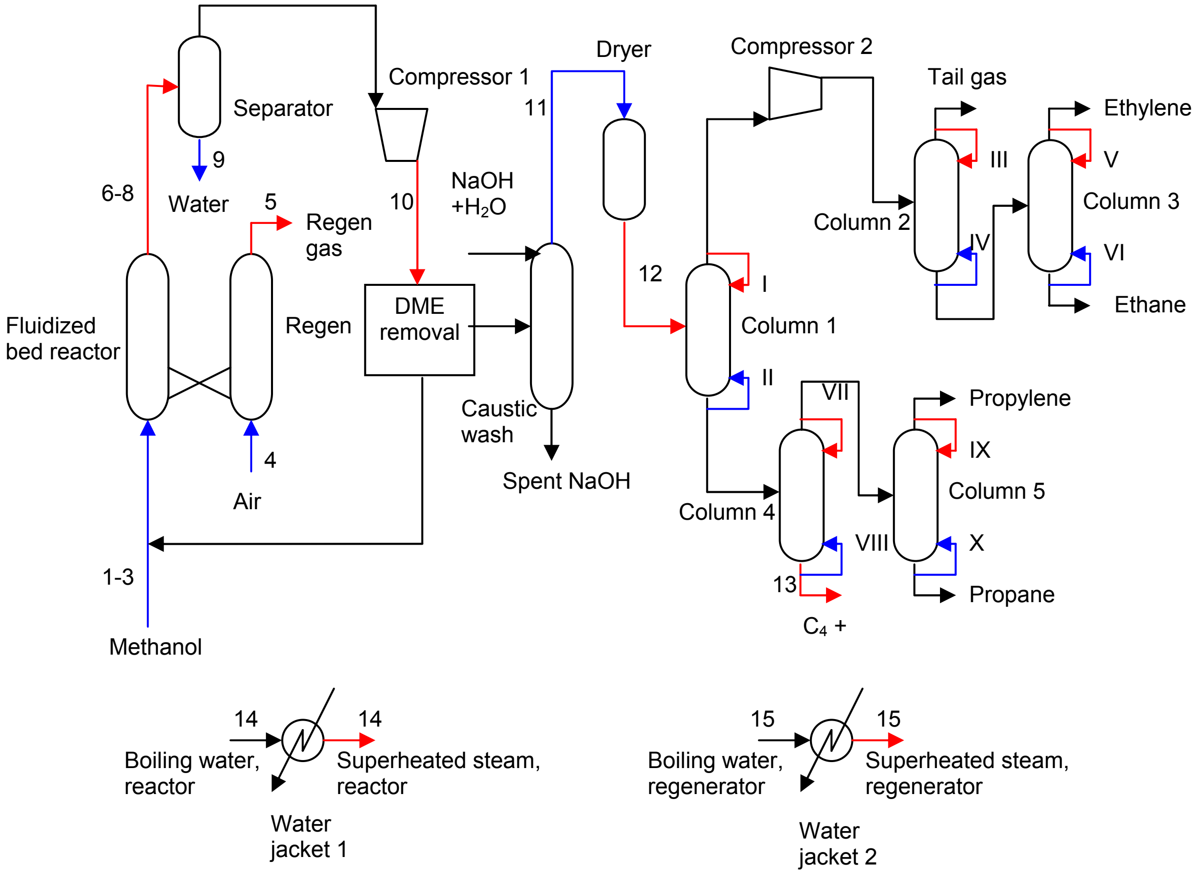


Figure A3.8: Heating and cooling within the MTO, background process

The streams with heating or cooling duties within the background process are given in Table A3.6, the stream numbers correspond to those given in Figure A3.8. Cooler 1 and 2 in the table are intercooling of the three-stage Compressor 1. Water jacket 1 in Figure A3.8 is cooling of the fluidized bed reactor, whereas water jacket 2 is cooling of the regeneration reactor "Regen". The background process does not include the separation process or the refrigeration section.

Table A3.6: Stream data in the MTO background process

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Cold	Sensible	30.7	60.0	2.30
2	Cold	Sensible	60.0	83.9	15.0
3	Cold	Sensible	83.9	400.0	7.20
4	Cold	Sensible	25.0	500.0	0.11
5	Hot	Sensible	550.0	25.0	0.14
6	Hot	Sensible	450.0	92.5	8.70
7	Hot	Sensible	92.5	55.0	17.40
8	Hot	Sensible	55.0	2.0	2.80
9	Cold	Sensible	2.0	32.0	0.95
10	Hot	Sensible	107.5	38.0	0.65
11	Cold	Sensible	38.0	212.4	1.10
12	Hot	Sensible	212.4	10	1.75
13	Hot	Sensible	125	38	0.096
Cooler 1	Hot	Sensible	73.8	32	0.29
Cooler 2	Hot	Sensible	101.4	32	0.49

The water jackets are not included in the process integration of the background process as they are seen as utilities. The duties of the two jackets are:

Water jacket 1: 11.6 MW, steam at 250.4°C and 40 bar
Water jacket 2: 2.7 MW, steam at 250.4°C and 40 bar

Saturated steam is produced in the water jackets, stream 14 and 15 in Figure A3.8. Production of power from the steam is discussed later.

The two compressors in the MTO background process have the following duty:

Compressor 1: 1.3 MW
Compressor 2: 0.05 MW

Compressor 1 is a three-stage compressor, whereas compressor 1 is one stage.

Integration of separation columns with the background process

The duties of the distillation columns given in Figure A3.8 are summarized in Table A3.7. Separation columns can be integrated with the background process if condensers are above pinch or reboilers are below pinch. In the background process, the pinch temperature is 70°C /60°C.

Table A3.7: Reboiler and condenser specifications

Stream no	Type	Temp [°C]	Heat [MW]
I	Condenser	-24	0.32
II	Reboiler	69	0.74
III	Condenser	-87	0.65
IV	Reboiler	-11	1.3
V	Condenser	-12	0.96
VI	Reboiler	10	2.2
VII	Condenser	57	1.2
VIII	Reboiler	125	0.74
IX	Condenser	57	4.3
X	Reboiler	66	3.7

All of the condenser duties are below the pinch temperature, and cannot be integrated with the cold streams in the background process. Reboiler duties IV and VI are below the pinch temperature. As reboiler duties are cold streams, the modified temperatures are -6°C and 15°C, respectively. Both reboilers can be integrated below pinch, as shown in Figure A3.9.

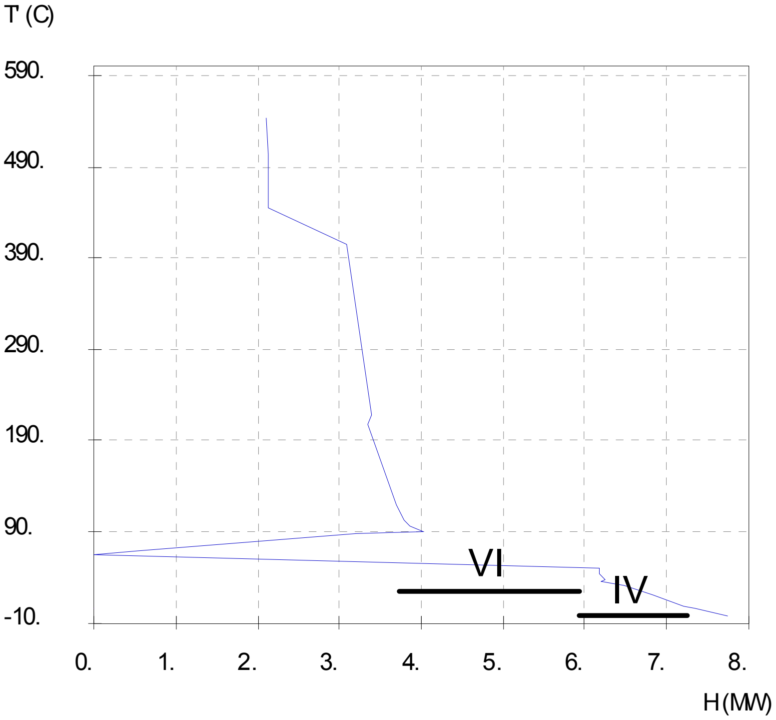


Figure A3.9: Possibility for integration of reboilers IV and VI

If the reboilers are integrated with the background process, the remaining cooling demand in the background process is 4.3 MW. Condensers VII and IX are cooled by cooling water, whereas reboilers II, VIII and X are heated by steam, requiring a total of 5.16 MW of heat.

Integration of the refrigeration cycle

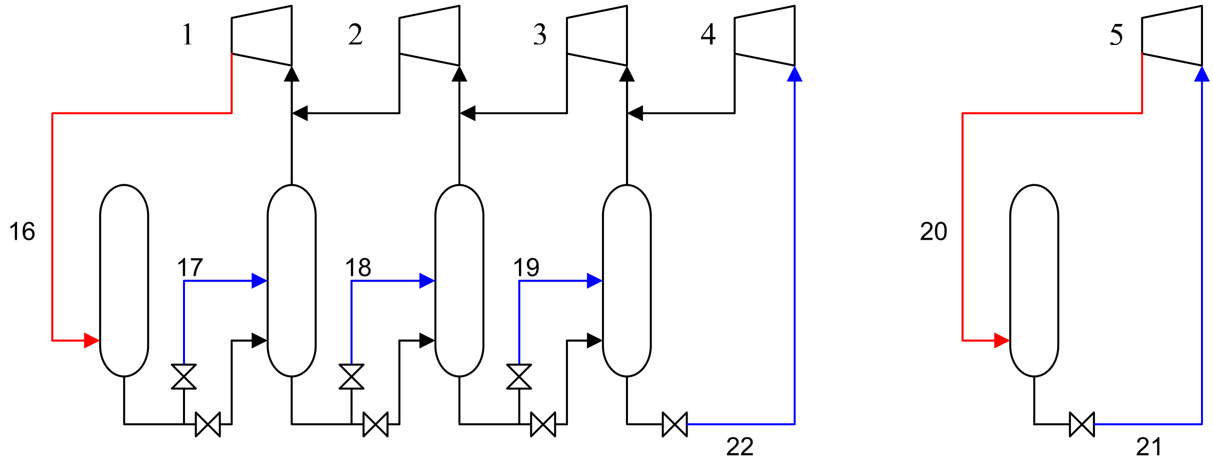


Figure A3.10: Flowsheet for the refrigeration cycle, propylene cycle to the left, ethylene to the right

Cooling water is usually available at 10-20°C, depending on the local climate. For temperatures below this, refrigeration is necessary. The refrigeration cycle given in Figure A3.10 provides low temperature cooling for the separation columns via the following matches (Table A3.6, Table A3.7 and Table A3.8):

Stream 17 and Stream 12 and 8
Stream 18 and Condenser V
Stream 19 and Condenser I
Stream 21 and Condenser III

Table A3.8: Stream data for the refrigeration cycle

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
16	Hot	Sensible	73	27	2.85
17	Cold	Latent	-5.9	-5.9	0.69
18	Cold	Latent	-26.2	-26.2	0.96
19	Cold	Latent	-36	-36	0.32
20	Hot	Sensible	89	-40	0.16
21	Cold	Latent	-101.5	-101.5	0.65
22	Cold	Sensible	-50	-46	0.094

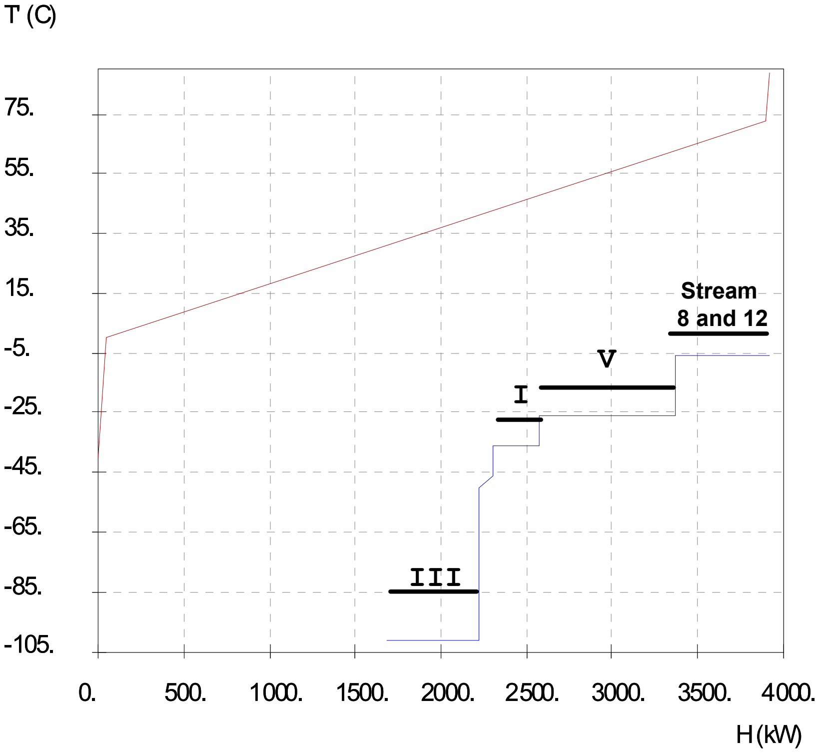


Figure A3.11: Composite curves for the refrigeration cycle

The composite curves for the refrigeration cycle are given in Figure A3.11, where the integration with condensers and streams in the separation and background process is indicated. Stream 22 is providing cooling for the cold end of stream 20. All heating of cold streams are covered by hot streams, whereas utility cooling is required, with cooling water as the utility source. In addition, power for the compressors are required (1-5 in Figure A3.10), and an overview of duties are given in Table A3.9.

Table A3.9: Compressor duties in the refrigeration cycle

Compressor	Duty [MW]
1	0.73
2	0.23
3	0.050
4	0.037
5	0.30
Total	**1.35**

Production of power from steam

Production of power from the steam produced in the two water jackets is given in Figure A3.12. Boiling feedwater is fed to the water jacket, and saturated steam is produced at 250.4°C and 40 bar. The saturated steam is superheated in E-101, and is then expanded to 20 bars in K-102. After the first expansion, the steam is heated in E-104 and expanded further to 0.07 bars in K-103. In order to condense the steam, the stream is cooled in E-105 before it is pumped to the desired pressure of 40 bars and finally heated in E-106 to the boiling temperature (250.4°C).

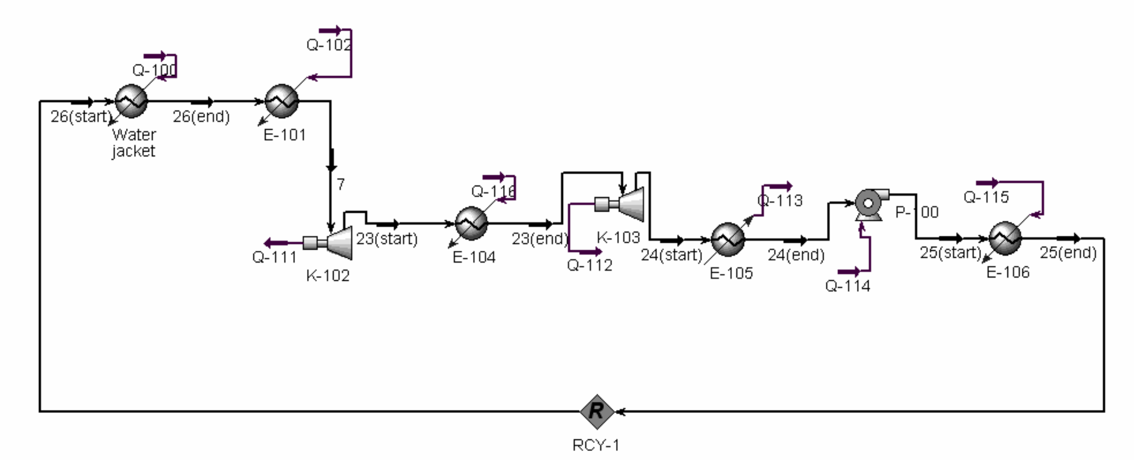


Figure A3.12: Power production from the steam produced in the water jacket

In addition to the hot streams given in Figure A3.8, heat is available from combustion of the tail gas (also given in Figure A3.8). As for the methanol unit, the heating value of the tail gas is used in the evaluation. For combustion at 1000°C, the heating value of the tail gas is 4.47 MW.

In order to utilize the steam produced in the water jackets of the MTO reactor, various levels of superheat and reheat can be chosen. In water jacket 1 11.6 MW of steam is available, whereas 2.7 MW is available from water jacket 2, both with a steam level of 250.4°C and 40 bar. The configurations investigated here are set to cover the power demand in the MTO process, but not produce excess power, and heat should be available in the process. The power needed is 2.7 MW.

The steam available from water jacket 2 is not sufficient for production of the required power. The steam available from water jacket 1 can produce more than the required power, and only 6 MW of this stream will be used. With a two-stage expansion with superheating and intermediate heating as given in Table A3.10, a total of 2.75 MW of power is produced in the two stage steam turbine. The streams in Table A3.10 are included in the GCC in Figure A3.13.

Table A3.10: Stream data for the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
23	Cold	Sensible	319.4	400	0.59
24	Hot	Sensible	40.01	40.0	8.16
25	Cold	Sensible	40.4	250.4	3.14
26	Cold	Sensible	250.4	400	1.18

The remaining of the steam from water jacket 1 (5.2 MW), or the steam from water jacket 2 (2.7 MW) can be used for the heating required up to 240°C. For temperatures above this level, the heat available in the combustion of the tail gas is the only alternative. 5.2 MW of steam is needed for the reboilers in the separation section, hence the steam from water jacket 1 can be used for this purpose. The remaining steam at 250°C covers 2.7 MW (water jacket 2) of the heating required, whereas the remaining 2.21 MW is covered by combustion of the tail gas. This leaves 2.26 MW of the high temperature heat from the combustion of tail gas. Cooling of the hot stream 24 is done by cooling water, 8.16 MW.

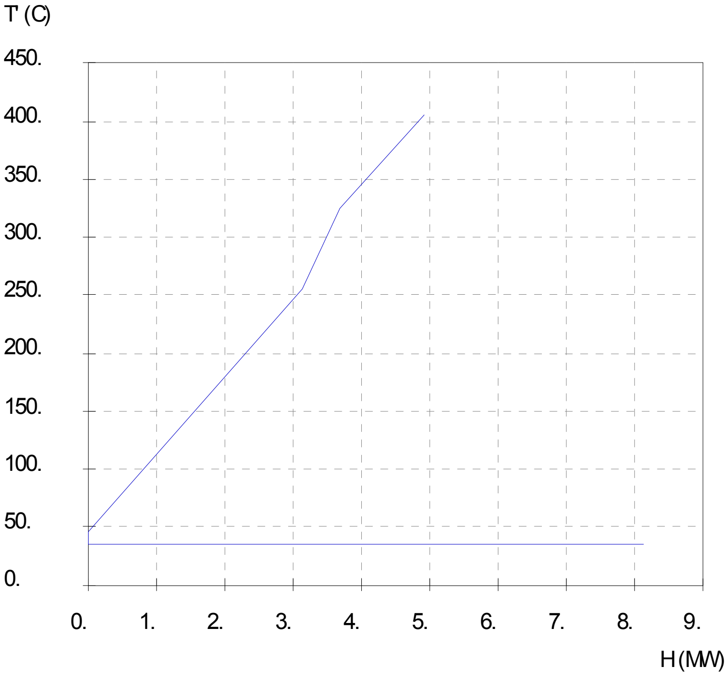


Figure A3.13: Heating and cooling demand in the power production of the MTO

Summary of the MTO process

The background process needs 2.1 MW of utility heating at 60°C to 80°C and 7.8 MW of utility cooling at 60°C to 2°C. The refrigeration cycle provides cooling of the cold end of stream 12 and 8, taking them down to 10°C and 2°C, respectively. Reboilers IV and VI are integrated with the background process as shown in Figure A3.9, leaving a cooling demand in the background process of 4.3 MW. The condensers in the separation columns are integrated with the refrigeration cycle as given in Figure A3.11, leaving a heating demand of 5.2 MW and cooling demand of 5.5 MW in the separation section. The heat demand can be covered by the steam in water jacket 1 (5.2 MW at 250°C), whereas the cooling is provided by use of cooling water. The refrigeration section needs 2.9 MW of external cooling, which is done at elevated pressure against cooling water.

In addition to heating and cooling, there is a need of power in the MTO process. The total power duty needed is 2.7 MW, which is covered by expansion of part of stream 14 (water jacket 1). There is a surplus of 2.26 MW of high temperature heat from the combustion of tail gas, this heat can be used to cover the 2.1 MW of heating needed in the background process (60°C to 80°C).

Process integration between units

A summary of the utilities needed in the various units, when the integration within each unit has been maximized, are given in Table A3.11.

Table A3.11: Summary of the utilities needed when integration within each unit has been maximized

Process [MW]	Surplus heat >200°C	Surplus heat Total	Heat deficit (cold streams)	Power (required)	Surplus heat (steam/ off gases)
Gasification	0	134.7	0	10	0
WGS	0	0	1.2	0	0
Methanol	2.1	37.2	0	0	4.7
MTO	0	20.9	0	0	0.2

The heat deficit in the WGS can be covered by the available heat in the methanol unit. The power required in the gasifier can, however, not be covered by the available steam from the other processes. There is a large surplus of low temperature heat in the system, which can not be utilized with the current configuration.

The approach so far has been to utilize the available steam and process streams for process integrations within each unit. Another approach is also investigated, sending all available steam and combustion of off-gasses to a common utility system, which provide utilities for all units. In this approach, all process to process integration is carried out within the unit, and only steam and purge/tail gasses are sent to the common utility system. The reasons for not looking at process to process integration between the units are the controllability, piping and other operational considerations.

With a common utility system for all units, power is produced centrally and electricity is sent to the grid to power the compressors. This is in contrast to the single shaft compressor which can be used when the steam is utilized within each unit. The main advantage with the common utility system, is the ability to use a larger steam turbine which have a higher efficiency.

The steam and combustion of off-gasses from the methanol unit and the MTO unit are led to the common utility plant, where production of electricity and extraction of steam levels are carried out to fulfill the needs within the entire process train. The available steam levels and off-gases as well as the required heat and power are given in Table A3.12.

Table A3.12: Heat and power fed to and required from the utility plant

Unit	Heat [MW]	T [°C]	P [bars]	Power [MW]	Comment
Gasifier	47.4	180	10.0		Cooling of process
Gasifier	11.6	175	8.9		Cooling of process
Gasifier				-10	Without ASU
WGS	-1.2	25-224			Heating of process
Methanol	26	225	25.5		Water jacket
Methanol	4.1	200	15.5		Cooling of process
Methanol	2.1	175	8.9		Cooling of process
Methanol				-6.3	Compressor
MTO	11.6	250.4	40		Water jacket
MTO	2.7	250.4	40		Water jacket
MTO	-2.1	60-80			Background process
MTO	-5.2	66-125			Separation section
MTO				-2.7	Compressor

The first task is to cover the heating demands within the processes (given as negative numbers in Table A3.12) by utilizing the heat available as steam from cooling of the other processes. When heat is provided by a central utility system, heat is exchanged as steam as opposed to process to process heat exchange. In order to limit the number of steam levels and piping needed, only one steam level is used for distribution of heat within each unit. The heat required and available is summarized in Table A3.13.

Table A3.13: Heat available and required for process heating and cooling

Stream	Unit	Heat [MW]	Temperature [°C]	Modified temp [°C]
1	Methanol	4.1	200	195
2	Gasifier	47.4	180	175
3	Methanol and Gasifier	13.7	175	170
4	MTO (background)	2.1	80	85
5	MTO (separation)	5.2	125	130
6	WGS	1.2	224	229

In Figure A3.14, the streams in Table A3.13 are plotted. The heat available as steam is plotted to the right, whereas heat required is plotted to the left. From the figure it can be seen that the heat required in stream 4 and 5 (MTO unit) can be covered by the steam available in stream 1, 2 or 3. The heat needed in stream 6 (WGS), however, cannot be covered by the heat available.

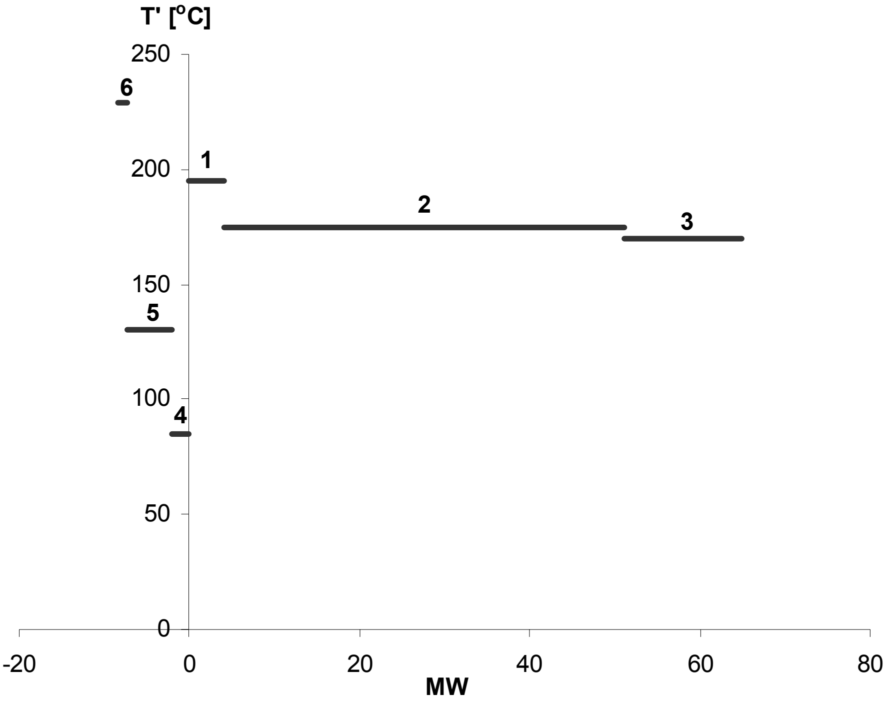


Figure A3.14: Steam levels available (right) and required (left)

The heat required in stream 4 and 5 will be covered by stream 3. When considering steam levels, it is, however, important to keep the number of steam levels at a reasonable level, and it is probably not convenient to have a steam levels at both 175°C and 180°C. With this in mind, stream 3 might be omitted, and the heat needed in stream 4 and 5 are covered by stream 2. The heat needed in the WGS, stream 6, can be covered by the combustion of off-gases (methanol or MTO), steam in the MTO water jackets or by extracting steam from the steam turbine used for power production. The approach by using steam available in the MTO water jacket is chosen.

Next task is production of power. Production of power is done in a multistage steam turbine, with superheat and reheat of the steam. Power production will be maximized with the available heat for superheat and reheat. The configuration is given in Figure A3.15.

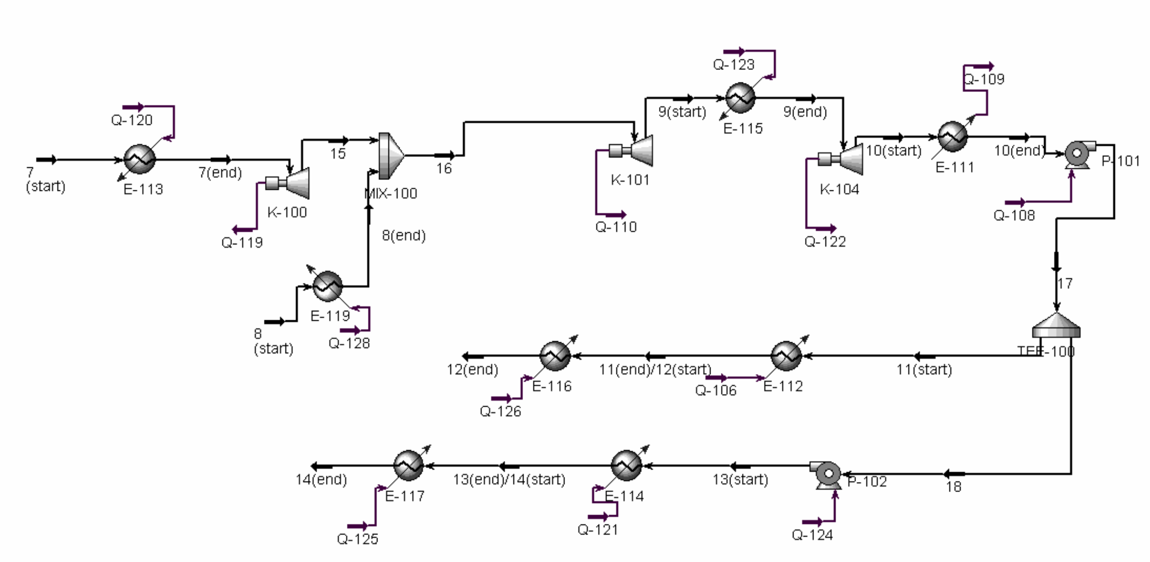


Figure A3.15: Power production in the central utility plant

Power is produced in the three turbines, yielding net 14.1 MW electricity (after the power required in the pumps are covered). Stream 7 is the steam at 40 bar available from the MTO (water jacket 1), this is superheated to 350°C, and then expanded to 25.5 bars in the turbine K-100. At this stage the steam from the methanol unit at 25.5 bars (water jacket) is added, after superheating in E-119. The next expansion takes place in turbine K-101, from 25.5 bars to 5 bars. The product gas (Stream 9) is then heated, before the final expansion to 0.05 bars. The steam is condensed in E-111, before it is pumped to 25.5 bars in P-101 and further to 40 bars in P-102. Streams 11 and 12 is heated to the boiling temperature of 225°C (25.5 bars), whereas streams 13 and 14 are heated to 250.4°C (40 bars). The hot and cold streams are given in Table A3.14, whereas the grand composite curve with the steam levels used in the superheat and reheat is given in Figure A3.16.

Table A3.14: Heating and cooling required in the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
7	Cold	Sensible	250.4	350.0	1.53
8	Cold	Sensible	225.0	300.0	2.23
9	Cold	Sensible	151.8	254.3	4.30
10	Hot	Sensible	32.50	32.49	48.8
11	Cold	Sensible	32.8	170.0	7.42
12	Cold	Sensible	170.0	225.0	3.47
13	Cold	Sensible	32.9	170.0	3.76
14	Cold	Sensible	170.0	250.4	2.55

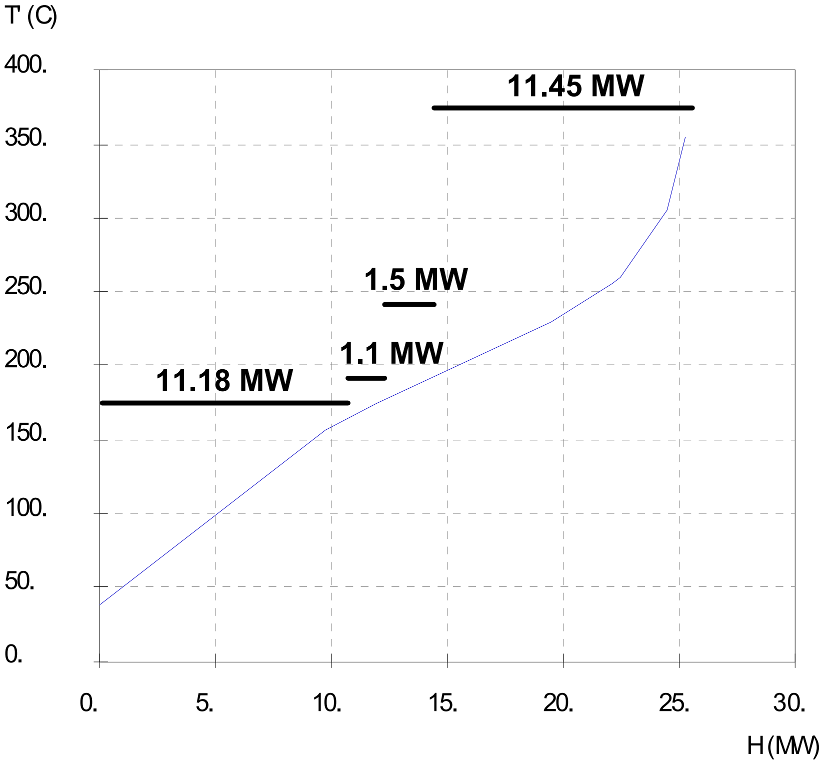


Figure A3.16: Steam levels used to cover the heat demand in the power production

The GCC given in Figure A3.16 does not include the cooling requirement of 48.77 MW. The steam levels in the figure, starting from the lowest, are 11.2 MW of steam from the gasifier (180°C), 1.1 MW of steam from the methanol process (200°C), 1.5 MW steam from water jacket 2 in the MTO unit (250.4°C), and finally 11.45 MW available from combustion of off-gases (1000°C). The off-gases should have been drawn at 1000°C, but for the illustration it is given at a lower temperature level in Figure A3.16.

The summary of the utilities needed after production of power and steam in the central utility plant is given in Table A3.15.

Table A3.15: Summary of the utilities needed when a central utility plant is used

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off gases)**
Gasification	0	116.2	0	4.9	0
WGS	0	0	0	0	0
Methanol	0	15.1	0	0	0
MTO	0	12.7	0	0	0
Utility plant	0	48.8	0	0	0

A4 Assignment of CO_2 emissions in the process train

The system consists of many process units, and the challenge is to assign the CO_2 emissions (and other emissions) to the “right” unit. Only the process waste emissions, as defined in Chapter 6.2.5, are discussed here. Utility waste is normally easier to assign to the right unit since utility consumption is often given for each unit operation.

If a traditional approach is used, the emissions are assigned to the unit where the emissions are “vented”. However, it seems to be beneficial for understanding and search for improvement within the system, to assign emissions to where they are formed. The difference is illustrated in Figure A4.1.

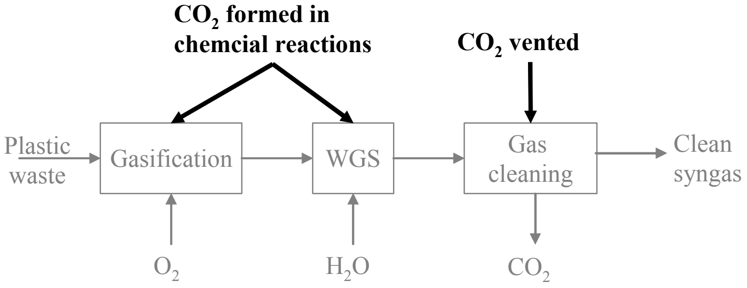


Figure A4.1: Illustration of CO_2 formation and vent

CO_2 is formed in the gasifier and WGS, and vented in the gas cleaning unit. Without process knowledge of each unit, CO_2 might be assigned to the gas cleaning process, rather than the gasifier or WGS. The gas cleaning unit can not be improved to reduce the overall emissions of the system, it just removes emissions that are already formed.

Based on the process model, it is possible to assign the CO_2 emissions to the gasifier or WGS, which enable us to do a more thorough process evaluation. All the CO_2 that is formed in the gasifier is an example of technology restrictions in the gasifier. This can be decreased by better performance of the gasifier [Technology]. Second, the CO_2 formed in the shift reactor is due to the need for a higher H_2/CO-ratio in the methanol production. These emissions can not be decreased by improved technology in each unit, only by improving the system [System restrictions].

To summarize the findings above, the process waste CO_2 emissions from this system can be divided into two categories:

- CO_2 as a result of the technology available
- CO_2 caused by “system restrictions”

Based on these findings, the following assignment f the process waste CO_2 has been used:

Gasifier = All CO_2 leaving the gasification reactor
WGS = All CO_2 leaving theWGS reactor subtracted the CO_2 from the Gasifier
Steam (utility) = All CO_2 from combustion of purge gas from the methanol reactor
MTO = All CO_2 from the reactor (regeneration of catalyst)
+ Combustion of purge gas (C_{5+}, H_2 and CO)

A5 Electricity mix

The electricity mix used in the Excel LCA model, the EU mix, is compared to the electricity mix used in the Ecoinvent database, Electricity medium voltage production UCTE at grid.

The EU mix includes the share of all EU and EEA countries, Table A5.1. UCTE is short for Union for the Co-ordination of Transmission of Electricity and covers continental Europe, numbers given in Table A5.2.

Table A5.1: EU mix (Edwards et al., 2003)

Electricity source	Share
Nuclear	37.5 %
Coal	22.4 %
Gas	15.5 %
Hydro	12.4 %
Oil	9.6 %
Waste	1.8 %
Wind	0.4 %
Other renewables	0.3 %

Table A5.2: Electricity medium voltage production UCTE at grid (Ecoinvent, 2004)

Electricity source	Share
Nuclear	31.3 %
Fossil	53.3 %
Hydro	11.6 %
Renewable	3.8 %

References:

Ecoinvent Centre, Ecoinvent data v1.1, Final report ecoinvent 2000 No. 1-15, Swiss Centre for Life Cycle Inventories, Dübendorf, 2004, CD-ROM.

Edwards, R., Griesemann, J-C., Larivé, J-F. and Mahieu, V., Well to wheels analysis of future automotive fuels and powertrains in the European context, EUCAR, CONCAWE, JRC, 2003.

A6 Hysys models

Flowsheets with stream data for the Hysys models are given for the PtP reference case, ATR3 and SMR3. In addition, the modeling of each unit operation and calculation is described. The Hysys models are used in LCA of the PtP concept in Section 6.2 and Chapter 7.

Table A6.1: Input variables to the Hysys models

Input variable	Model	Description
Syngas from gasifier	All	Import the syngas composition, temperature, pressure and mass flow from Future Energy (2003).
Steam/methane ratio	ATR, SMR	The steam/methane ratio is set for the various scenarios tested. Steam/carbon ratio varied between 2 and 3.
Oxygen/methane ratio	ATR	The oxygen/methane ratio is set for the various scenarios tested. Oxygen/methane ratio varied between 0.5 and 0.8.
Conditions input streams	All	Temperature and pressure for all input streams are specified.
H_2/CO-ratio in treated gas	All	The H_2/CO ratio in the treated syngas is set to 2.

Table A6.2: Unit operations in the Hysys models

Unit operation	Reactor type/	Description
SMR	Gibbs reactor	Temperature and pressure set. Components in Gibbs reactions; CH_4, H_2O, CO, CO_2, N_2 and H_2, all other components inert
ATR	Gibbs reactor	Pressure set, adiabatic reactor. Components in Gibbs reactions; CH_4, H_2O, CO, CO_2, N_2, O_2 and H_2, all other components inert
Sulfur removal (sulferox)	Component splitter	Sulferox process modeled as a component splitter. Energy use is calculated in the Excel model. Component split as given in Ekbom et al., 2003
CO_2 removal	Component splitter	CO_2 removal modeled as two component splits. First splitter is for recycle of CO_2 to the gasifer, second goes to vent. Energy use is

		calculated in the Excel model. Component splits as given in Ekbom et al., 2003
Methanol reactor	Conversion reactor	Methanol reactor modeled as a conversion reactor with total conversion of 92%. The total conversion is based on the methanol model given in Chapter 5.2.4. Energy use is calculated in the Excel model. A detailed Hysys model is used for process integration.
Heat required for SMR	Gibbs reactor	Combustion of methane in air for production of the heat required in the SMR. The methane flow is calculated with “adjust”, giving the required output temperature of 1000°C.
Combustion of flue gas	Gibbs reactor	Combustion in air of the flue gas from the methanol plant.
Component splitter - methanol	Component splitter	Separation of methanol/water and flue gas. All methanol and water in one stream, all other components in the flue gas. Energy use calculated in Excel. Component split as given in Ekbom et al., 2003
Component splitter - water	Component splitter	Possibility for removal of water in the syngas from the ATR case, not used.

Spreadsheets	**Calculation**	**Description**
Calculate steam flow	Steam	Calculate the amount of steam from set methane flow and steam/carbon ratio.
Calculate oxygen flow	Oxygen	Calculate the amount of oxygen from set methane flow and oxygen/carbon ratio.
Air for combustion	Air	Calculate the amount of air needed in the combustion of methane for heat.
Heat required for SMR	Heat	Input to the “combustion for heat” reactor, amount of heat required.

Figure A6.1: Flowsheet PtP reference case

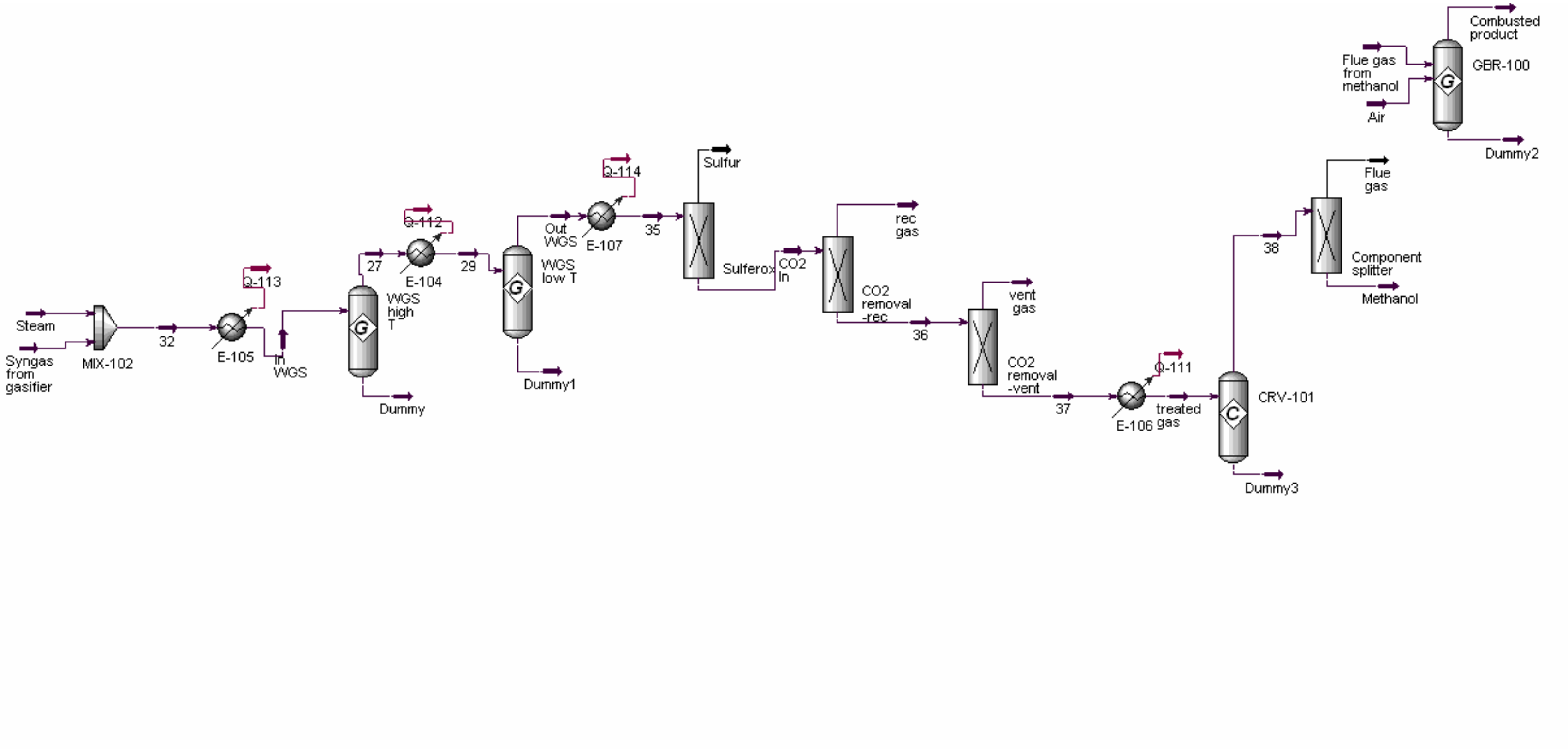


Table A6.3: Stream data in PtP reference case

Stream	**Steam**	**Syngas from gasifier**	**In WGS**	**Out WGS**	**Treated gas**	**Methanol**	**Flue gas**	**Combusted product**
Mass flow [[kg/h]	8107	79263	87370	87370	38178	28232	9946	16975
H_2 [[kg/h]	-	2872	2872	3674	3644	-	228	-
CO [[kg/h]	-	38856	38856	27623	27493	-	3534	-
CO_2 [[kg/h]	-	36080	36080	53731	5411	-	4736	12645
O_2 [[kg/h]	-	-	-	-	-	-	-	-
H_2O [[kg/h]	8107	-	8107	887	182	182	-	2883
CH_4 [[kg/h]	-	-	-	-	-	-	-	-
Methanol [[kg/h]	-	-	-	-	-	28050	-	-
Others [[kg/h]	-	1455	1455	1455	1448	-	1448	1448
Temperature [^{o}C]	400	35	350	294	38	46	46	1000
Pressure [bar]	25	21	21	19	19	7	7	7

Figure A6.2: Flowsheet ATR3 case

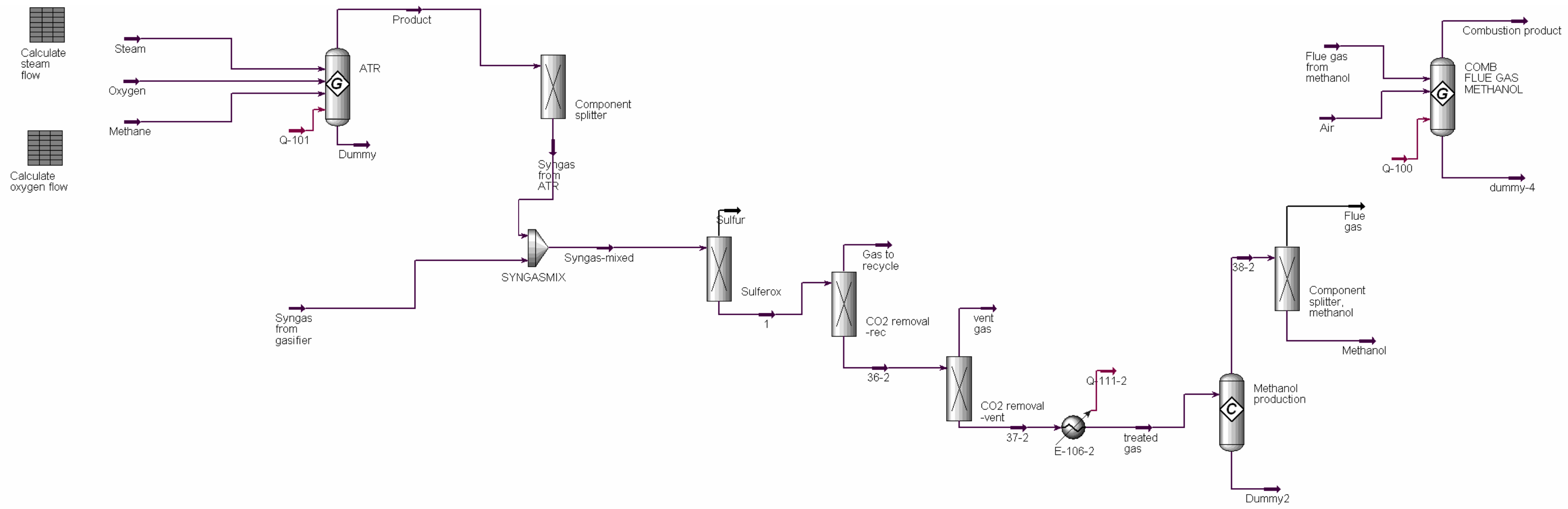


Table A6.4: Stream data in the ATR3 case

Stream	**Steam**	**Oxygen**	**Methane**	**Syngas from ATR**	**Syngas from gasifier**	**Syngas -mixed**	**Treated gas**	**Methanol**	**Flue gas**	**Combusted product**
Mass flow [[kg/h]	68400	42560	30400	141360	79079	220438	94238	79957	14281	32913
H_2 [[kg/h]	-	-	-	7463	2865	10327	10251	-	888	-
CO [[kg/h]	-	-	-	32724	38766	71490	71241	-	5634	-
CO_2 [[kg/h]	-	-	-	31738	35996	67734	6830	-	6141	18665
O_2 [[kg/h]		42560	-	-	-	-	-	-	-	-
H_2O [[kg/h]	68457	-	-	69276	-	69276	4310	5050	-	12800
CH_4 [[kg/h]	-	-	30482	160	-	160	158	-	158	-
Methanol [[kg/h]	-	-	-	-	-	-	-	74907	-	-
Others [[kg/h]	-	-	-	-	1452	1452	1448	-	1448	1448
Temperature [^oC]	200	200	200	848	35	567	38	46	46	1000
Pressure [bar]	20	20	20	20	21	19	19	7	7	7

Figure A6.3: Flowsheet SM3 case

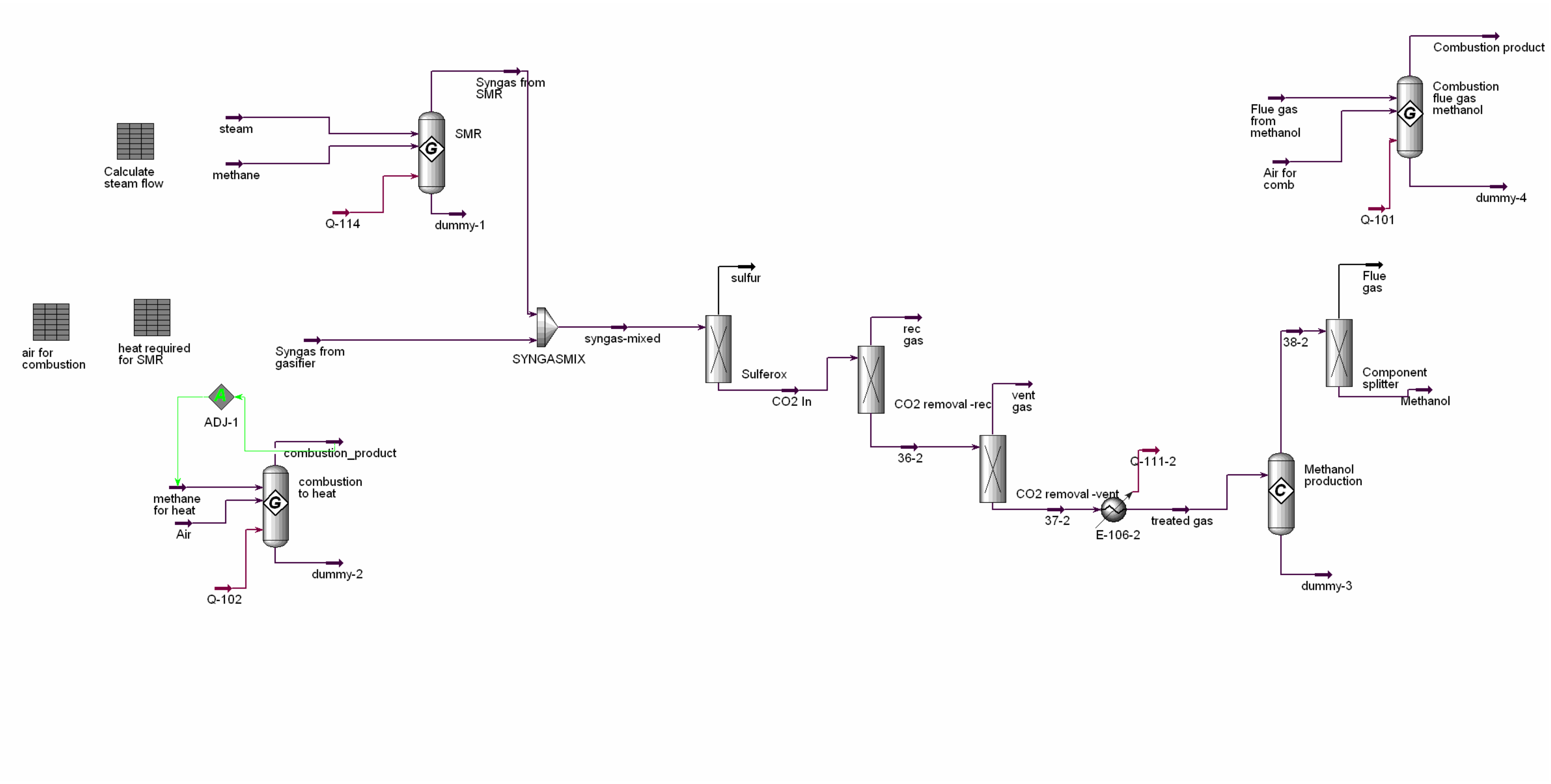


Table A6.5: Stream data in the SMR3 case

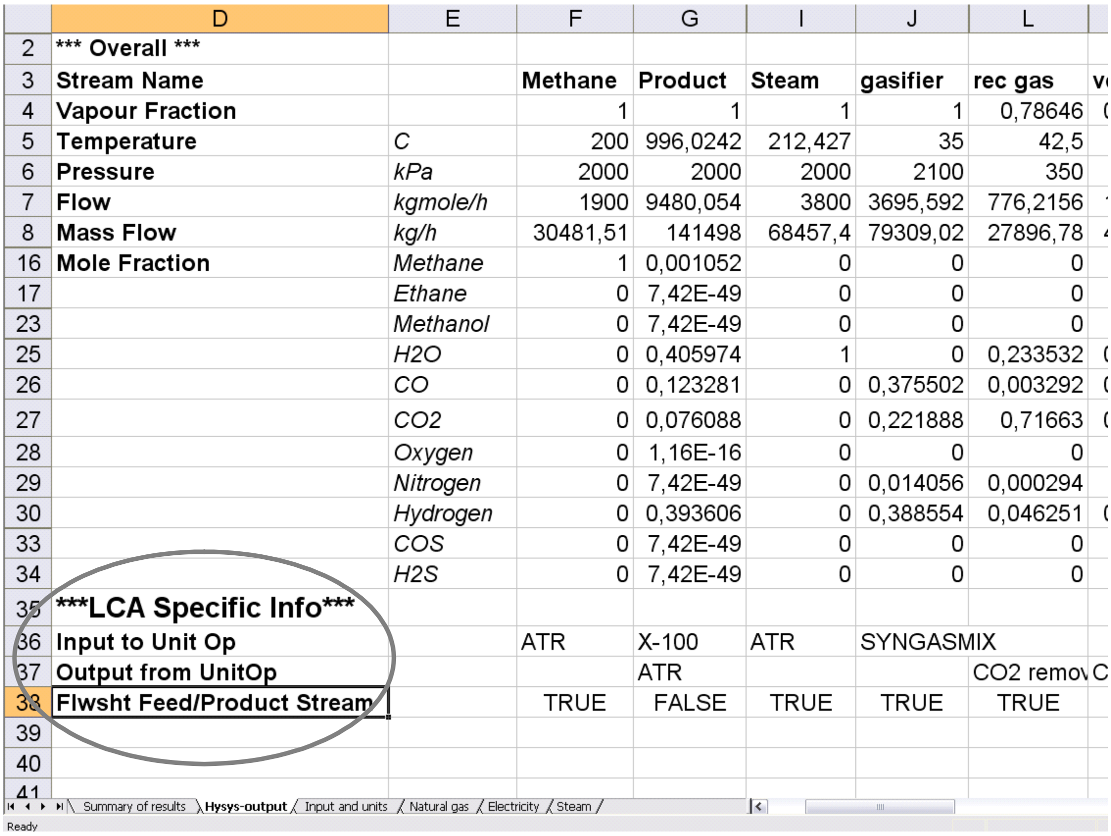
Stream [kg/h]	**Steam**	**Methane**	**Methane for heat**	**Combutsion _product**	**Syngas from SMR**	**Syngas from gasifier**	**Syngas-mixed**	**Treated gas**	**Methanol**	**Flue gas**	**Combusted product**
Mass flow	43200	12800	7523	37634	56000	79078	135078	74493	63736	108757	16976
H_2	-	-	-	-	5094	2865	7959	7902	-	661	-
CO	-	-	-	-	16495	38766	55261	55089	-	4355	-
CO_2	-	-	-	20688	8577	35996	44573	4498	-	4045	12645
O_2	-	12800	-	-	-	-	-	-	-	-	-
H_2O	43200	-	-	16946	25578	-	25578	5303	5812	-	2883
CH_4	-	-	7523	-	256	-	265	253	-	248	-
Methanol	-	-	-	-	-	-	-	-	57924	-	-
Others	-	-	-	-	-	1452	1452	1448	-	1448	1448
Temp. [°C]	200	200	1000	1000	1000	35	592	38	46	46	1000
Pressure [bar]	20	20	20	20	20	21	19	19	7	7	7

A7 Excel models

This appendix describes the Excel model used to calculate the greenhouse gas emissions for the extended PtP concept. The example shown here is taken from the ATR3 case.

1. Import stream data from Hysys

The stream data from Hysys is imported by use of a Hysys-Excel link. An overview of the screen is given in Figure A7.1.



	D	E	F	G	I	J	L
2	*** Overall ***						
3	**Stream Name**		**Methane**	**Product**	**Steam**	**gasifier**	**rec gas**
4	**Vapour Fraction**		1	1	1	1	0,78646
5	**Temperature**	*C*	200	996,0242	212,427	35	42,5
6	**Pressure**	*kPa*	2000	2000	2000	2100	350
7	**Flow**	*kgmole/h*	1900	9480,054	3800	3695,592	776,2156
8	**Mass Flow**	*kg/h*	30481,51	141498	68457,4	79309,02	27896,78
16	**Mole Fraction**	*Methane*	1	0,001052	0	0	0
17		*Ethane*	0	7,42E-49	0	0	0
23		*Methanol*	0	7,42E-49	0	0	0
25		*H2O*	0	0,405974	1	0	0,233532
26		*CO*	0	0,123281	0	0,375502	0,003292
27		*CO2*	0	0,076088	0	0,221888	0,71663
28		*Oxygen*	0	1,16E-16	0	0	0
29		*Nitrogen*	0	7,42E-49	0	0,014056	0,000294
30		*Hydrogen*	0	0,393606	0	0,388554	0,046251
33		*COS*	0	7,42E-49	0	0	0
34		*H2S*	0	7,42E-49	0	0	0
35	*****LCA Specific Info*****						
36	**Input to Unit Op**		ATR	X-100	ATR	SYNGASMIX	
37	**Output from UnitOp**			ATR			CO2 remov
38	**Flwsht Feed/Product Stream**		TRUE	FALSE	TRUE	TRUE	TRUE
39							
40							
41							

Figure A7.1: Imported stream data from Hysys

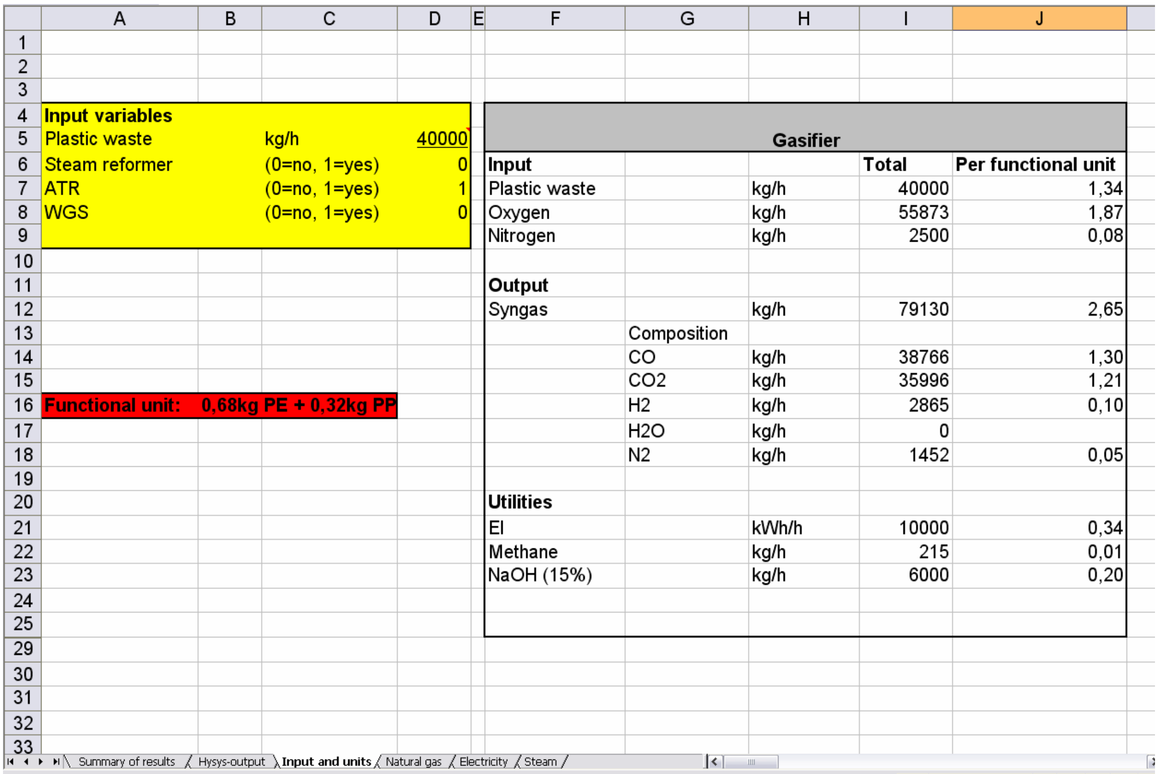
The “LCA specific info” gives information of whether the stream is an intermediate, input or output from a unit operation. This is utilized to establish mass flows to the various unit operations.

2. Numbers transferred to “Inputs and units”

Next step is to establish the mass flows in and out of the unit operations based on the Hysys outputs in step 1. This is done by looking up numbers for each unit by use of the LCA specific info and if-sentences, an example of an if-sentence used for the methane flow into the ATR reactor is the following (B6 contains the molecular weight of methane): =SUM(IF(F38:CC38;IF(F36:CC36="ATR";F16:CC16*F7:CC7;0);0))*B6

3. Summary of input and output for each unit

The numbers from step 2 are then combined with the process information given directly in the Excel model. Information of what is included in the Hysys models are given in Appendix 6. In Figure A7.2 part of the screen showing the mass and energy flows are given. The Input variables are set by the user, as well as the functional unit. The gasifier unit shows an example of how the mass flows and utilities are represented; all unit operations are given in an analogous box.



Input variables		
Plastic waste	kg/h	40000
Steam reformer	(0=no, 1=yes)	0
ATR	(0=no, 1=yes)	1
WGS	(0=no, 1=yes)	0

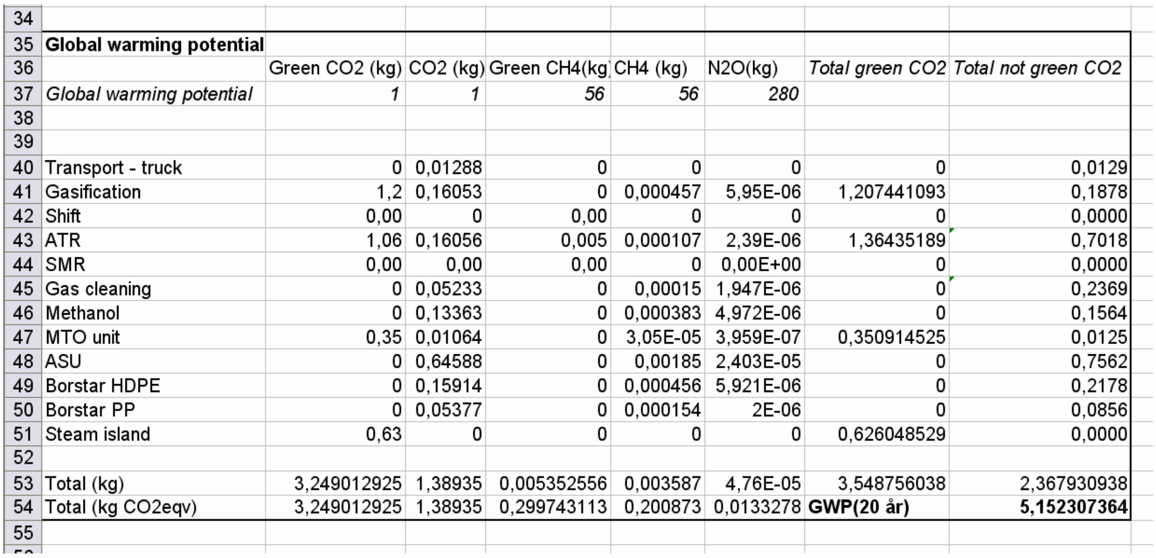
Functional unit: 0,68kg PE + 0,32kg PP

Gasifier				
Input			**Total**	**Per functional unit**
Plastic waste		kg/h	40000	1,34
Oxygen		kg/h	55873	1,87
Nitrogen		kg/h	2500	0,08
Output				
Syngas		kg/h	79130	2,65
	Composition			
	CO	kg/h	38766	1,30
	CO2	kg/h	35996	1,21
	H2	kg/h	2865	0,10
	H2O	kg/h	0	
	N2	kg/h	1452	0,05
Utilities				
El		kWh/h	10000	0,34
Methane		kg/h	215	0,01
NaOH (15%)		kg/h	6000	0,20

Figure A7.2: Mass flows and utilities of the unit operations

4. Global warming potential for each unit

In this step, the global warming potential of each unit is divided into green and not green CO_2 and then summarized. The category “green” correspond to renewable emissions (originate from the waste material), whereas “not green” correspond to non-renewable emissions (all other emissions). The summary is shown in Figure A7.3. In order to calculate the CO_2 equivalents from electricity, natural gas use and steam production, the numbers are multiplied with the global greenhouse gas emissions from production of electricity and natural gas, respectively. The overview of the emissions from production is given in separate tabs in the spreadsheet, natural gas, electricity and steam, respectively (Figure A7.2).

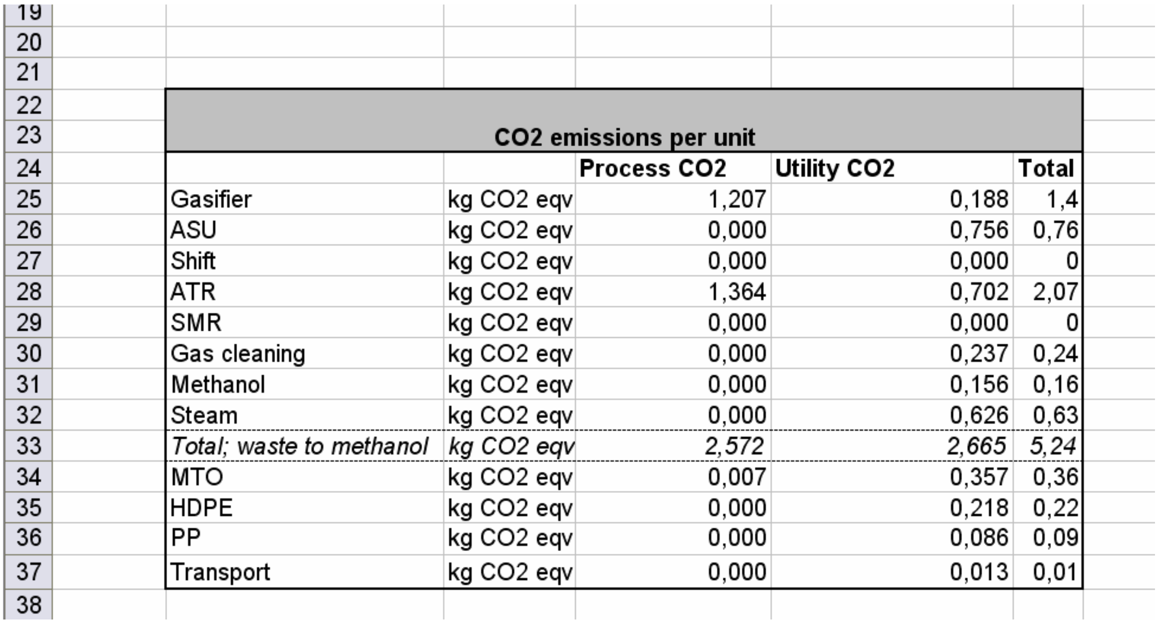


Global warming potential							
	Green CO2 (kg)	CO2 (kg)	Green CH4(kg	CH4 (kg)	N2O(kg)	*Total green CO2*	*Total not green CO2*
Global warming potential	*1*	*1*	*56*	*56*	*280*		
Transport - truck	0	0,01288	0	0	0	0	0,0129
Gasification	1,2	0,16053	0	0,000457	5,95E-06	1,207441093	0,1878
Shift	0,00	0	0,00	0	0	0	0,0000
ATR	1,06	0,16056	0,005	0,000107	2,39E-06	1,36435189	0,7018
SMR	0,00	0,00	0,00	0	0,00E+00	0	0,0000
Gas cleaning	0	0,05233	0	0,00015	1,947E-06	0	0,2369
Methanol	0	0,13363	0	0,000383	4,972E-06	0	0,1564
MTO unit	0,35	0,01064	0	3,05E-05	3,959E-07	0,350914525	0,0125
ASU	0	0,64588	0	0,00185	2,403E-05	0	0,7562
Borstar HDPE	0	0,15914	0	0,000456	5,921E-06	0	0,2178
Borstar PP	0	0,05377	0	0,000154	2E-06	0	0,0856
Steam island	0,63	0	0	0	0	0,626048529	0,0000
Total (kg)	3,249012925	1,38935	0,005352556	0,003587	4,76E-05	3,548756038	2,367930938
Total (kg CO2eqv)	3,249012925	1,38935	0,299743113	0,200873	0,0133278	**GWP(20 år)**	**5,152307364**

Figure A7.3: Summary of the global warming calculations

5. Summary of results

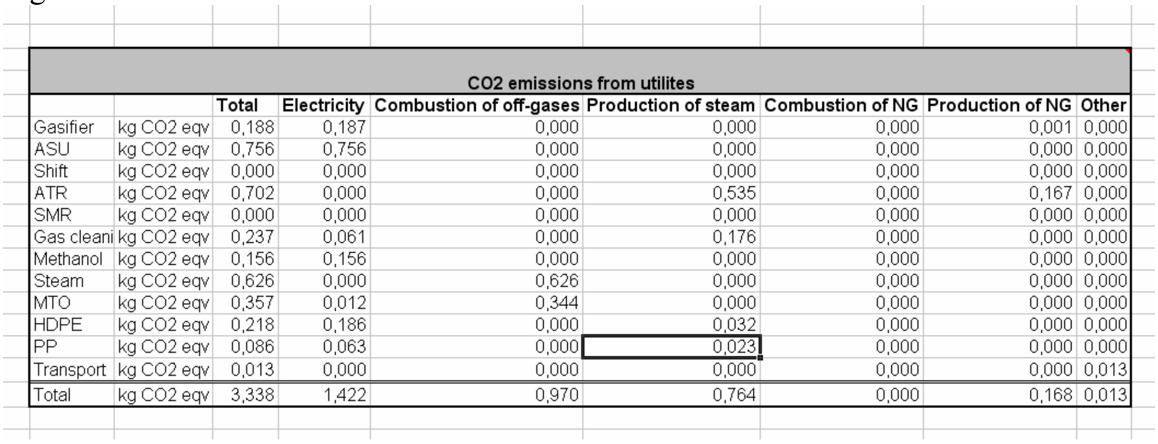
In the last step, the CO_2 equivalents per unit are then summarized for both process and utility CO_2. The definition of utility and process waste is used to assign the emissions to the correct waste type. The summary is given in Figure A7.4.



CO2 emissions per unit				
		Process CO2	**Utility CO2**	**Total**
Gasifier	kg CO2 eqv	1,207	0,188	1,4
ASU	kg CO2 eqv	0,000	0,756	0,76
Shift	kg CO2 eqv	0,000	0,000	0
ATR	kg CO2 eqv	1,364	0,702	2,07
SMR	kg CO2 eqv	0,000	0,000	0
Gas cleaning	kg CO2 eqv	0,000	0,237	0,24
Methanol	kg CO2 eqv	0,000	0,156	0,16
Steam	kg CO2 eqv	0,000	0,626	0,63
Total; waste to methanol	*kg CO2 eqv*	*2,572*	*2,665*	*5,24*
MTO	kg CO2 eqv	0,007	0,357	0,36
HDPE	kg CO2 eqv	0,000	0,218	0,22
PP	kg CO2 eqv	0,000	0,086	0,09
Transport	kg CO2 eqv	0,000	0,013	0,01

Figure A7.4: Summary of the CO_2 equivalents per unit, divided into process and utility waste

Finally the utility waste is broken down into the various contributions, this is shown in Figure A7.5.



CO2 emissions from utilites

		Total	Electricity	Combustion of off-gases	Production of steam	Combustion of NG	Production of NG	Other
Gasifier	kg CO2 eqv	0,188	0,187	0,000	0,000	0,000	0,001	0,000
ASU	kg CO2 eqv	0,756	0,756	0,000	0,000	0,000	0,000	0,000
Shift	kg CO2 eqv	0,000	0,000	0,000	0,000	0,000	0,000	0,000
ATR	kg CO2 eqv	0,702	0,000	0,000	0,535	0,000	0,167	0,000
SMR	kg CO2 eqv	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Gas cleani	kg CO2 eqv	0,237	0,061	0,000	0,176	0,000	0,000	0,000
Methanol	kg CO2 eqv	0,156	0,156	0,000	0,000	0,000	0,000	0,000
Steam	kg CO2 eqv	0,626	0,000	0,626	0,000	0,000	0,000	0,000
MTO	kg CO2 eqv	0,357	0,012	0,344	0,000	0,000	0,000	0,000
HDPE	kg CO2 eqv	0,218	0,186	0,000	0,032	0,000	0,000	0,000
PP	kg CO2 eqv	0,086	0,063	0,000	0,023	0,000	0,000	0,000
Transport	kg CO2 eqv	0,013	0,000	0,000	0,000	0,000	0,000	0,013
Total	kg CO2 eqv	3,338	1,422	0,970	0,764	0,000	0,168	0,013

Figure A7.5: CO_2 equivalents from the various utilities

A8 LCA and Process Integration

ATR3 case

The main units in the ATR3 case are the gasifier, ATR, gas cleaning, methanol unit, MTO and plastic production. The gasifier, ATR and the methanol unit are included in the process integration study. The MTO unit is self sufficient with respect to heating and power required and no excess heat is available. The other units are of course included in the LCA.

Gasifier

The gasifier is the same as used in the process integration study in Section 6.3., and has a heat surplus of 134.7 MW. From the heat available, 47.4 MW of steam can be produced at 180°C. In addition to the 10 MW of power needed in the gasifier, 40 MW of electricity is needed in the ASU and nitrogen liquefaction.

Methanol unit

The methanol unit has changed from the case in Section 6.3, as more syngas is processed in the ATR3 case. The process train is, however, the same. The hot and cold streams in the methanol unit are given in Table A8.1.

Table A8.1: Hot and cold streams in the methanol unit, ATR3 case

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Syngas	Hot	Sensible	325	215	7.5
2	Methanol	Hot	Sensible	250	125	27.4
3	Methanol	Hot	Sensible	125	80	8.5
4	Methanol	Hot	Sensible	80	40	6.2
5	Steam	Hot	Latent	250	250	65.4
6	Syngas	Cold	Sensible	38	82	5.3

Compared to the methanol process in Appendix 3, Figure A3.5, stream 6 is added. Stream 6 is heating of the syngas before compression in K-100.

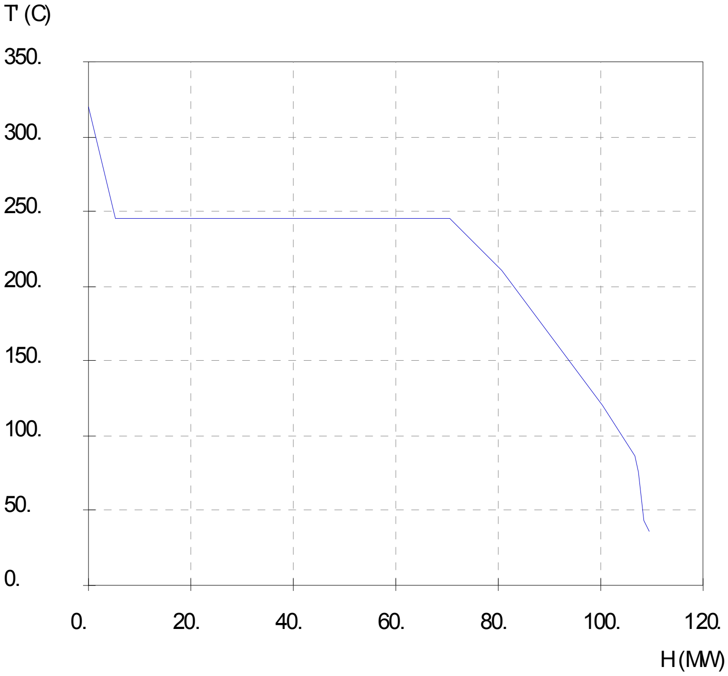


Figure A8.1: GCC of the methanol unit in the ATR3 case

The GCC of the methanol unit is given in Figure A8.1. 65.4 MW of steam is available from the water jacket surrounding the reactor (stream 5). In addition, there are heat available from the surplus of heat in the methanol unit, 16.3 MW of steam can be produced at 200°C or 20.7 MW at 180°C. Cooling water required for the low temperature heat is 28 MW if the steam level is 200°C, or 23.6 MW if the steam level is 180°C.

Power required in the compressor: 19.83 MW

Heat available from combustion of the purge gasses (again heating value is used, as in Appendix 3): 41.5 MW
(The reason for the large increase in heat available compared to the reference case in Section 6.3 is the higher hydrogen content in the syngas)

<u>ATR unit</u>
The hot and cold streams in the ATR unit are given in Figure A8.2 and Table A8.2. Methane (stream 2), oxygen (stream 1) and steam (stream 4 and 5) are heated by the product stream (stream 3). No heat is added or removed from the reactor. Production of saturated steam is divided into heating of water to the boiling temperature (stream 4) and evaporation (stream 5).

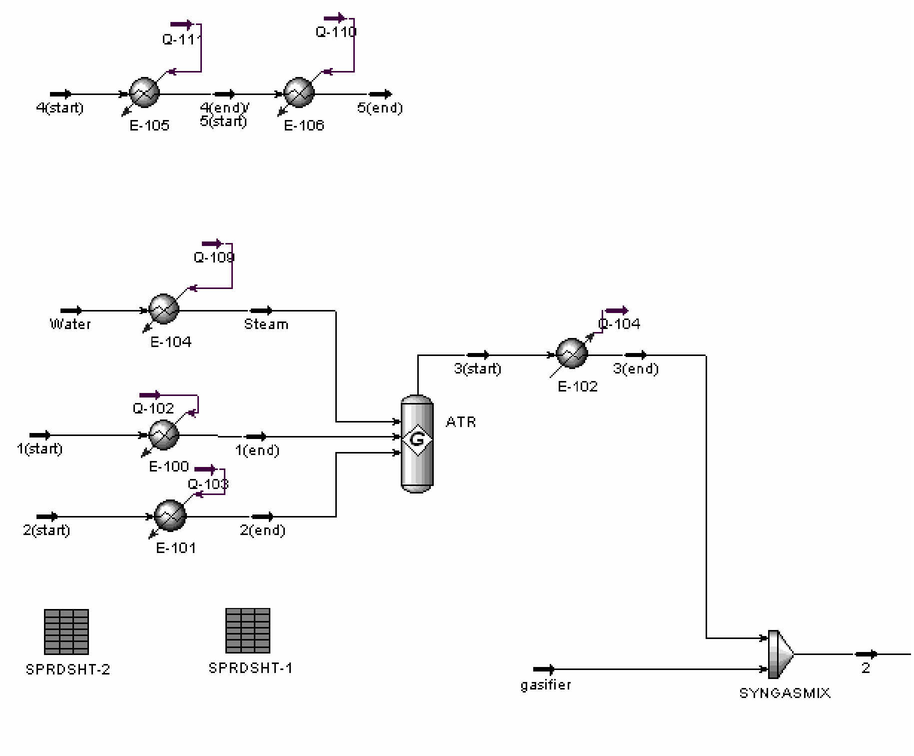


Figure A8.2: Hysys model of the ATR unit.

Table A8.2: Hot and cold streams in the ATR unit

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Oxygen	Cold	Sensible	25	200	2.0
2	Methane	Cold	Sensible	25	200	3.8
3	Syngas	Hot	Sensible	996	175	78.2
4	Steam	Cold	Sensible	25	212.4	15.1
5	Steam	Cold	Latent	212.4	212.4	36.8

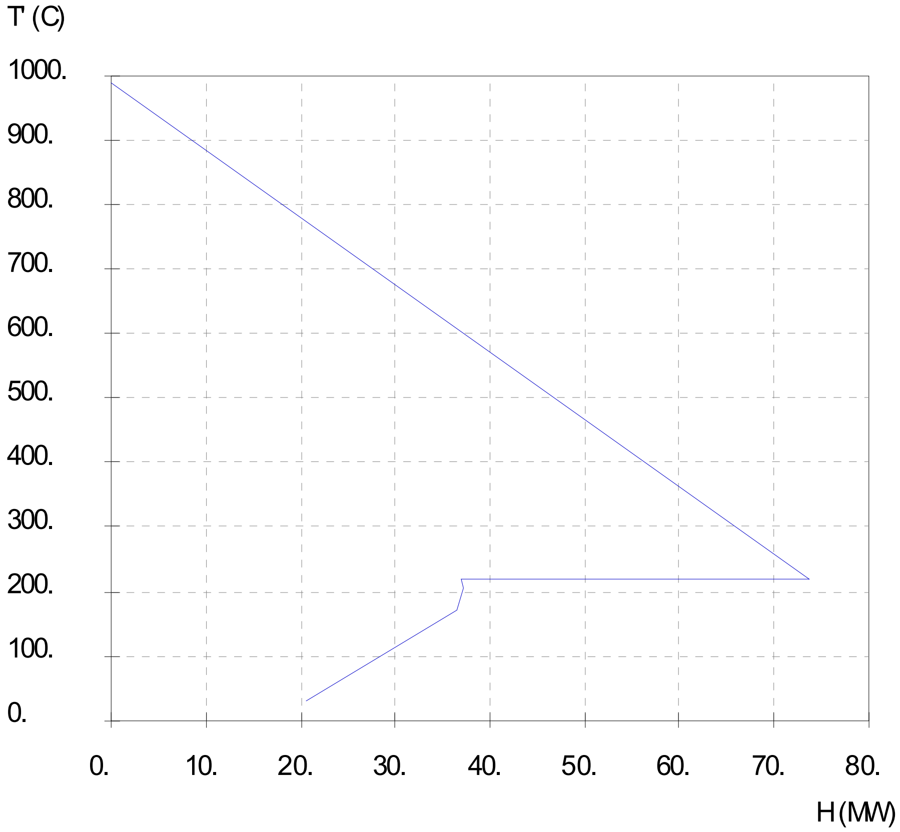


Figure A8.3: The grand composite curve of the ATR unit

The GCC of the ATR unit is given in Figure A8.3. In the ATR, 20.5 MW of heat can be exported as saturated steam at 100 bars and 311°C. No cooling water is required. In addition the electricity needed in the ASU for O_2-production is 17.52 MW

Process integration between the units in the ATR3 case

The power required as well as hot and cold streams not covered by process to process integration within each unit are given in Table A8.3.

Table A8.3: Summary of the ATR3 case, after process integration within the units

Process [MW]	Surplus heat >200°C	Surplus heat Total	Heat deficit (cold streams)	Power (required)	Surplus heat (steam/ off-gases)
Gasification	0	134.7	0	10	0
ATR	20.5	20.5	0	17.5	0
Methanol	16.3	44.3	0	19.8	65.4+41.5

From Table A8.3, it can be seen that there is no heat deficit in the system, and the available heat can be used for power production to cover the demand in the methanol unit, ATR and the gasification unit. All the surplus steam and off-gases are sent to the central utility plant that produces power in a steam turbine with superheat and reheat of the steam. In addition to the units included in the process integration study, power is needed in the gas cleaning section as well as in the plastic production.

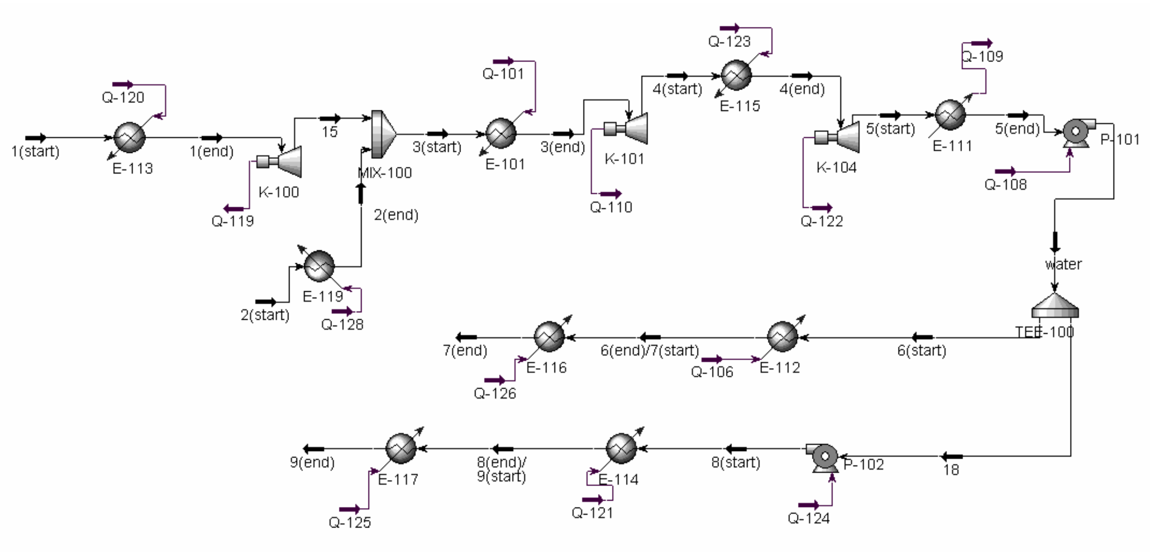


Figure A8.4: Power production in the ATR3 case

Table A8.4: Heating and cooling required in the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Cold	Sensible	310.7	400.0	6.3
2	Cold	Sensible	225.1	346.0	9.2
3	Cold	Sensible	346.0	400.0	6.1
4	Cold	Sensible	165.5	236.1	7.1
5	Hot	Sensible	32.50	32.49	12.4
6	Cold	Sensible	32.8	170.0	19.8
7	Cold	Sensible	170.0	225.1	8.9
8	Cold	Sensible	33.5	170.0	9.3
9	Cold	Sensible	170.0	250.4	6.4

The Hysys model of the power production is given in Figure A8.4. Power is produced in the three turbines, yielding a net production of 43.1 MW electricity (when the power required in the pumps is covered). Stream 1 is the steam at 100 bars available from the ATR (cooling of product stream) which is superheated to 400°C and then expanded to 25.5 bars in the turbine K-100. At this stage the steam from the methanol unit at 25.5 bars (water jacket) is added after superheating in E-119. After mixing the two streams, the steam is heated to 400°C before expansion from 25.5 bars to 2 bars in turbine K-101. The resulting steam (Stream 4) is then heated before the final expansion to 0.05 bars. The steam is condensed in E-111, before it is pumped to 25.5 bars in P-101 and further to 100 bars in P-102. Streams 6 and 7 are heated to the boiling temperature of 225.1°C (25.5 bars), whereas streams 8 and 9 are heated to 310.7°C (100 bars). The hot and cold streams are given in Table A8.4, whereas the grand composite curve is given in Figure A8.5.

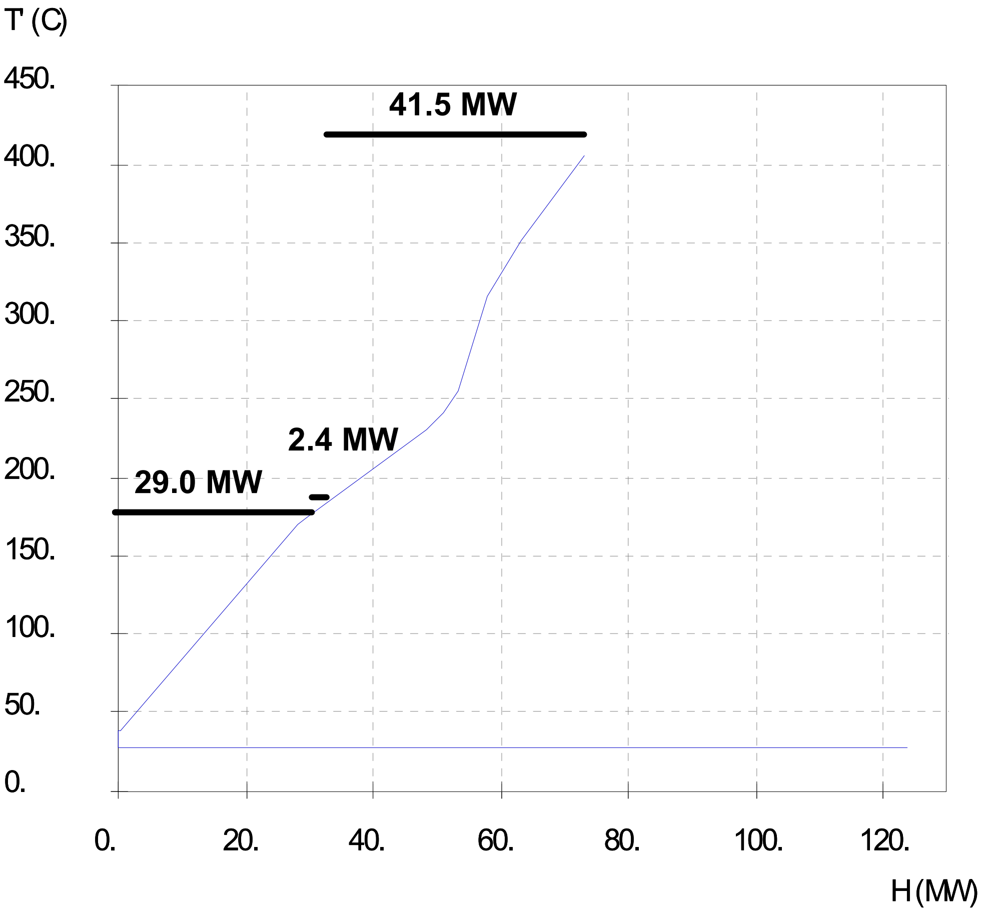


Figure A8.5: Steam levels used to cover the heat demand in the power production

The GCC, Figure A8.5, shows a cooling demand of 123 MW below pinch. Above pinch, there is a heating demand which is covered by steam at three different levels. The steam levels in the figure, starting from the lowest, are 29.0 MW of steam from the gasifier (180°C), 2.4 MW of steam from the methanol process (200°C), and finally 41.5 MW available from combustion of off-gases in the methanol unit (1000°C). The off-gases should have been drawn at 1000°C, but for the illustration it is given at a lower temperature level in Figure A8.5.

The summary of the utilities needed in the processes after production of power and steam in the central utility plant is given in Table A8.5.

Table A8.5: Summary of the utilities needed when a central utility plant is used

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	105.7	0	1.4	0
ATR	0	0	0	1.4	0
Methanol	13.7	41.7	0	1.4	0

SMR3 case

The main units in the SMR3 case are the gasifier, SMR, gas cleaning, methanol unit, MTO and plastic production. As for the ATR3 case, the gasifier, reformer and the methanol unit are included in the process integration study. The MTO unit is self sufficient with respect to heating and power required, no excess heat is available. The other units are of course included in the LCA.

Gasifier

Again, the gasifier is not changed form the process integration study in Section 6.3., and has a heat surplus of 134.7 MW. From the heat available, 47.4 MW of steam can be produced at 180°C. In addition to the 10 MW of power needed in the gasifier, 40 MW of electricity is needed in the ASU and nitrogen liquefaction.

Methanol unit

The methanol unit has changed from the case in Section 6.3, as more syngas is processed in the SMR3 case. The process train is, however, the same. The hot and cold streams in the methanol unit are given in Table A8.6.

Table A8.6: Hot and cold streams in the methanol unit, SMR3 case

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Syngas	Hot	Sensible	344	215	7.0
2	Methanol	Hot	Sensible	250	125	22.5
3	Methanol	Hot	Sensible	125	80	6.5
4	Methanol	Hot	Sensible	80	40	4.8
5	Steam	Hot	Latent	250	250	50.7
6	Syngas	Cold	Sensible	38	93.4	6.0

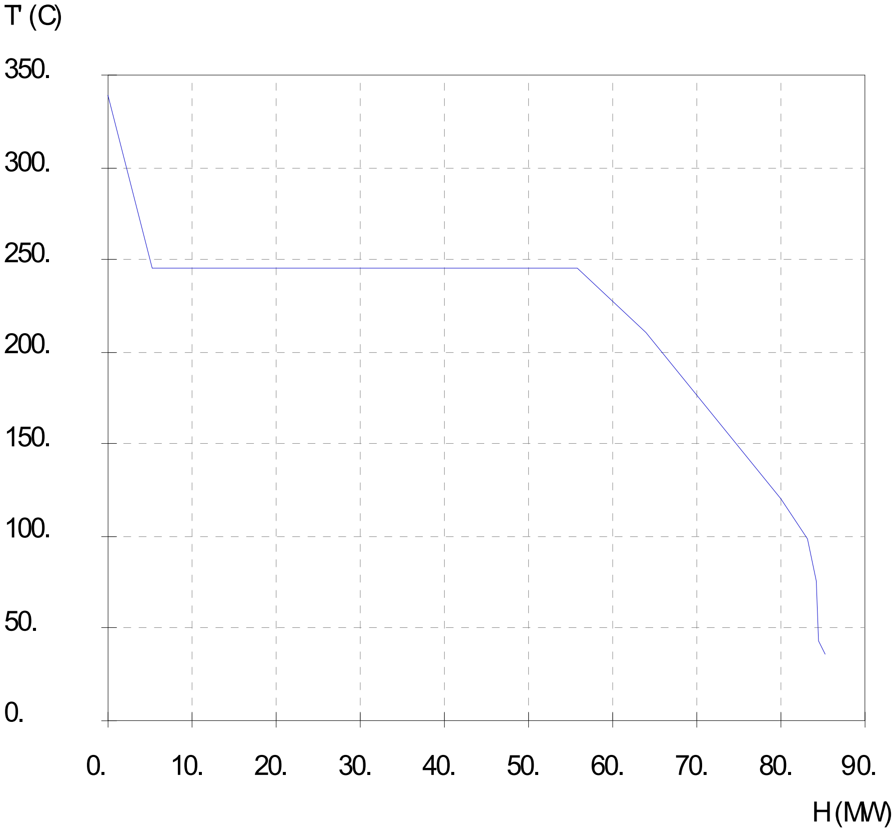


Figure A8.6: GCC of the methanol unit in the SMR3 case

The GCC of the methanol unit is given in Figure A8.6. 50.7 MW of steam is available from the water jacket surrounding the reactor (stream 5). In addition, there is a surplus of heat in the methanol unit where14.6 MW of steam can be produced at 200°C or 17.8 MW at 180°C. Cooling water required for the low temperature heat is 20.2 MW if the steam level is 200°C, or 17.0 MW if the steam level is 180°C.

Power required in the compressors: 15.87 MW

Heat available from combustion of the purge gasses (heating value): 31 MW

<u>SMR unit</u>

The hot and cold streams in the SMR unit are given in Figure A8.7 and Table A8.7. Methane (stream 1) and steam (stream 3, 4 and 5) are heated by the product stream (stream 2). Heat is added to the reactor by combustion of methane in the Gibbs reactor “Combustion to heat”.

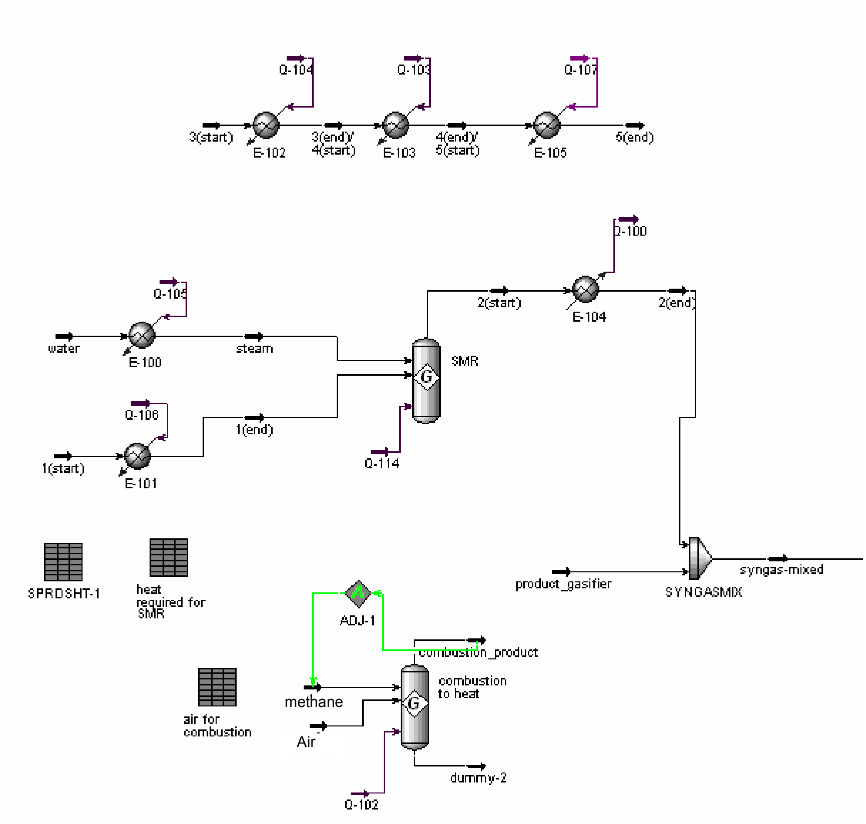


Figure A8.7: Hysys model of the SMR unit.

Table A8.7: Hot and cold streams in the SMR unit

Stream	Composition	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Methane	Cold	Sensible	25	315	2.9
2	Syngas	Hot	Sensible	1000	156	38.3
3	Steam	Cold	Sensible	25	212.4	9.5
4	Steam	Cold	Latent	212.4	212.4	23.2
5	Steam	Cold	Sensible	212.4	315	2.6

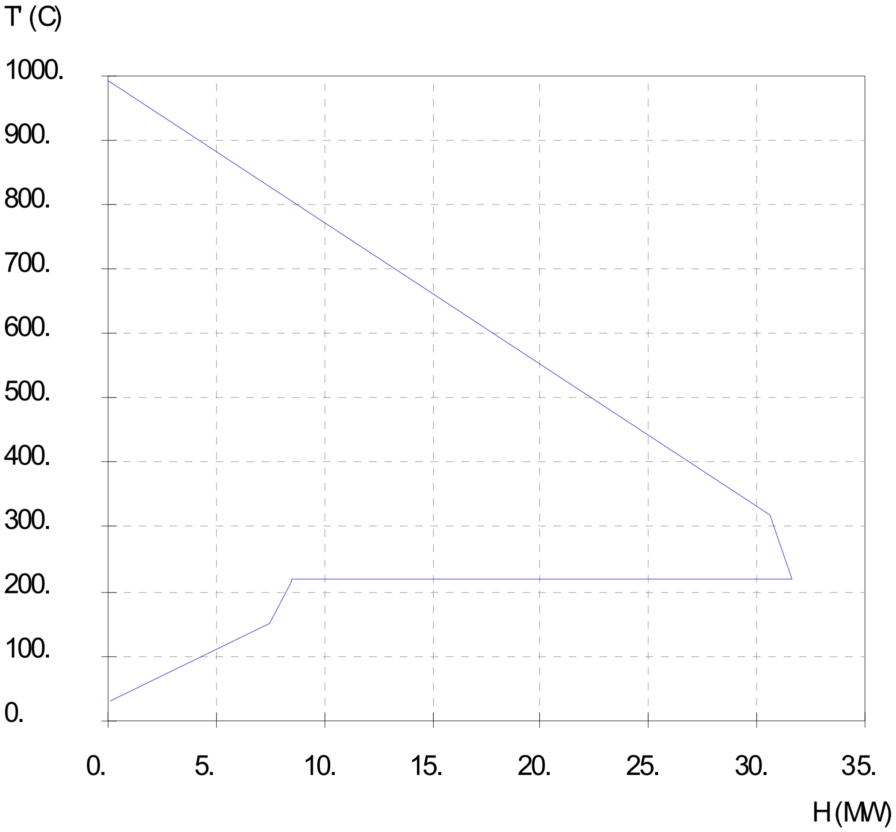


Figure A8.8: The grand composite curve of the SMR unit

The GCC of the SMR unit is constructed in Figure A8.8. The heat available in the product stream is used for production of steam and preheating of the reactants, resulting in no excess heat. In addition, 76.9 MW of heat is required for the reactor (at 1000°C).

Process integration between the units in the SMR3 case

The power required as well as hot and cold streams not covered by process to process integration within each unit are given in Table A8.8.

Table A8.8: Summary of the SMR3 case, after process integration within the units

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	76.9	0	0
Methanol	14.6	34.8	0	15.9	50.7+31.0

From Table A8.8, it can be seen that heat is required in the SMR. In addition there is a requirement for power in the gasifier and the methanol unit. All the surplus steam and off-gases are sent to the central utility plant, which produces steam and power in a steam turbine with superheat and reheat of the steam. In the SMR3 case there will be a trade off between covering the heat demand or production of power.

Only the 31 MW of heat available from combustion of off-gases is warm enough to heat the SMR reactor, the off-gases will then be sent to the SMR and are combusted together with methane. If all the high temperature heat available from the off-gases is used for heating the SMR, no heat is available for superheat and reheat of the steam in the power production. Without superheat of the steam, only small amounts of power can be produced. The utilities needed, heat available and total CO_2 emission from this approach are given in Table A8.9.

Table A8.9: Summary of the SMR3 case, with heating of the SMR reactor

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	45.9	0	0
Methanol	14.6	34.8	0	15.9	50.7
Total CO_2-eqv emitted from the SMR3 with this approach					**5.35**

An alternative configuration is to use part of the steam available for preheat of the steam and methane used in the SMR, the product gas can then be used for heating of the streams at high temperatures. If the reactants (steam and methane) are heated to the reaction temperature (1000°C), 47.6 MW heat is needed to cover the heat of reaction within the reactor. This reduces the need for methane in the combustion. The streams in the SMR unit, by use of this approach are given in Table A8.10. As the product gas is 1000°C, it is only capable of heating the reactants to 990°C, leaving a heating demand within the reactor of 48.1 MW. It is, however, not possible with to today's technology to carry out process to process heat exchange at such high temperatures, and the following two examples (Table A8.11 and A8.13) are to be seen as a purely theoretical approach.

Table A8.10: Hot and cold streams in the SMR unit, with heating of the reactants

Stream	**Composition**	**Description**	**Heat type**	**T_1 [°C]**	**T_2 [°C]**	**H [MW]**
1	Methane	Cold	Sensible	25	990	13.1
2	Syngas	Hot	Sensible	1000	156	38.3
3	Steam	Cold	Sensible	25	212.4	9.5
4	Steam	Cold	Latent	212.4	212.4	23.2
5	Steam	Cold	Sensible	212.4	990	38.3

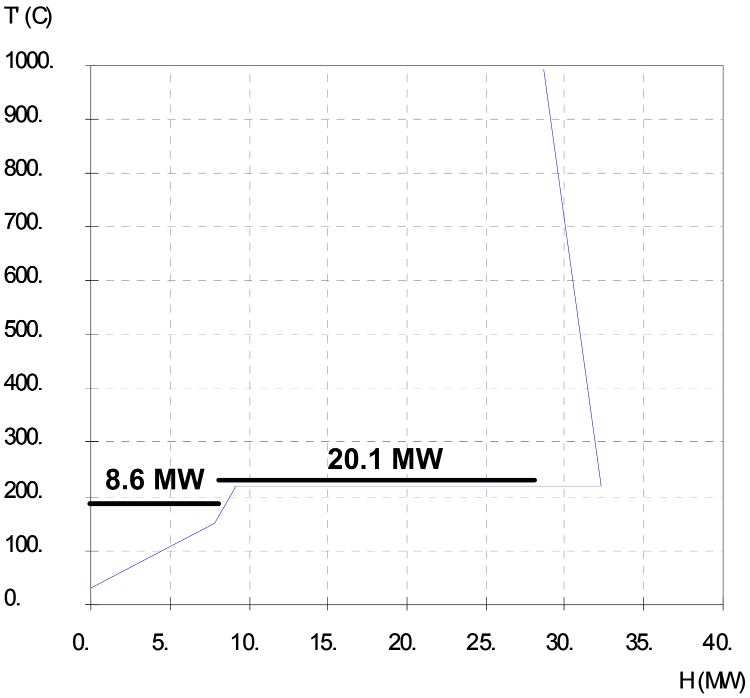


Figure A8.9: The GCC of the SMR unit with preheat of the reactants to 990°C

In Figure A8.9 the GCC of the SMR3 case with heating of the reactants to 990°C are shown. The product gas is used for heating at high temperatures, whereas 20.1 MW of steam from the methanol water jacket (225.1°C) and 8.6 MW of steam from cooling of the methanol process stream (200°C) are used to cover the remaining heating requirement. The steam and off-gases left, can then either be used in power production or in heating of the reactor. In the case where the off-gases are used for heating of the reactor, no power is produced, but only 17.1 MW of methane is needed for heating of the reactor. The approach is summarized in Table A8.11.

Table A8.11: Summary of the SMR3 case, with heating of reactants and the SMR reactor (theoretical)

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	134.7	0	10	0
SMR	0	0	17.1	0	0
Methanol	6.0	26.2	0	15.9	30.6
Total CO_2-eqv emitted from the SMR3 with this approach					**5.08**

An alternative approach is to utilize the remaining heat, after heating of the reactants, for power production. Power production is done in a central utility plant by expansion of steam in a three stage steam turbine. The configuration is given in Figure A8.10.

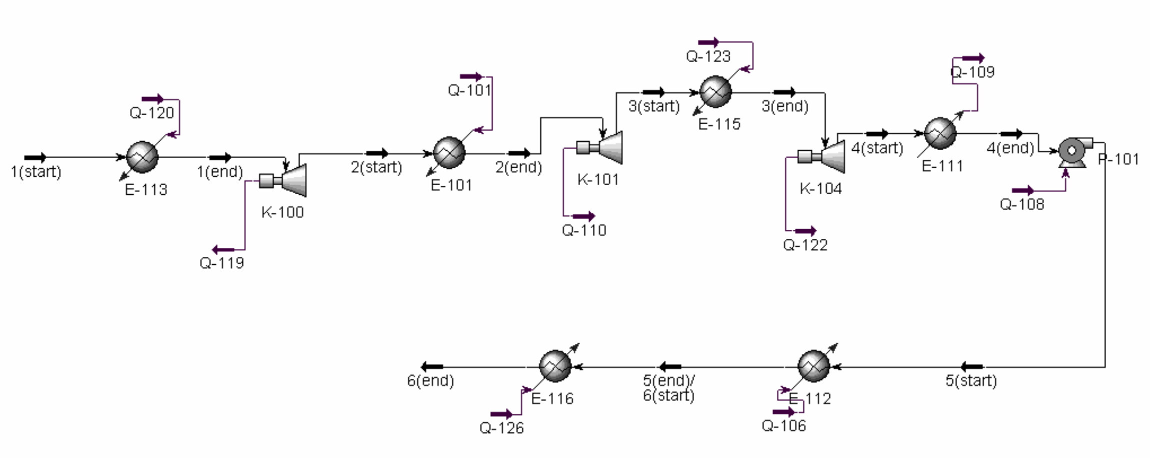


Figure A8.10: Power production in the SMR3 case

Power is produced in the three turbines, yielding a net production of 18.7 MW electricity (when the power required in the pump is covered). Stream 1 is the steam at 25.5 bars available from the methanol reactor (water jacket) which is superheated to 450°C and then expanded to 10 bars in the turbine K-100. The steam is then reheated to 450°C, before expansion in turbine K-101 from 10 bars to 2 bars. The resulting steam (Stream 3) is then heated before the final expansion to 0.05 bars. The steam is condensed in E-111 before being pumped to 25.5 bars in P-101. Streams 5 and 6 are heated to the boiling temperature of 225.1°C (25.5 bars). The hot and cold streams in the power production are given in Table A8.12, whereas the heating demand and how it is covered are shown in Figure A8.11.

Table A8.12: Heating and cooling required in the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Cold	Sensible	225.1	450.0	8.0
2	Cold	Sensible	342.8	450.0	3.7
3	Cold	Sensible	282.5	450.0	5.6
4	Hot	Sensible	139.2	32.5	42.5
5	Cold	Sensible	32.8	170.0	9.2
6	Cold	Sensible	170.0	225.1	4.2

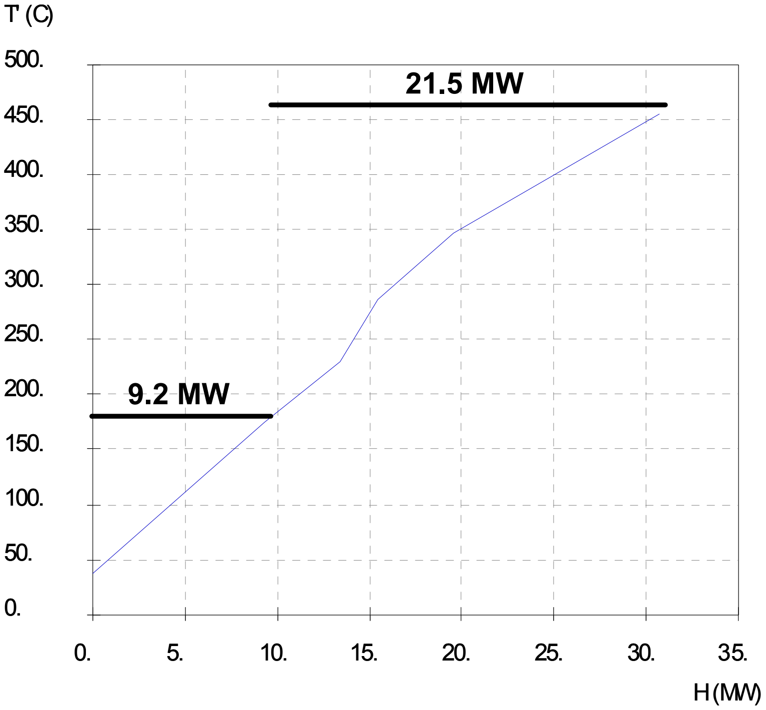


Figure A8.11: Steam levels used to cover the heat demand in the power production

The GCC, Figure A8.11, shows the steam levels used for superheat and reheat in the power production, 9.2 MW of steam from the gasifier (180°C) and 21.5 MW available from combustion of off-gases in the methanol unit (1000°C). The off-gases should have been drawn at 1000°C, but for the illustration it is given at a lower temperature level in Figure A8.11. In addition there is a cooling demand of 42.5 MW, stream 4.

There is 8.54 MW of heat available from the off-gases, after the power generation. The heat will be used for heating of the SMR reactor. There is not enough power to cover the demand in the gasifier and the methanol unit, and the remaining 7.2 MW of power is divided evenly among the two units. The summary of this approach, heating of reactants and power production, is given in Table A8.13.

Table A8.13: Summary of the SMR3 case, with heating of reactants and SMR reactor, and power production (theoretical)

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	125.5	0	3.6	0
SMR	0	0	39.6	0	0
Methanol	6.0	26.2	0	3.6	0
Utility	0	42.5	0	0	0
Total CO_2-eqv emitted from the SMR3 with this approach					**5.06**

The last approach is production of power from all the available steam and off-gases, heating of the SMR is then done by combustion of methane only. The configuration used for power production is given in Figure A8.10.

Table A8.14: Heating and cooling required in the power production

Stream	Description	Heat type	T_1 [°C]	T_2 [°C]	H [MW]
1	Cold	Sensible	225.1	400.0	10.3
2	Cold	Sensible	297.6	400.0	5.8
3	Cold	Sensible	241.6	388.0	8.0
4	Hot	Sensible	99.51	32.49	68.4
5	Cold	Sensible	32.8	170.0	15.3
6	Cold	Sensible	170.0	225.1	6.9

Power is produced in the three turbines, yielding a net production of 28.6 MW electricity (when the power required in the pump is covered). Stream 1 is the steam at 25.5 bars available from the methanol (water jacket) which is superheated to 400°C, and then expanded to 10 bars in the turbine K-100. The steam is then reheated to 400°C, before expansion in turbine K-101, from 10 bars to 2 bars. The product steam (Stream 3) is then heated, before the final expansion to 0.05 bars. The steam is condensed in E-111, before it is pumped to 25.5 bars in P-101. Streams 5 and 6 are heated to the boiling temperature of 225.1°C (25.5 bars). The hot and cold streams are given in Table A8.14, whereas the grand composite curve with the steam levels used in the superheat and reheat is given in Figure A8.12.

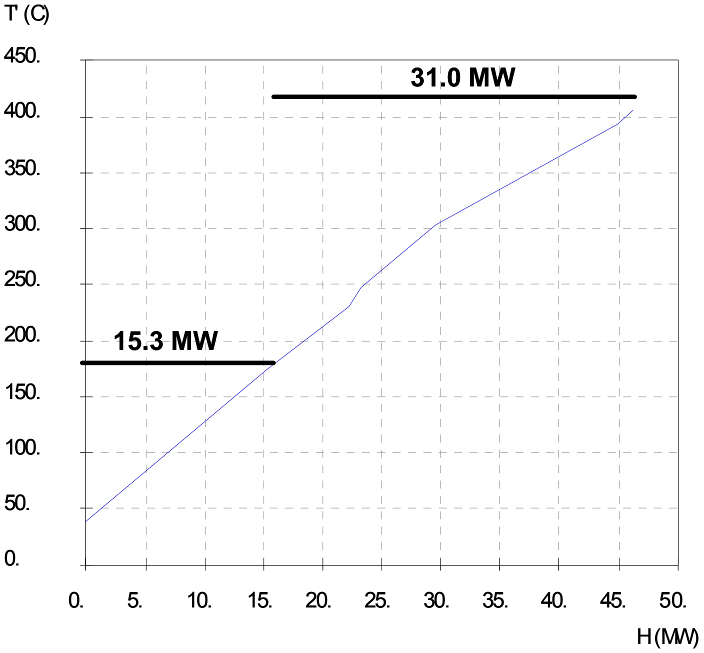


Figure A8.12: Steam levels used to cover the heat demand in the power production

The GCC, Figure A8.12, shows the steam levels used for superheat and reheat in the power production, starting from the lowest, 15.3 MW of steam from the gasifier (180°C) and 31.0 MW available from combustion of off-gases in the methanol unit (1000°C). The off-gases should have been drawn at 1000°C, but for the illustration it is given at a lower temperature level in Figure A8.12. In addition there is a cooling demand of 68.4

MW. There is a surplus of power from the system (2.7 MW), which can be utilized in the gas cleaning section, ASU or plastic production. The power has been utilized in the system prior to the calculation of total CO_2-eqv. The findings are summarized in Table A8.15.

Table A8.15: Summary of the SMR3 case, with power production

Process [MW]	**Surplus heat >200°C**	**Surplus heat Total**	**Heat deficit (cold streams)**	**Power (required)**	**Surplus heat (steam/ off-gases)**
Gasification	0	119.4	0	0	0
SMR	0	0	76.9	0	0
Methanol	14.6	33.5	0	0	0
Utility	0	67.2	0	0	0
Total CO_2-eqv emitted from the SMR3 with this approach					**5.24**

A9 Comparison of LCA results with SimaPro results

In Table A9.1 the LCA results for the PtP reference case, ATR3 and SMR3 are compared to results from the SimaPro 7.0 Educational software. Each of the three scenarios has been modeled in SimaPro, using the mass flows calculated in the Excel spreadsheet.

The characterization method used in SimaPro is the IPCC 2001 GWP 100a, which gives the CO_2 equivalents for a 100 years perspective. The Ecoinvent database (2004) is used as the data source. The electricity production used is “Electricity, medium voltage, production UCTE at grid”, whereas the natural gas is “Natural gas to UCPTE S”.

Table A9.1: CO_2-equivalents in the PtP, ATR and SMR case, calculated in SimaPro and the Excel model

		Total CO_2-equivalents [kg]										
		Gasifier	**ASU**	**WGS**	**ATR**	**SMR**	**Gas cleaning**	**Methanol**	**Steam (utility)**	**MTO**	**Plastic**	**Total**
PtP (ref)	SimaPro	3.68	1.0	1.75	-	-	0.25	0.64		0.35	0.25	**7.92**
	Process	3.23	0	1.58	-	-	0	0	0	0	0	**8.21**
	Utility	0.50	1.15	0.17	-	-	0.25	0.17	0.50	0.35	0.30	
ATR (3)	SimaPro	1.37	0.66	-	2.16	-	0.24	0.75		0.36	0.25	**5.79**
	Process	1.21	0	-	1.36	-	0	0	0	0	0	**5.91**
	Utility	0.19	0.76	-	0.70	-	0.24	0.16	0.63	0.36	0.30	
SMR (3)	SimaPro	1.78	0.48	-	-	2.22	0.24	0.69		0.36	0.25	**6.02**
	Process	1.56	0	-	-	0.99	0	0	0	0	0	**6.39**
	Utility	0.24	0.56	-	-	1.48	0.19	0.16	0.55	0.36	0.30	

The results from the SimaPro software are given as aggregated numbers for both process and utility waste, whereas the results for the LCA carried out in Excel are divided into utility waste and process waste. For the SimaPro results, the methanol unit and steam (utility) is one category.

For all numbers the SimaPro software gives slightly lower total CO_2 equivalents than the LCA model built in Excel. The largest deviations are found for the SMR, ATR and ASU. All these units require input from the technosphere; electricity and natural gas. For the SMR and ATR the reason for the lower contribution from the SimaPro software is the lower CO_2 potential used for methane in SimaPro, compared to the LCA model in Excel. The sensitivity of the CO_2 potential is discussed in Section 7.3. For ASU the reason is a difference in the electricity mixed used in the SimaPro software compared to the Excel model. The different composition of the electricity mix is given in Appendix 5.

References

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SimaPro 7.0 Educational, PRé Consultants, The Netherlands, 2006