

## A comparison of the eco-efficiency of two production routes for methanol

J.A. Hugill  
J.P. Overbeek  
S. Spoelstra

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<b>Made by</b> J.A. Hugill		ECN Energy Efficiency in Industry  Processes & Systems
<b>Approved by</b> S. Spoelstra		
<b>Checked by</b> J.P. Overbeek		
<b>Issued by</b> J.A. Hugill		

## Preface

This document is the final report of the ENGINE project 'Eco-efficiency of chemical processes' (project nr. 76188) which was carried out in the period August 1999 – December 2000.

## Abstract

To achieve sustainable development in the chemical industry, there is a need for methodologies to assess the eco-efficiency of alternative and novel technologies.

The aim of this project was to use a case study to investigate the application of existing tools to assess eco-efficiency. The case study compared the conventional methanol production process with a novel route using a photo-electrochemical (PEC) reactor.

The Exergy Analysis showed that the exergetic efficiency (for the production phase) of the PEC process was much lower than that of the conventional process. However, exergy from the sun is free and abundant, and in such processes there can be large exergy losses without direct environmental consequences.

The Life Cycle Analysis revealed that the two process routes have a similar overall environmental impact. The impact is dominated by the production phase for the conventional process, but by the construction phase for the PEC process. To improve the PEC process, priority should in principle be given to optimising the materials of construction, rather than improving the exergetic efficiency as such. Nevertheless, insofar as the large size of the PEC reactor is related to its low exergetic efficiency, we can still conclude that it makes no sense to squander exergy, even free exergy.

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## SUMMARY

In order to achieve sustainable development in the chemical industry, there is a need for a set of methodologies with which to assess the relative merits of alternative and novel technologies on the basis of sustainability or eco-efficiency. However there is a gap between the existing methods of chemical process synthesis/design and those of Life Cycle Analysis LCA.

The aim of this project was to use a case study to investigate the possibilities and pitfalls of applying existing tools - the process design tool Aspen Plus together with the exergy subroutine EXERCOM, and the LCA tool SimaPro - to assess eco-efficiency. The case study was based on a process of industrial interest, namely the production of methanol. Two totally different routes to produce methanol were compared. One is the conventional route, by reforming of natural gas and synthesis of methanol. The other route uses a photo-electrochemical (PEC) reactor in which CO<sub>2</sub> and water are used as feedstock and the reaction is driven by solar energy.

A considerable effort was required to perform the exergy analysis and the LCA on the conventional process, starting from the process flowsheet. In addition to modelling the process flowsheet as such, attention had also to be given to modelling of the steam system, and the heat integration, before even an approximate overall steam/electricity balance could be obtained. Furthermore, the program EXERCOM was found to have a limited functionality. Exergies of material streams are calculated, but exergies of heat streams, exergy losses in (sub)systems, and exergetic efficiencies all had to be calculated manually. We conclude that such a detailed modelling approach is probably only justified when it is desired to identify the specific causes of the exergy losses or environmental impacts in a process. If we only wish to calculate overall values for the process, then it is preferable to adopt a black box approach at the highest possible level of agglomeration – however this approach requires data on the overall process performance which may not always be readily available.

The exergy analysis showed that the exergetic efficiency of the conventional process is about 68 %, while that of the PEC process is only about 5 %. However, exergy from the sun is free and abundant, and in such processes there can be large exergy losses without direct environmental consequences. We conclude that exergetic efficiency as normally defined (based on the production phase only) is not a useful concept when comparing processes driven by solar energy with their conventional counterparts. To be of more use, the exergy analysis would have to be extended to include (like the LCA) the construction/demolition phases.

The LCA revealed that the two process routes have a similar overall environmental impact. For the conventional process, the construction/disposal phases make a negligible contribution to the total environmental impact, which is dominated by the production phase. For the PEC process, although the production and disposal phases are beneficial to the environment, the total (adverse) environmental impact is dominated by the construction phase.

We conclude that LCA is a useful tool to compare novel processes with their conventional counterparts. For novel processes based on solar energy (and probably other renewable energy sources) LCA can reveal the potentially key contribution made by the construction/demolition phases to the total environmental impact. Such observations can help guide process development.

To improve the PEC process, priority should in principle be given to optimising the materials of construction, rather than improving the exergetic efficiency as such. Nevertheless, insofar as the large size of the PEC reactor is related to its low exergetic efficiency, we can still conclude that it makes no sense to squander exergy, even free exergy.

## 1. INTRODUCTION

In the framework of sustainable development, the chemical industry is interested in indicators for sustainability or eco-efficiency. Not only does it realise that sustainable thinking can provide business benefits, the chemical industry also tries to project a more sustainable image towards the consumers/public. Producing in a sustainable way will in the end lead to a sustainable company.

This calls for a need of a set of methodologies with which to assess the relative merits of alternative and novel technologies on the basis of sustainability or eco-efficiency. These methodologies must take into account factors such as exergy efficiency (i.e. use of primary energy), environmental impact, and depletion of natural resources, in the context of the entire life cycle of the process/product. But the currently applied methodologies for chemical process synthesis and design (e.g based on flowsheeting programs such as Aspen Plus) are limited insofar as they are mainly concerned with existing technologies, do not have a specific focus on eco-efficiency, and miss the insights of a life cycle approach. On the other hand, currently applied methodologies for environmental life cycle analysis LCA (e.g. based on the program SimaPro) have been rarely applied to chemical processes, and never applied at the stage of process synthesis and design. To put it crudely, a gap exists between the methods of process design and the methods of LCA. We have to bridge that gap if we want to develop a sustainable chemical industry.

In the long term, the objective is to develop a methodology or instrument to assess the sustainability or eco-efficiency of industrial processes/process chains. For the present project the objective is to further investigate the possibilities and pitfalls of applying existing tools as a process design tool (Aspen Plus) together with an LCA tool (SimaPro) to do so. Previous studies have been performed on a chemical heat pump and on two production routes for Methyl Isobutyl Ketone, see [1, 2].

In the current project, one case study is used to further investigate the above and other issues. The case study is based on a process of industrial interest, namely the production of methanol. Two totally different routes to produce methanol are compared. One consists of the conventional way by reforming of natural gas and synthesis of methanol. The other way uses a photo-electrochemical (PEC) reactor in which CO<sub>2</sub> and water are used as feedstock and the reaction is driven by solar energy.

Chapter 2 describes both the conventional methanol production process and the production of methanol in a photo-electrochemical reactor. The concept of eco-efficiency as well as the methods of exergy analysis and Life Cycle Assessment are addressed in Chapter 3. Chapter 4 deals with the analysis results, followed by the conclusions and recommendations in Chapter 5.



## 2. METHANOL PRODUCTION ROUTES

This chapter describes the two production routes for methanol which have been studied in this project.

### 2.1 Conventional

There are about 95 methanol plants worldwide with a total capacity of 34 Mt/y. About 80% of methanol is produced from natural gas, and methanol production is concentrated in regions where natural gas is cheap and available. In the Netherlands, Methanor (a joint venture of Akzo-Nobel, DSM, and Dyno) produces 780 kt/y (about 14 % of European production) in Delfzijl.

The main applications of methanol are as a solvent (4% worldwide), in gasoline blending (2%) and in the manufacture of formaldehyde (35%), MTBE (27%), acetic acid (10%) and other chemicals.

The conventional methanol process is licensed by

- Syntex (formerly ICI) (60% of production worldwide, including the Methanor plant).
- Lurgi (30%).
- Others (Haldor Topsoe, Kellogg, Krupp Uhde).

The conventional process consists of four main sections, see Figure 2.1.

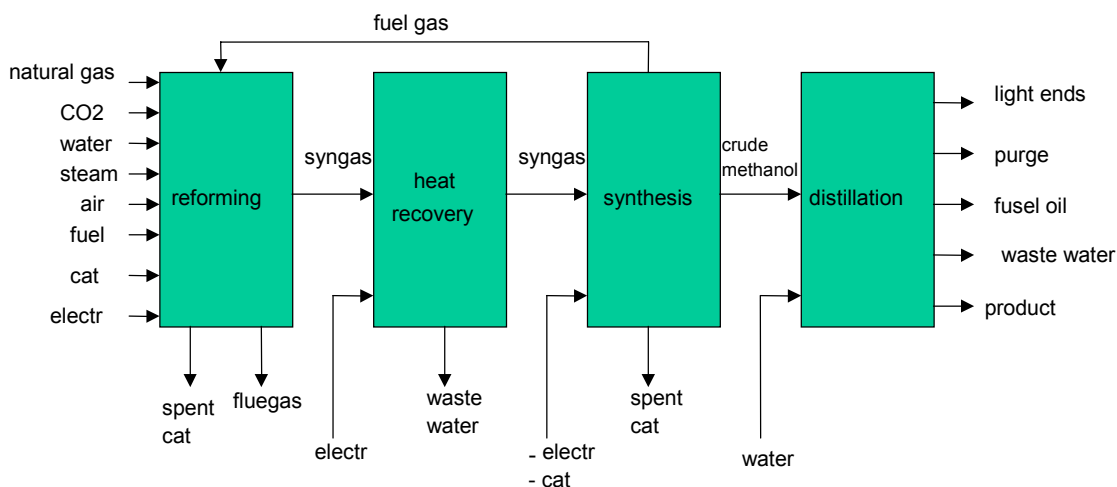
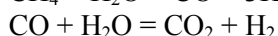
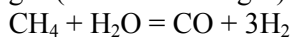


Figure 2.1 *Conventional process for methanol production*

#### *Reforming (syngas production):*

Usually (e.g. Syntex), syngas is produced by steam reforming of natural gas in a multitubular fixed-bed reactor with a nickel catalyst at about 860-880 °C and 18-20 bar. Energy for the strongly endothermic reaction is provided by heating the reactor tubes by combustion of natural gas (and some fuel gas) in a furnace. The main (equilibrium) reactions are:



Steam reforming gives syngas with a H<sub>2</sub>/CO ratio which is too high for the methanol synthesis step. This can be dealt with by:

- hydrogen purge downstream of the synthesis reactor (e.g. Syntex),
- addition of CO<sub>2</sub> to the syngas (either upstream or downstream of the reformer).

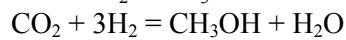
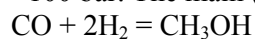
CO<sub>2</sub> addition is most often practised when CO<sub>2</sub> is available from a nearby ammonia plant. In some processes (e.g. Lurgi), syngas of an optimum composition is produced by using partial oxidation of natural gas in addition to steam reforming.

*Heat recovery:*

The syngas is cooled and compressed before entering the synthesis loop.

*Methanol synthesis:*

The methanol synthesis reactor uses a fixed bed of copper-based catalyst at 200 – 280 °C and 80 - 100 bar. The main (equilibrium) reactions are:



Both reactions are exothermic, so the reactor is normally cooled in order to maximise the equilibrium conversion. Different process licensors use various methods of reactor cooling. The methanol concentration at the reactor outlet is only about 7-8 %. The reactor effluent is cooled to 40-45 °C to condense the crude methanol product, and the unreacted gases are recycled back to the reactor inlet. A purge is taken from the recycle gas to remove inerts and any surplus hydrogen. The purge gas is used as fuel in the reformer furnace.

*Distillation (methanol purification):*

A two- or three-column distillation system removes water and other by-products.

More details about conventional methanol production are given in a recent report [3].



## 2.2 Photo-electrochemical

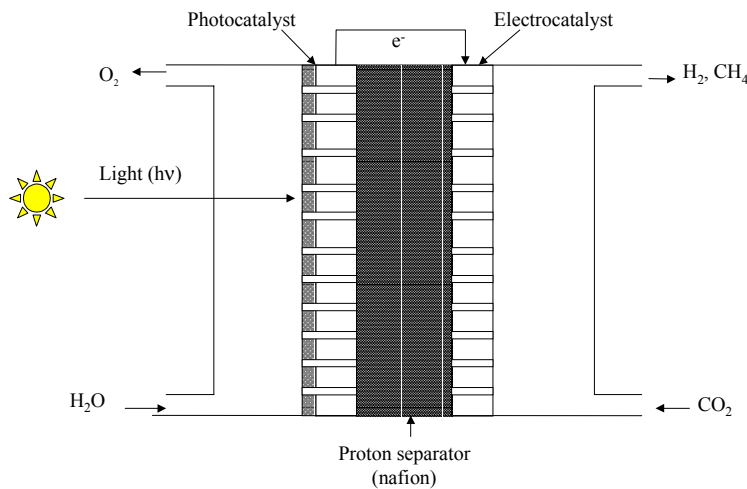
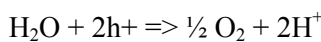
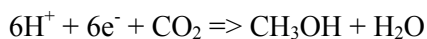


Figure 2.2 *Concept of a photo-electrochemical reactor for methanol production*

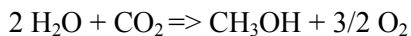
The concept under study is shown below in Figure 2.2. The concept works in the following way. A semiconductor photocatalyst on the left (anode) side absorbs light resulting in the promotion of an electron from the valence band to the conduction band, leaving a hole behind. This charge separation is the first essential step. For a n-type semiconductor, the holes will move to the interface with the water. The reaction between the water and the holes results in the formation of oxygen and protons.



The protons are able to diffuse to the right (cathode) side through a proton conducting membrane. The electrons that were created in the semiconductor are also able to move to the cathode by an electrical connection and possibly a bias voltage. At the cathode the proton and electrons react with the carbon dioxide present to form chemicals. To form for example methanol, the following reaction occurs.



The type of product that is formed depends on the electrocatalyst that is used at the cathode side. The overall reaction for the production of methanol becomes:



For this principle to work the bandgap of the photocatalyst semiconductor should be larger than the redox potentials of both half reactions. However, a too large bandgap would imply that the semiconductor would not absorb visible light. In addition, the band edges potentials at the interface between the photocatalyst and the water should match the redox potentials needed to split the water. The most widely used semiconductor is titanium dioxide (TiO<sub>2</sub>) due to the fact that it is very stable, its bandgap is high enough, it is not toxic, it is widely available, and low in cost. The disadvantage of TiO<sub>2</sub> is that it has a bandgap of about 3 eV (rutile), implying only absorption of UV-light.

More information on this reactor can be obtained from for example [4].



### 3. METHODOLOGY

The concept of eco-efficiency was first coined in 1992 by the Business Council for Sustainable Development. It was further defined at the first Antwerp workshop on Eco-efficiency in 1993 as being ‘reached by the delivery of competitively priced goods and services that satisfy human needs and bring quality of life, while progressively reducing ecological impacts and resource intensity throughout the life cycle, to a level at least in line with the earth’s estimated carrying capacity’. Eco-efficiency is a management philosophy. It encourages businesses to become more competitive, more innovative and more environmentally responsible. Eco-efficiency links the goals of business excellence and environmental excellence. Eco-efficiency embraces cleaner production concepts such as efficient use of raw materials, pollution prevention, source reduction, waste minimisation and internal recycling and reuse. It captures the idea of pollution reduction through process change as opposed to the earlier end-of-pipe approaches. Eco-efficiency also features a life cycle perspective that follows products from the raw material through to final disposal stages. Put in simple terms, the vision of eco-efficiency is to ‘produce more from less’. Reducing waste and pollution, and using less energy and fewer raw materials is obviously good for the environment. It is also self-evidently good for business because it cuts companies’ costs, and eventually avoids potential environmental liabilities. It is, therefore, a prerequisite to the long-term sustainability of business.

The World Business Council of Sustainable Development (WBCSD) has identified seven success factors for eco-efficiency:

- reduce the material intensity of goods and services,
- reduce the energy intensity of goods and services,
- reduce toxic dispersion,
- enhance material recyclability,
- maximise sustainable use of renewable resources,
- extend material durability,
- increase the service intensity of goods and services.

Translating Eco-efficiency into numbers is a difficult task. While indices such as energy and water use are easy to measure, others such as non-product output (or waste) are not uniformly defined. In turn, this makes it difficult to compare the figures of different companies. The relevance of various types of emissions and environmental burdens also varies from business to business. The elements to be included in an Eco-efficiency performance profile are therefore a matter of intense debate.

There is no shortage of measurement methods. The problem is that there is no standard methodology and no agreed, common set of indicators to quantify Eco-efficiency. Because companies and organisations use different systems, there is confusion, and even scepticism, about some of industry's claims. The need for co-ordination and standardisation is critical.

Eco-efficiency is the merging of product or service value and ecological aspects into an efficiency ratio. This means maximising value while minimising adverse environmental impact, i.e. minimising use of resources and adverse environmental consequences from emissions. WBCSD developed the following basic formula to estimate eco-efficiency:

$$eco - efficiency = \frac{product\ or\ service\ value}{environmental\ influence}$$

However, there is no universally accepted set of terms for the numerator and de-nominator elements in this formula. Therefore, numerous ways to calculate eco-efficiency exist, and specific parameters must be established based on the individual needs of companies and their stakeholders. For example, 'product or service value' may be defined in terms of the number of products, their economic value, or a measure of the need they fulfil for the public. Environmental influence encompasses elements of the use of resources and energy, as well as emissions of substances to air, water, and land that could have adverse environmental impacts. The use of eco-indicator points per kg product resulting from a Life Cycle Assessment or the use of cumulative exergy losses per kg product represent a way of indicating environmental influence per product quantity.

### *Exergy analysis*

Exergy is a concept which follows from a combination of the first and second laws of thermodynamics. Exergy is a measure for the quality of energy and corresponds to the maximum available work which can be obtained when taking a system through reversible processes to equilibrium with the environment. In real processes, irreversibilities always occur. This leads to a loss of exergy or loss of available work.

An exergy analysis is a powerful tool for providing insight into the inefficiencies of processes. It pinpoints the exact location of the losses. A decrease of the exergy loss of a process automatically leads to a decrease of the demand of primary fuels for that process. Exergy analysis is not a new concept but has up till now mainly been applied to energy conversion processes, like gas turbines, combined heat and power stations, combined cycles, etc... The use of exergy analysis in the chemical industry is increasing.

The quantity of exergy can be subdivided into three components, namely the physical, mixing, and chemical exergy. The physical exergy is the maximum amount of work which can be obtained when a system comes to thermal and mechanical equilibrium with the environment ( $p_0, T_0$ ). The mixing exergy corresponds to the minimum necessary work to separate a mixture at thermal and mechanical equilibrium ( $p_0, T_0$ ) into the separate components. Alternatively, it is the maximum amount of work which is released by this process.

The chemical exergy is the maximum amount of work which can be obtained from a component when taking this component from thermal and mechanical equilibrium ( $p_0, T_0$ ) to chemical equilibrium with the substances occurring in the natural environment. This also equals the minimum amount of work necessary to create this component from environmental substances.

In calculating exergy, it is very important to define a reference or environmental condition. It is common to use  $p_0 = 1.01325$  bar and  $T_0 = 298.15$  K as these reference conditions. These are based on [5]. This reference also states the reference substances and their environmental concentrations for use in the calculation of the chemical exergy. Reference [5] contains tables with the standard chemical exergy (i.e. the chemical exergy at reference conditions) of a large number of substances.

### *Life Cycle Assessment*

A Life Cycle Assessment (LCA) is a cradle-to-grave approach to a specific product or process. It evaluates the environment impact of any product or process considering the total life cycle, including design, construction, use, dismantling, and recycling. The purpose of an LCA is to compare different products or processes which have the same function. The methodology is already very well developed and in the Netherlands there is a very good description of how to perform an LCA, see [6, 7]. An LCA consists of the following components.

### *Goal and Scope*

The specific application of the LCA is defined within this component. Elements hereof are the objective of the study (product information, product innovation, product regulation, policy strategies), the target group (consumers, producers, authorities), and the depth of the study. Another element of this component is the definition of the functional unit of the system under consideration. This unit describes the central function of the product or process. For the purpose of this study the functional unit is the production of 100 kton of methanol by either the conventional process or in a photo-electrochemical reactor.

### *Inventory*

Within this component an overview is compiled which contains all processes which make up the life cycle, the so called process tree. This also determines the system boundaries within which the LCA will be performed. Thereafter data collection starts of all processes under consideration. This is a labour-intensive task and concerns data about the in- and outflows from/to the economy (products, services, materials, energy, waste to be treated) and in- and outflow from/to the environment (raw materials, energy carriers, space, emissions, radiation, noise, heat, light, disasters). Hereafter rules have to be applied which allocate the impacts to multiple economic products, if this is the case. The last step of the inventory component consists of making an impact table. This table contains the quantified environmental impact or emissions of each process/product per functional unit.

### *System boundaries*

In order to establish the material use for the construction phase for both production routes an educated guess must be made to estimate the amount of construction materials needed. The environmental impact of transporting the materials to the site is included. The other information needed regarding the construction phase is the energy use during construction, required tools, additional overhead/infrastructure and capital goods as well as the use of land. It is almost impossible to make an estimate of these figures and their environmental impact. Accordingly, we consider these aspects to fall outside the system boundaries – it is implicitly assumed that their environmental impact is negligible in comparison to the other contributions.

The transport of feedstock as well as maintenance activities during the production phase also fall outside the system boundaries – again, it is implicitly assumed that these activities have a negligible effect. The remaining aspects such as feedstock, energy use, emissions, waste, products and by-products all fall within the system boundaries.

Although from previous studies it is known that the demolition phase of a system or product makes a very small contribution to the overall environmental impact, an attempt has been made to take the demolition phase into account.

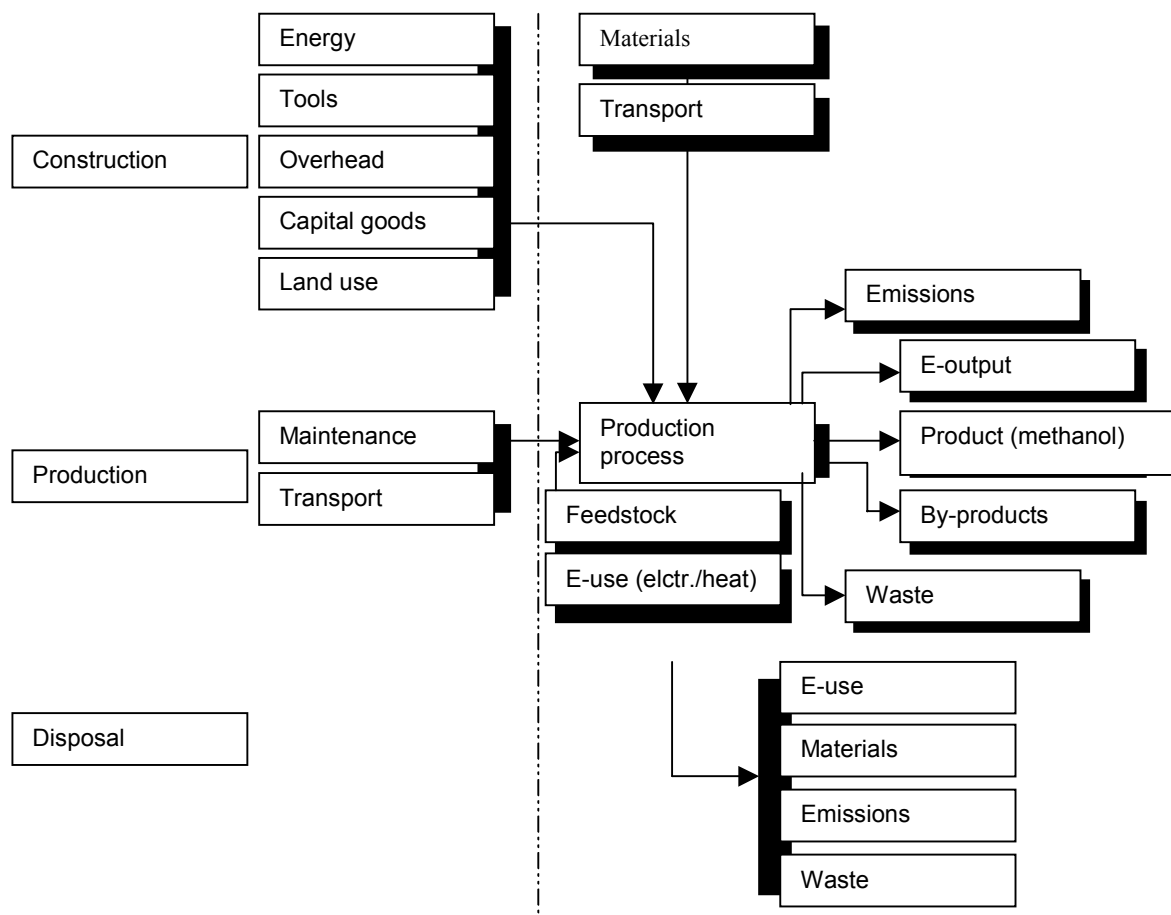


Figure 3.1 System boundaries for the methanol production case

### Classification

The classification component translates the environmental impacts to relevant environmental effects. These effects present the contribution to environmental problems like acidification, green house effect, ozone layer destruction, etc. For each emission there is a classification factor which determines the contribution of that particular emission to a specific environmental problem. For each environmental problem the emission is multiplied with the classification factor and summed up. This results in total scores for each problem. To be able to compare the different scores, they are normalised. In practice, this means that the contribution of a specific process/product to an environmental problem is compared to the contribution of for example the European Union to the same problem.

### Evaluation

During the evaluation, the profile consisting of the scores on the individual environmental problems is assessed. For this one needs a way to compare the different problems with each other. One way to do this is to multiply each score with a weighting factor and sum them up. The Eco-indicator '95 method (see Appendix A) is such a way to come up with one number for the total environmental effect.

The analysis described above can be followed by an improvement analysis in which the knowledge that has been gathered is used to improve the product/process. The analyses reported in this document have been performed with the commercially available software package SimaPro, version 4.0, see [8, 9].





## 4. ANALYSES

### 4.1 Conventional process

#### *Process flowsheet modelling*

The starting point for the process modelling was a flowsheet and data provided in the documentation of an Aspen Plus course [10]. It would have been preferable to have data from an actual plant, or from a generic design provided by a process licensor. However we were unable to acquire sufficient information from either an end-user (Methanor) or the process licensors (Synetix, Lurgi). The advantage of the source used is that we knew from the outset that sufficient information was available to construct a reasonably detailed and self-consistent Aspen Plus model. The disadvantage is that although we know the flowsheet is that of a 'typical' methanol plant, the exact origin of the data is not known.

The overall flowsheet of the process modelled was already shown in Figure 2.1. The detailed flowsheet is given in Appendix B. In this particular flowsheet, only steam reforming is used to produce syngas, as in the Synetix process, but carbon dioxide is added to the natural-gas feedstock in order to produce an optimal syngas composition. The methanol synthesis reactor uses direct cooling, as in the Lurgi process. The flowsheet was modelled using Aspen Plus 10.1. (One small feature of the flowsheet, a water recycle loop, was not modelled in Aspen Plus but dealt with by an approximate procedure; this is explained in Appendix C.) The resultant heat and material balances are given in Appendix D. The production of methanol is 61809 kg/h.

#### *Steam system modelling*

In order to provide a sufficient basis for the exergy analysis, it was necessary to complement the process model with a model for the associated steam system. The function of the steam system is to use the heat extracted from various parts of the process (ultimately from the exothermic reactors) to generate steam at various pressure levels and to generate electricity. The steam is then used at other points in the process (as process steam and as a heat source for e.g. the

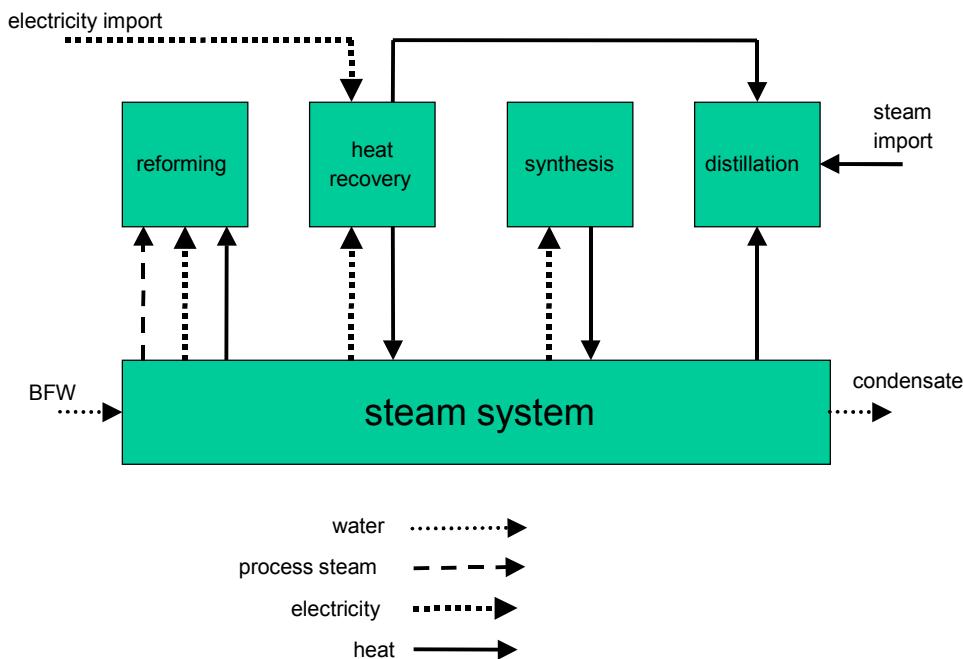


Figure 4.1 *The relationship of the steam system to the process*

reboilers of distillation columns). The electricity is used to drive equipment such as compressors. The relationship of the steam system to the process is illustrated in Figure 4.1.

The flowsheet for the steam system was designed on the basis of a global description given by Lurgi [11] and is shown in Appendix E. It is very simple, feasible system. No attempt was made to develop an optimum flowsheet, which would certainly be much more complicated. The flowsheet was modelled using Aspen Plus 10.1 (a separate model from the process model). The resultant heat and material balances are given in Appendix F.

#### *Heat integration*

Most of the heat sources and heat sinks in the process/steam-system flowsheets were tied together by links already defined in the flowsheet structures. However, once the flowsheets had been modelled, it remained to deal with a number of ‘unassigned’ heat sources and heat sinks. In practice this concerned four heaters in the reforming section whose heating requirements could be met by use of heat recovered from the reformer-furnace flue-gas cooler, together with MP/LP steam from the steam system. A simple, feasible heat integration scheme was designed which takes into account the temperature levels of the various heat sources/sinks. Details of this design are given in Appendix G. A more optimum design could probably be made by use of a rigorous pinch analysis, but such an analysis would logically have to include optimisation of the steam system and indeed a re-assessment of all source/sink links defined in the original flowsheet. Such an exercise was not justified in the scope of the current work.

#### *Electricity and steam imports*

After completion of the flowsheet models and the heat integration study, the requirement for import of electricity and steam could be assessed on the basis of the overall balances. Details are given in Appendix H. An import of 13160 kW electricity and 18676 kW LP steam is required. The former figure corresponds to 213 kWh/ton methanol, which is an order of magnitude greater than the value quoted by Lurgi, 20 kWh/ton [11]. Furthermore, the information from Lurgi suggests that no import of steam should be required. Some of these differences may be due to the fact that our steam system and heat integration are not fully optimised. Nevertheless such large differences are somewhat surprising.

### 4.1.1 Exergy analysis

#### *Exergies of material and heat streams*

The subroutine EXERCOM Version 2 (licensed from Jacobs Comprimo) was used together with the Aspen Plus flowsheet models to generate exergy values for all the material streams. These exergy values are given together with the heat and material balances in Appendices D and F. However, EXERCOM does not provide exergy values for the heat streams. In the EXERCOM User Manual it is recommended to calculate such exergy values from the corresponding enthalpies (heat duties) by use of Carnot factors. This is unambiguous only in cases where heat is derived from a material stream under isothermal conditions (e.g. condensation of steam in a reboiler). However in general the material stream will change in temperature (e.g. a process stream in a heat exchanger) in which case the use of Carnot factor must be based essentially on some approximation for the average temperature (unless the entire enthalpy-temperature profile of the stream would be available, which is not the case with the Aspen Plus output). To avoid the use of approximations in such cases, we opted for a calculation based on a simple exergy balance for the unit in question, by adopting the convention that the internal exergy loss in the unit is zero. This is illustrated for the case of a cooler in Figure 4.2.

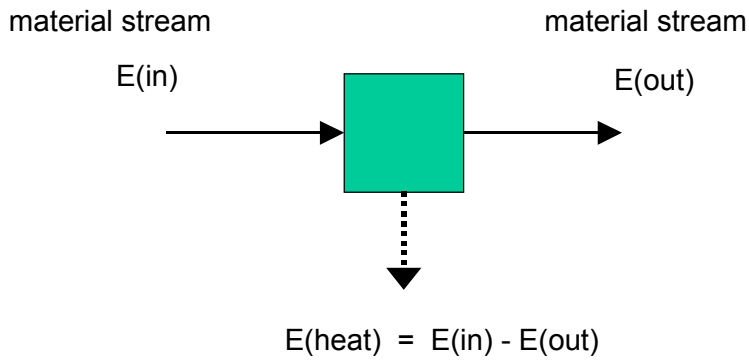


Figure 4.2 Calculation of the exergy of a heat flow

In effect, any internal exergy loss in this unit is assigned to the heat stream and will be ultimately be accounted for as part of the exergy loss at the point where the heat stream encounters another unit (in this case a heater) or crosses a system boundary (see below). Although this convention is obviously not realistic, this lack of realism has no effect on the final results – it is a convenient means of ‘book-keeping’ the exergy flows without any loss of accuracy.

*Exergy losses at system boundaries*

The internal exergy loss within any defined system can be calculated as the sum of the exergy flows into the system minus the sum of the exergy flows out of the system. Boundaries between systems present no problem for material flows but care must be taken with heat flows. This is because the heat is usually generated in one system at a high temperature and used in another system at a lower temperature. There is then an exergy loss associated with this temperature decrease which is not accounted for in either system separately. (This is true independent of which of the methods mentioned above is used to calculate the exergies of the heat flows). It is therefore necessary to check all system boundaries for exergy losses associated with heat flows. This is illustrated in Figure 4.3.

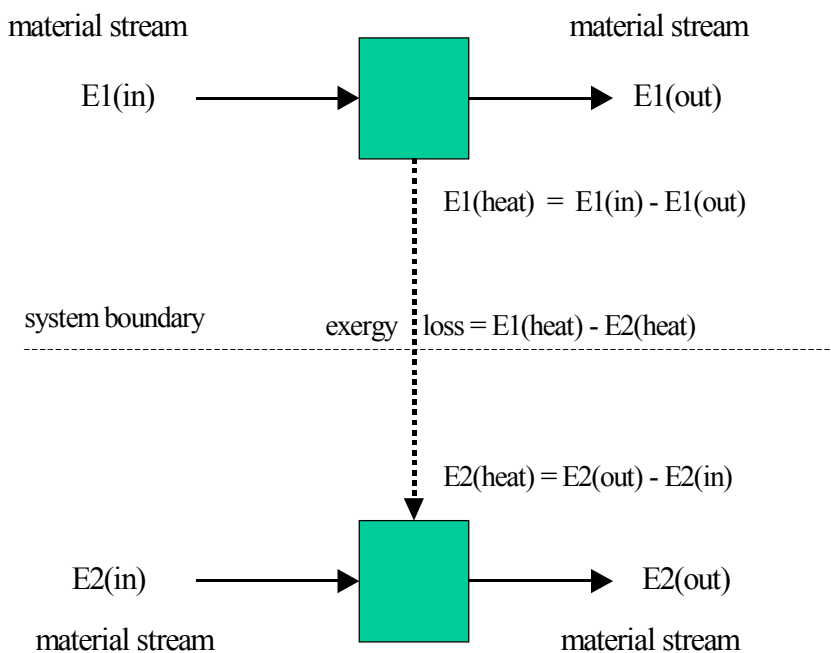


Figure 4.3 Calculation of exergy losses at system boundaries

We see that in this case the exergies of the heat flows in each system have been calculated as mentioned above, by conventionally assuming that internal energy losses in the units concerned (cooler and heater) are zero. All exergy loss is then calculated at the point where the heat flow crosses the system boundary. At first sight it may seem to be a disadvantage of this approach that no attempt is made to calculate the distribution of this exergy loss between the cooler and the heater. In physical reality however, the cooler/heater combination must be a single heat exchanger and so it is actually quite realistic just to calculate a single exergy loss. The apparent split between cooler and heater is actually just an artifact of the process flowsheet model. If the above case had been considered as one system, and modelled as a single heat exchanger, then the internal exergy loss of the heat exchanger would have been calculated (exergies of material flows in minus flows out) exactly equal to the loss calculated here.

#### *Cumulative exergy losses for electricity and steam imports*

The procedures described above enable the exergy losses to be calculated for the overall system (process plus steam system). In the present context, most of the input streams (natural gas, CO<sub>2</sub>, water) can be considered to be primary resources. This means that we neglect any cumulative exergy loss which may have been incurred in producing these streams from the environment. However, for the electricity and steam imports, this cumulative exergy loss is not negligible, and should be included in the exergy analysis. This is equivalent to extending the system boundaries to include the production of the electricity and steam from primary resources (e.g. natural gas, coal, or oil). This question was addressed in a previous project, and here we make use of the correlation derived in that work [2]:

cumulative exergy loss = 1.32 \* exergy output (electricity or steam).

This correlation was based on co-generation of electricity and steam based on an oil-fired furnace – it corresponds to an overall exergetic efficiency (output/input) of 43 %.

#### *Results*

Exergy losses were calculated for each of the main flowsheet sections, and for all the boundaries between sections. Details of the calculations are given in Appendix I. The results are summarised in Table 4.1.

It can be seen that about 40 % of the exergy loss occurs in the reforming section, with a further 7 % lost at its interface (A), which includes the recycle of heat from the flue-gas cooler. The remaining 53 % is fairly evenly divided among the other sections. This result is not unexpected because it is well known that steam reforming with a gas-fired furnace is exergetically very inefficient.

The exergy losses could easily be calculated a lower agglomeration level (e.g. at unit operation level) in order to identify the main causes of the exergy losses more precisely. However such a detailed exergy analysis is beyond the scope of the current project.

The calculated total specific exergy loss of 10.8 GJ/t can be compared with the value of 14.3 GJ/t which has been given for the Methanor plant in Delfzijl [12]. It is interesting that the model calculation predicts a lower total loss than the literature value, despite the fact (mentioned above) that the electricity and LP steam imports may have been overestimated in the model. This may be because the modelled process uses CO<sub>2</sub> in addition to natural gas as a feedstock, whereas the Methanor plant does not do this. Such a use of CO<sub>2</sub> can be expected to improve the exergetic efficiency.

Table 4.1 *Exergy losses for the conventional methanol process*

Exergy losses		Internal kW	External kW	Total kW	Total %
Section 1	reforming	67097	7052	74149	40,1
Section 2	heat recovery	135	8556	8691	4,7
Section 3	synthesis loop	12850	9150	22000	11,9
Section 4	distillation	290	16694	16984	9,2
Section 5	steam system	15358	2440	17798	9,6
Section 6	steam system	2534	1077	3611	2,0
Interface A	1 with 5,6	13078	0	13078	7,1
Interface B	3 with 6	805	0	805	0,4
Interface C	4 with 2,6,BL	3594	0	3594	1,9
Import LP steam	exergy 5187 kW	6847	0	6847	3,7
Import electricity	exergy 13160 kW	17371	0	17371	9,4
TOTALS		139959	44969	184928	100
Methanol production:					
mass flow	kg/h	61809			
exergy of product	kW	384176			
specific exergy of product	kJ/kg methanol	22376			
	GJ/ton methanol	22,4			
Specific exergy loss in process	kJ/kg methanol	10771			
	GJ/ton methanol	10,8			
Relative exergy loss (exergy loss/exergy product)		0,4814			
Efficiency (exergy product/exergy input)		0,6751			
Exergy of feedstock:					
Natural gas	kW	425478			
Carbon dioxide	kW	3747			
Total	kW	429225			
Exergy feedstock/exergy product		1,1173			
Total specific exergy loss including feedstock	GJ/ton methanol	33,1			

Notes:

- (Cumulative) exergy losses for imported LP steam and electricity are calculated using the factor (exergy loss/exergy output) = 1.32 [2]. See further explanation in the text. They are here classified as internal losses, but in fact they would be partly external (CW etc.)
- The total specific exergy loss ‘including feedstock’ is calculated by adding the specific exergy loss to the specific exergy of the product. This sum is equal to the total specific exergy input for the process.

### 4.1.2 Life-Cycle Assessment

The ecological impact of the three different life stages of the conventional methanol plant will be discussed separately.

#### *Construction phase*

The materials needed for the construction of the conventional methanol plant are mainly concrete and steel. In [13] a detailed LCA-study has been performed on a hydrogen production plant. The second column in Table 4.2 presents the material quantities for a 1.5 million Nm<sup>3</sup>/day hydrogen plant. When these quantities are normalised to the capacity of the plant (about 210 MW, HHV) the third column in Table 4.2 is calculated. Then these values are extrapolated to a methanol plant under the assumption that the two processes are to some extent similar and the plants, on a MW-basis, need the same amount of construction materials. The fourth column shows the calculated quantities for a 434 MW (HHV) methanol plant. This capacity corresponds to 550 kton methanol per year.

Table 4.2 *Material quantities for construction of a conventional methanol plant*

Material	H <sub>2</sub> -plant (ton)	H <sub>2</sub> -plant (kg/MW)	Methanol plant (ton)
Concrete	12041	56736	24623
Steel	3272	14872	6454
Aluminium	27	123	53
Iron	40	182	79

The environmental impacts of the materials needed for the construction of the methanol plant have been taken from the SimaPro database. Likewise this has been done for the energy use. All construction materials are assumed to be transported over an average distance of 100 km to the construction site.

For the allocation of the construction phase of the plant to the production of methanol the following is used. The production plant has a capacity of 550 kton methanol per year and a life time of 30 years. The production of 100 kton methanol (functional unit) has therefore an allocation factor of 0.00606.

The contribution of the construction phase to the environmental impact of the production of 100 kton methanol amounts to 483 Ecopoints. The use of oxysteel has by far the largest contribution (about 90 %). Other materials, transport and operations hardly make any impact on the result.

#### *Production phase*

The data concerning the energy use and product flows have been obtained from the Aspen Plus model. Data on emissions have been obtained from the SimaPro database.

The methanol synthesis catalyst is known to be cuprous oxide on ceramic pellets. The reformer uses a nickel catalyst. No specific information could be found about the quantity of catalysts nor about the regeneration processes. The amounts of catalyst have been calculated from the estimated sizes of the reactors. Generic data about catalyst regeneration processes (e.g. energy requirement) have been taken from Ullmann's Encyclopedia of Industrial Chemistry; however no information on emissions was available. The energy required for regeneration was found to have a negligible environmental impact.

Table 4.3 presents the calculated Ecopoints for the production phase of the conventional process. Subdivision has been made to allocate the contribution of the separate processes. Clearly the process-related emissions and the use of electricity constitute the largest contributions. (However, as mentioned in section 4.1, the electricity import calculated from the Aspen Plus model may be an over-estimate compared to an actual plant.)

Table 4.3 *Ecological impact of the production phase of 100 kton methanol by the conventional process*

Process	Ecological impact (kPt)	Share (%)
Emissions	31.8	47.7
Electricity use (import)	34.0	50.9
Heat use (LP steam import)	0.96	1.4
Total	66.8	100

#### *Disposal phase*

It is assumed that the used materials at the end of life of the methanol plant are processed with available recycling techniques. This recovery of materials has a beneficial effect which outweighs the impact of the transport, emissions, and energy use in this disposal phase. As with the construction phase, an allocation factor of 0.00606 has been applied to convert the lifetime production of methanol to 100 kton. Table 4.4 presents the results for the disposal phase.

Table 4.4 *Ecological impact of the disposal phase of the conventional process responsible for the production of 100 kton methanol*

Process	Ecological impact (Pt)
Transport	7.03
Emissions and energy use	17.7
Recycling and recovering	-102
Total	-77

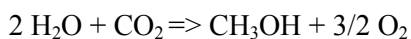
## 4.2 Photo-electrochemical process

This section describes both the exergy analysis and LCA on the PEC-reactor.

### 4.2.1 Exergy analysis

One could argue about the use of exergy analysis when solar energy is involved. Exergy analysis is normally used to locate losses of primary energy in order to reduce these losses. This is particularly useful when fossil energy carriers play an important role. It seems only of academic interest to look at exergy losses when the abundant energy supply of the sun is involved. Nevertheless, an exergy analysis of the PEC-system is carried out for the sake of completeness.

The exergy analysis is performed for the following reaction:



The reaction is driven by solar energy. If an energetic efficiency of 5 % is assumed, a solar radiation of 100 W will result in 5 W of methanol. This efficiency is a reasonable number that could be obtained by these devices, see also [4]. Based on a higher heating value of 22670 kJ/kg methanol this corresponds to 0.794 g/h, or 0.0248 mol/h. The mass balance becomes:

H <sub>2</sub> O in	: 0.0496 mol/h =	0.893 g/h
CO <sub>2</sub> in	: 0.0248 mol/h =	1.092 g/h
CH <sub>3</sub> OH out	: 0.0248 mol/h =	0.794 g/h
O <sub>2</sub> out	: 0.0372 mol/h =	1.191 g/h

The incoming water stream is assumed to be at 20 °C. The incoming CO<sub>2</sub>-stream and all outgoing streams are assumed at 80 °C. All streams are at atmospheric pressure and are assumed to consist of only one component. This leads to the following exergy values, based on EXERCOM. Petela in [14] has studied the exergy value of solar energy. Based on this the exergy of solar energy is equal to 0.9327 times its energy content.

H <sub>2</sub> O in	: 0.0496 mol/h =	0.0124 W
CO <sub>2</sub> in	: 0.0248 mol/h =	0.138 W
CH <sub>3</sub> OH out	: 0.0248 mol/h =	4.967 W
O <sub>2</sub> out	: 0.0372 mol/h =	0.0424 W
Solar energy	:	= 93.27 W

The total exergy loss or destruction equals  $(93.27 + 0.0124 + 0.138) - (4.967 + 0.0424) = 88.41$  W. In this calculation, the production of oxygen is considered to be a useful by-product. The total loss corresponds to 401 GJ/t methanol, with a total exergy input of 424 GJ/t.

The exergetic efficiency defined as outgoing/incoming equals 5.4 %. If the efficiency is defined as the change in exergy caused by the chemical reaction divided by the incoming solar exergy, the efficiency becomes 5.2 %. So the difference between the two definitions is very small. We see that there is very little additional information gained by doing an exergy analysis compared to the energy values.

#### 4.2.2 Life Cycle Assessment

##### *Construction phase*

The construction of the photo-electrochemical reactor consists mainly of steel and polyethylene for the housing of the device, see Table 4.5. Any wiring or infrastructure of the production site has not been taken into account. The presented data originates from internal ECN sources. It is based on a solar irradiation of 1000 kWh/m<sup>2</sup>/yr and an efficiency of 5 %.

Table 4.5 *Material quantities for the production of 1 ton methanol per year by a photo-electrochemical reactor*

Part	Material	Quantity (kg)
Support	Stainless steel	1259
Housing	Polyethylene (PE)	1008
Anode	Titanium	11
Photocatalyst	Titanium dioxide	0.054
Proton conductor	Nafion	9
Cathode	Copper	22
Electrocatalyst	Zinc oxide	0.065

All construction materials are supplied by truck across an average distance of 100 kilometres. In addition, the reactors produced are transported by truck over a distance of 100 kilometres to the place of destination. The manufacturing processes to construct the device from the materials (welding, extrusion, drying) have also been taken into account.

The functional unit of this study is set at a production of 100 kton of methanol. When a life time of 20 years is assumed for the photo-electrochemical reactor, 5000 reactors of the size presented in Table 4.5 are needed to produce this quantity of methanol. The ecological impact of the construction of these 5000 reactors is quite high and amounts to 101 kEcopoints.



### *Production phase*

As could be expected, the ecological benefit of the photo-electrochemical way of producing methanol is achieved during its production phase. When in operation, the reactor converts CO<sub>2</sub> and water into oxygen and methanol. The reactor does not exhaust any harmful emissions nor does it need any external energy input. There are avoided emissions because the conventional production of oxygen is avoided. The total of these contribution amounts to -24.9 kiloEcopoints

### *Disposal phase*

For the dismantling of the photo-electrochemical production system of methanol it is assumed that conventional recycling techniques are used. This assures a reuse of a large part of the materials. Transport necessary to take away the materials is taken into account. Table 4.6 gives an overview of the ecological impact during this phase.

Table 4.6 *Ecological impact of the disposal phase of a photo-electrochemical reactor responsible for the production of 100 kton of methanol*

Process	Ecopoints (Pt)
Transport	426
Emissions and energy use	6700
Recycling and recovering	-19000
Total	-11874

## 4.3 Comparison

Three kinds of comparisons will be made in this chapter. First, the results of the exergy analyses for both the conventional and the photo-electrochemical production are compared. Next, the same will be done for the LCA-results of both routes. The last comparison is made between the results of the exergy analysis and the LCA.

### *Exergy analysis*

The total exergy loss for the conventional process was found to be 10.8 GJ/ton methanol, for a total exergy input of 33.1 GJ/ton. This corresponds to an exergetic efficiency (exergy product/exergy input) of 68 %.

The total exergy loss for the photo-electrochemical methanol production is 401 GJ/ton methanol, for a total exergy input of 424 GJ/ton. This corresponds to an exergetic efficiency (exergy product/exergy input) of 5 %. However 99.8 % of the exergy input is solar energy.

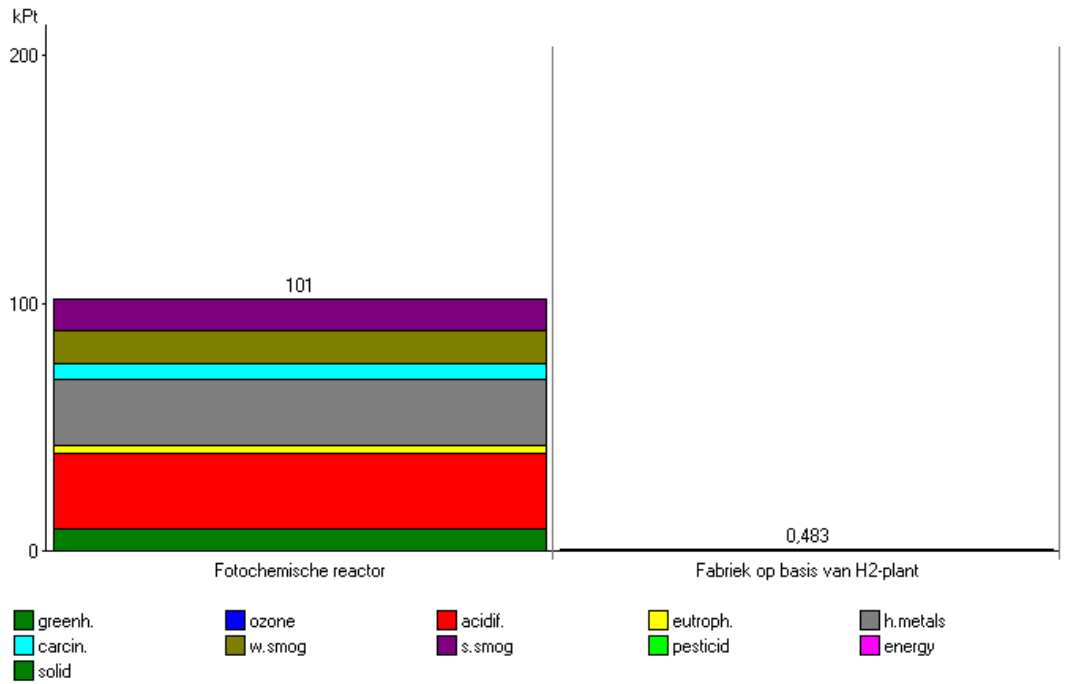
The first conclusion would be that the conventional process is by far more efficient with respect to the use of exergy. However, if one would not assign a exergy value to solar energy because it is free and abundant, the efficiency of the photo-electrochemical conversion would be far greater than 100 %. Clearly, exergetic efficiency is not a very useful concept for systems that involve solar energy.

### *Life Cycle Assessment*

The results of the LCA are separated into the three life stages construction, production, and disposal. The comparison will be made accordingly.

### *Construction phase*

Figure 4.4 presents the comparison of the production phase of the two routes. Clearly, the amount of materials needed for the construction of the photo-electrochemical reactor has a very large ecological impact compared to the conventional route.

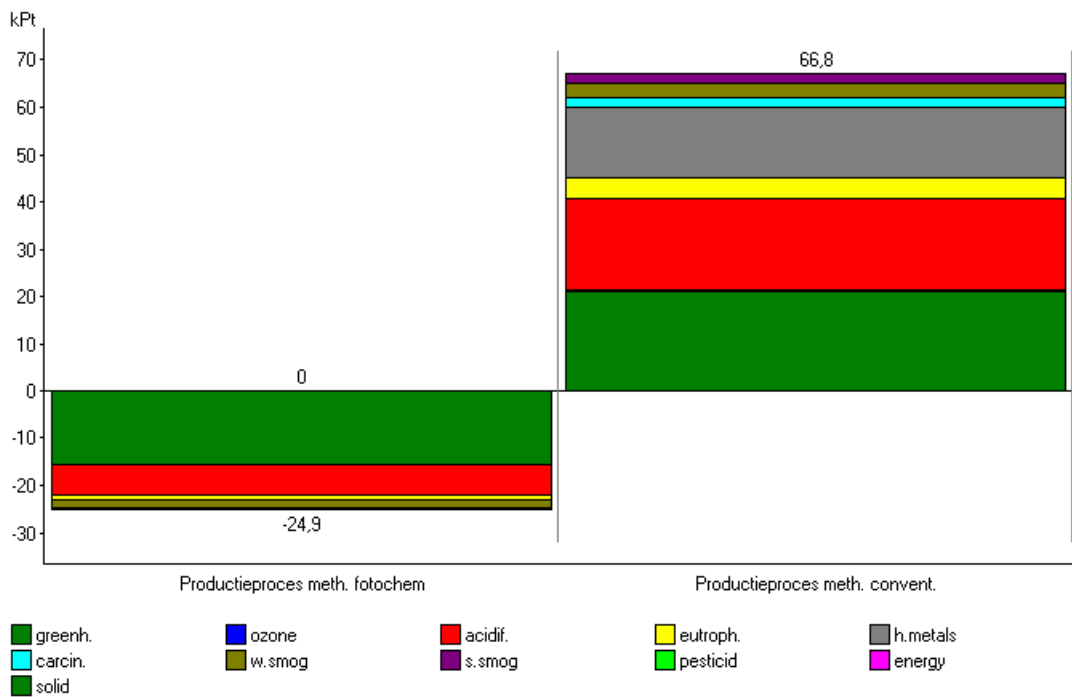


Analyse 1 p assembly 'Vergelijking construc processe'; Method: SimaPro 3.0 Eco-indicator 95 / Europe g / indicator

Figure 4.4 Comparison of the ecological impact of the construction phase of a plant producing 100 kton methanol

#### Production phase

Figure 4.5 shows the same comparison for the production phase of both routes.



Analyse 1 p assembly 'Vergelijking methanol processe'; Method: SimaPro 3.0 Eco-indicator 95 / Europe g / indicator

Figure 4.5 Comparison of the ecological impact of the production phase of 100 kton methanol

### Disposal phase

Since the SimaPro software does not provide for the option to show two disposal phases of different production routes in one figure, two figures are provided below. Figure 4.6 and Figure 4.7 show the construction and disposal phases compared to each other. This gives an indication of the amount of environmental benefit that is gained during recycling compared to the impact made during construction.

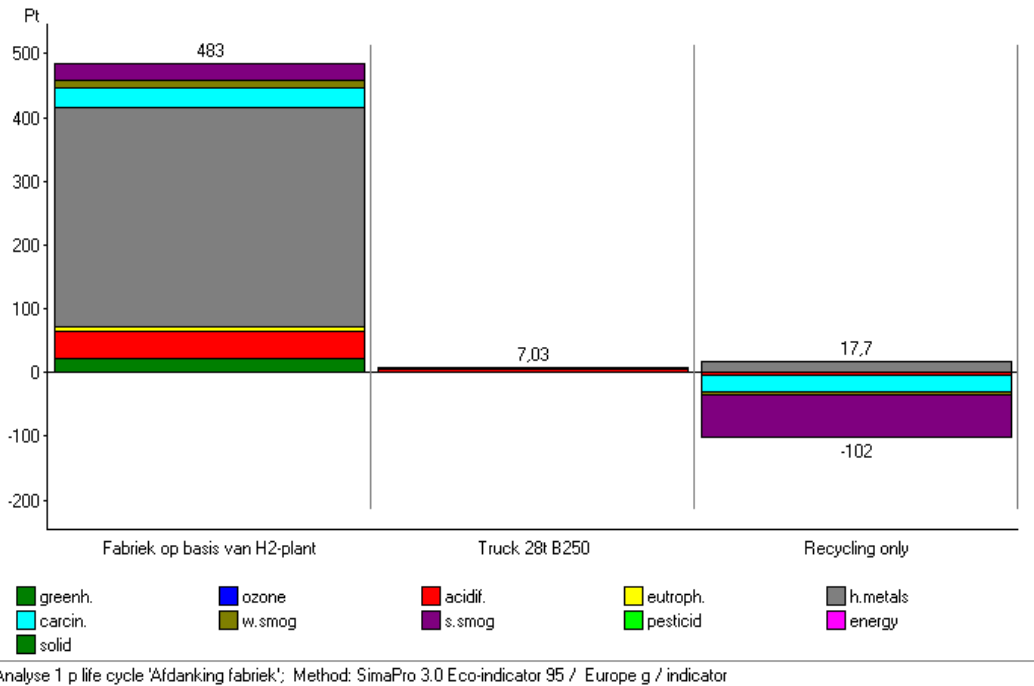


Figure 4.6 Comparison of the ecological impact of the construction and disposal phases of the conventional methanol process

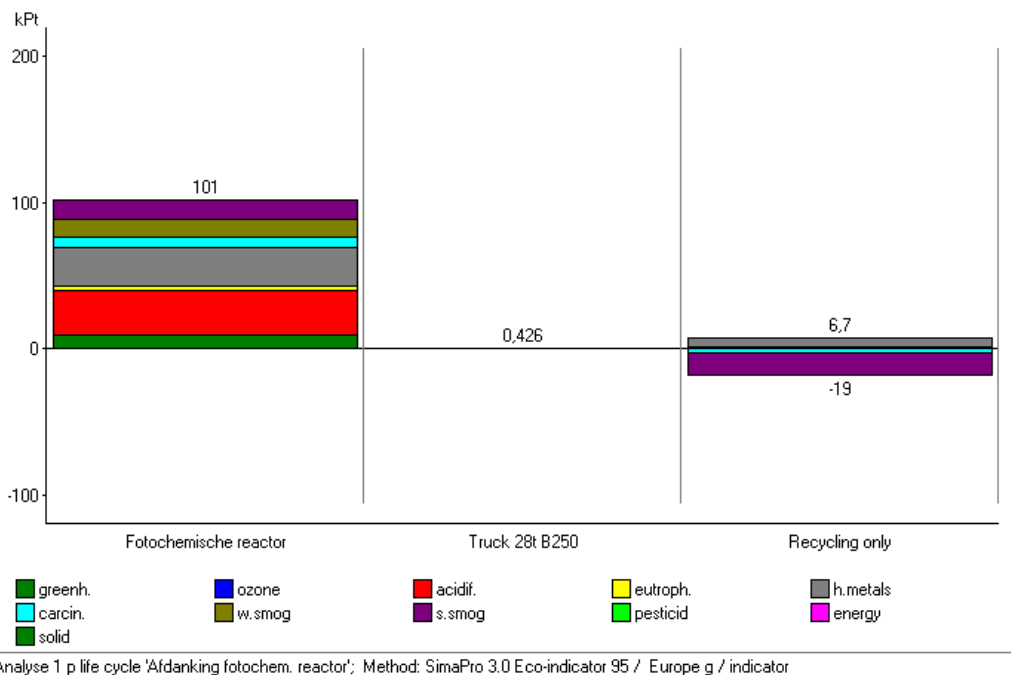


Figure 4.7 Comparison of the ecological impact of the construction and disposal phases of the photo-electrochemical methanol process

### *Total life cycle*

Table 4.7 below shows the comparison for the total life cycle, including construction, production, and disposal phase.

Table 4.7 *Comparison of the total life cycle ecological impact of both methanol production processes*

	Conventional process		Photo-electrochemical reactor	
	(Pt)	%	(Pt)	%
Construction phase	483	0.7	101000	157.3
Production phase	66800	99.4	-24900	-38.8
Disposal phase	-77	-0.1	-11874	-18.5
Total impact	67206	100	64226	100

This leads to the conclusion that based on the present information the photo-electrochemical production of methanol has a comparable environmental impact over its life cycle compared to the conventional process. In other words, the ecological pay-back time of this process equals its lifetime. This could of course improve if the efficiency of the reactor increases and therefore the amount of materials needed decreases. In addition, other materials can be considered for the construction of specifically the support. On the other hand, the analysis of the PEC reactor does not yet take into account all the peripheral systems (infrastructure) which will finally be required for a commercial plant.

### *Exergy versus LCA*

Traditionally, an exergy analysis is restricted to the production phase of a process, while an LCA often extends its system boundaries to include the construction/disposal phases as well. For the conventional methanol process, the LCA is anyway dominated by the production phase, so the difference has no significance in practice. It is likely that the same is true for bulk chemicals processes in general. However, for the PEC process, the LCA highlights the key role of the construction phase which the conventional exergy analysis cannot detect. This would probably also be true for other novel processes driven by solar energy.

In principle, there is no reason why an exergy analysis could not be extended to include the construction/disposal phases. In a way, this is already done implicitly as part of the LCA, insofar as this is concerned with the calculation of the primary energy use.

In our previous work comparing two conventional production routes for MIBK [2], we noticed a rough correlation between exergy losses and environmental impact. We suspected that such a correlation would apply to many chemical processes, since the total environmental impact will often result mainly from the use of primary energy in the production phase. However, the current work illustrates the fact that this correlation is not valid for processes powered by solar energy. In such processes there can be large exergy losses without environmental consequences in the production phase.

Nevertheless there may still be some less direct correlation. The low exergetic efficiency of the PEC process can perhaps be correlated with the low material efficiency (requirement for a large reactor) which in turn is related to the large environmental impact of the construction phase. So we could conclude that it never makes sense to squander exergy, even free exergy.

For the conventional process, the import of electricity contributes 9 % to the exergy loss, but 51 % to the environmental impact. However, this difference may be at least partly due to a lack of consistency between the calculation methods. Whereas the exergy analysis assumed that the electricity is produced on site (together with steam) by an oil-fired furnace, the LCA assumed that electricity is taken from the grid (average European electricity park). The latter would have a higher impact due to the contribution of coal-fired power stations.

## 5. CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Process routes

- For the conventional methanol process, the construction/disposal phases make a negligible contribution to the total environmental impact, which is dominated by the production phase. It seems likely that this is true for bulk chemical processes in general.
- For the PEC methanol process, the production and disposal phases are beneficial to the environment, and the total (adverse) environmental impact is dominated by the construction phase. It seems likely that this would also be true for other novel processes based on sun energy.
- Although the PEC process has a much lower exergetic efficiency than the conventional process, this observation is of little direct consequence because exergy from the sun is free and abundant.
- The rough correlation between exergy losses and environmental impact, which was previously observed for conventional processes [2], does not apply to processes powered by solar energy. In such processes there can be large exergy losses without environmental consequences.
- Overall the PEC process has an environmental impact comparable to that of the conventional process. This is not due to the low exergetic efficiency as such, but rather to the materials of construction.
- To improve the PEC process, priority should in principle be given to optimising the materials of construction, rather than improving the exergetic efficiency as such.
- Nevertheless, insofar as the large size of the PEC reactor is related to its low exergetic efficiency, we can still conclude that it makes no sense to squander exergy, even free exergy.
- The energy required for catalyst regeneration in the conventional methanol process makes no significant contribution to the environmental impact of the process. However, in the absence of more information (especially regarding emissions), we cannot yet extend this result to the entire use of the catalysts in the process. We can certainly not yet draw any conclusions for catalytic processes in general.

### 5.2 Methodology

A considerable effort is required to perform an exergy analysis and an LCA on a chemical process, when starting from the process flowsheet:

- Even when (as in the present work) a complete basis for an Aspen Plus model of the process itself is available, attention must also be given to modelling of the steam system, and the heat integration, before even an approximate overall steam/electricity balance is obtained.
- Regarding the exergy analysis, the program EXERCOM has a limited functionality. Exergies of material streams are calculated, but exergies of heat streams, exergy losses in (sub)systems, and exergetic efficiencies must all be calculated manually.

In view of this, we conclude that such a detailed modelling approach is probably only justified when it is desired to identify the specific causes of the exergy losses or environmental impacts in a process. If we only wish to calculate overall values for the process, then it is preferable to adopt a black box approach at the highest possible level of agglomeration – however this approach requires data on the overall process performance which may not always be readily available.

LCA is a useful tool to compare novel processes with their conventional counterparts. For novel processes based on solar energy (and probably other renewable energy sources) LCA can reveal the potentially key contribution made by the construction/demolition phases to the total environmental impact. Such observations can help guide process development.

Exergetic efficiency as normally defined (based on the production phase only) is not a useful concept when comparing processes driven by solar energy with their conventional counterparts. To be of more use, the exergy analysis would have to be extended to include (like the LCA) the construction/demolition phases.

### 5.3 Recommendations

During the course of this project, ECN management has decided that the subject of eco-efficiency (of industrial processes) will not be further developed as an R&D topic in its own right. Accordingly, the above-mentioned long-term objective, to develop a new methodology, will not be pursued. However, in view of the encouraging results obtained in this and previous studies, it is recommended to:

- apply the existing techniques on an ad-hoc basis in support of other technological developments,
- continue with a minimal gatekeeping activity to maintain awareness of developments in this field, especially of commercial software products and their applications.

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## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

E	exergy
$p_0$	reference pressure (for exergy calculation)
$T_0$	reference temperature (for exergy calculation)
BFW	boiler feed water
BL	battery limits (system boundary of entire site)
CW	cooling water
HHV	higher heating value
HP	high pressure (steam)
LCA	Life Cycle Analysis
LP	low pressure (steam)
MIBK	methylisobutylketone
MP	medium pressure (steam)
MTBE	methyltertiarybutylether
NG	natural gas
PEC	photo-electrochemical
Pt	eco-points
WBCSD	World Business Council for Sustainable Development





## APPENDIX A: ECO-INDICATOR '95

The description of the eco-indicator '95 method below is closely based on a CD-ROM which is distributed by PRé Consultants B.V. More information can be found in [15].

After the inventory and classification phases have been completed, the environmental effects of two products can be compared. The results however prove to be difficult to interpret. One product or process causes e.g. more winter smog and acidification, but scores better on the other environmental effects. Thus the LCA does not reveal which is the better product or process. What is missing is the mutual weighting of the effects. Although the LCA method describes how this should be, this weighting is almost never carried out because of a lack of data. The Eco-indicator '95 has plugged this gap.

The first step in any further interpretation consists of comparing the scores with another value. PRe Consultants B.V. developed an inhabitant-equivalent for this, i.e. the environmental effects that an average European causes in a year. In LCA terminology this is called the normalisation step. The values are normalised to the average European. The effects are now compared on the scale of inhabitant equivalents.

Normalisation reveals which effects are large and which are small in relative terms. However, it does not yet say anything about the relative importance of the effects. A small effect can very well be the most important. A weighting step is therefore necessary to achieve an overall result. All effects are now scaled to a certain measure of seriousness. In this example the seriousness is indicated in Eco-indicator points.

The problem, of course, lies in determining the weighting factors. Much consideration has been given to setting up the Eco-indicator value. After detailed analysis of the options the so-called Distance-to-Target principle was chosen for determining the weight factors. This principle has already been in use for some years in the Swiss Ecopoints weighting system. The underlying premise is that there is a correlation between the seriousness of an effect and the distance between the current level and the target level. Thus if acidification has to be reduced by a factor of 10 in order to achieve a sustainable society and smog by a factor of 5, then acidification is regarded as being twice as serious; the reduction factor is the weighting factor.

The term 'target level' still embodies a major problem. What is a good target level, and how can such a level be defined? The above-mentioned Swiss Ecopoints method uses political target levels from government policy papers. These levels are often defined on the basis of a compromise between feasibility (cost) and desirability.

For the Eco-indicator '95 it was decided to define target levels that are independent of politics and are based on scientific information. The problem then arises again that scientists have different views on what constitutes a good target level. One of the reasons for this is that different environmental problems cause different types of damage. Smog, for example, results in health complaints, while acidification causes major damage to forests. To ensure that the target level for acidification is equivalent to that for smog a correlation must be established with the damage caused by the effect. The premise is that the target level for each effect yields uniformly serious damage. The following damage levels are assumed to be equivalent:

- The number of fatalities as a consequence of environmental effects. The level chosen as acceptable is 1 fatality per million inhabitants per year.
- The number of people who become ill as a consequence of environmental effects. This refers in particular to winter and summer smog. The acceptable level set is that smog periods should hardly ever occur again.
- Ecosystem degradation. A target level has been chosen at which 'only' 5% ecosystem

degradation will still occur over several decades.

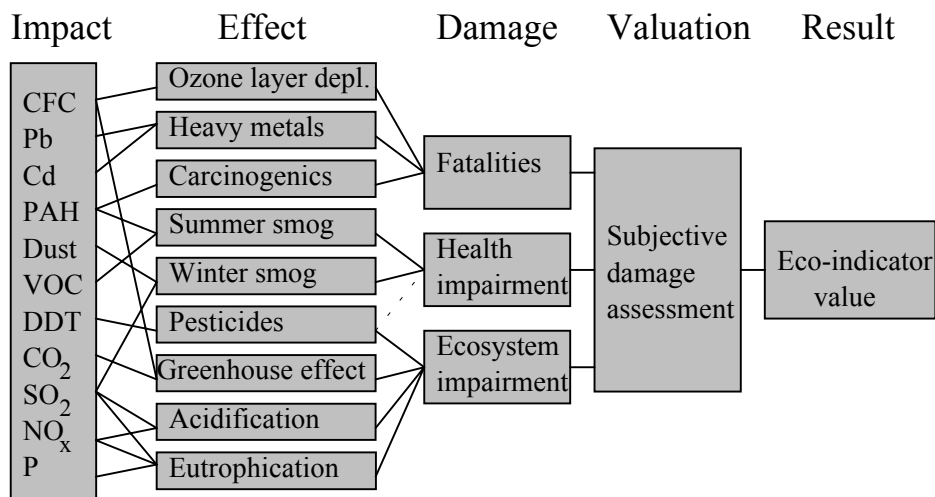
Setting equivalents for these damage levels is a subjective choice that cannot be scientifically based. It is therefore also possible to make different assumptions which could cause the weighting factors to change.

To establish a correlation between these damage levels and the effects a detailed study was carried out of the actual state of the environment in Europe. The current status of each effect was determined and by what degree a particular effect has to be reduced to reach the damage level defined for it. Much work has been carried out particularly by the Dutch National Institute for Public Health and Environmental Hygiene (RIVM) in this field. Detailed maps of Europe are now available in which the environmental problems are shown in a high degree of detail. These data were used to determine the current level of an environmental problem and by what factor the problem must be reduced to reach an acceptable level. The table below lists the weighting factors and the criteria applied.

Environmental effect	Weighting factor	Criterion
Greenhouse effect	2.5	0.1°C rise every 10 years, 5% ecosystem degradation
Ozone layer depletion	100	Probability of 1 fatality per year per million inhabitants
Acidification	10	5% ecosystem degradation
Eutrophication	5	Rivers and lakes, degradation of an unknown number of aquatic ecosystems (5% degradation)
Summer smog	2.5	Occurrence of smog periods, health complaints, particularly amongst asthma patients and the elderly, prevention of agricultural damage
Winter smog	5	Occurrence of smog periods, health complaints, particularly amongst asthma patients and the elderly
Pesticides	25	5% ecosystem degradation
Airborne heavy metals	5	Lead content in children's blood, reduced life expectancy and learning performance in an unknown number of people
Waterborne heavy metals	5	Cadmium content in rivers, ultimately also impacts on people (see airborne)
Carcinogenic substances	10	Probability of 1 fatality per year per million people

This table reveals that high priority must be given to limiting substances causing ozone layer damage and the use of pesticides. The latter is becoming a very serious problem in the Netherlands in particular. Furthermore, a great deal of consideration must be given to the diffusion of acidifying and carcinogenic substances.

The weighted environmental effects can now be added to obtain one single value: the eco-indicator. The figure below shows the weighting method in a schematic way.



It is apparent from the table that a number of effects that are generally regarded as environmental problems have not been included. The following reasons can be advanced for the omission of a number of effects:

- Toxic substances that are only a problem in the workplace*

Many substances are only harmful if they occur above a certain concentration. Such harmful concentrations can occur relatively easily in the workplace, while the concentration in the outside atmosphere often remains very low and well below the damage threshold. This happens because the substances are generally greatly diluted and because many substances disappear from the atmosphere because of natural decomposition processes. Only substances that actually occur in harmful concentrations in the atmosphere are included in the Eco-indicator, while the rest are disregarded. This means that a product with a low Eco-indicator score can still cause poor working conditions because substances are released that are harmful locally.
- Exhaustion (depletion) of raw materials*

If a product made of very rare raw materials is used this rarity is not expressed in the indicator; after all, the fact that a substance is rare does not cause any damage to health. The emissions arising from extraction of the raw materials are included and are usually extensive because ever lower-grade ores have to be used. Incidentally, the term 'exhaustion' is very difficult to define. Alternatives are available for most raw materials, and recycling could enable raw materials to remain in circulation for much longer. In fact minerals never disappear from the Earth; at worst they are diffused in an unfortunate manner.
- Waste*

The fact that waste occupies space is not particularly important in environmental terms because the amount of ecosystem lost to the mountains of waste is relatively small compared with the damage to ecosystems caused, for example, by acidification. However, the substances released by waste (heavy metals, or CO<sub>2</sub> on incineration) are very important. These latter effects are included in the indicator, but the quantity of waste in itself is not part of the assessment process.
- Other environmental effects*

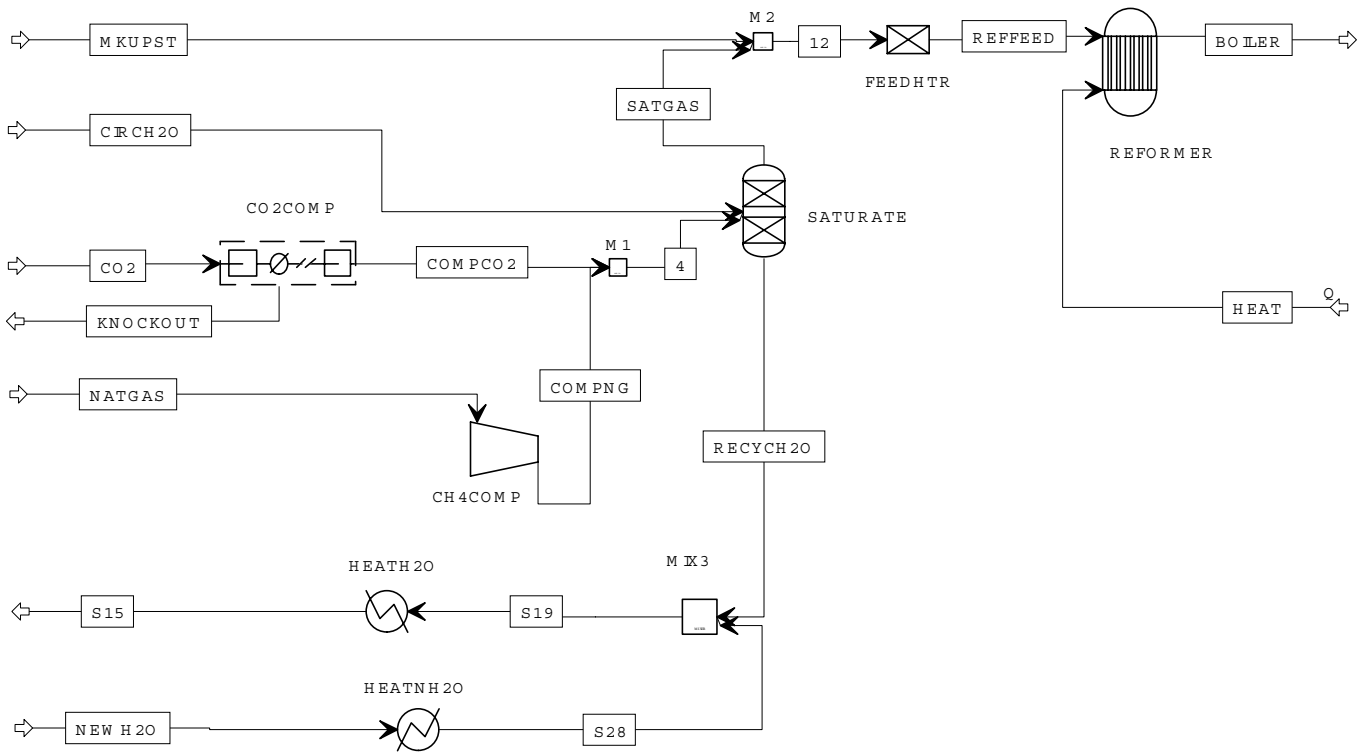
There are a number of local environmental effects which are recognised as having an effect on our society but which are not included in the eco-indicator. Examples of this are the thermal pollution of surface water, the occupation of space, the emission of foul-smelling gases, noise, and the emission of radiation.

As a result of these differences the Eco-indicator can be seen as an indicator of emissions, and raw materials depletion and the use of space by waste must be evaluated separately at present.

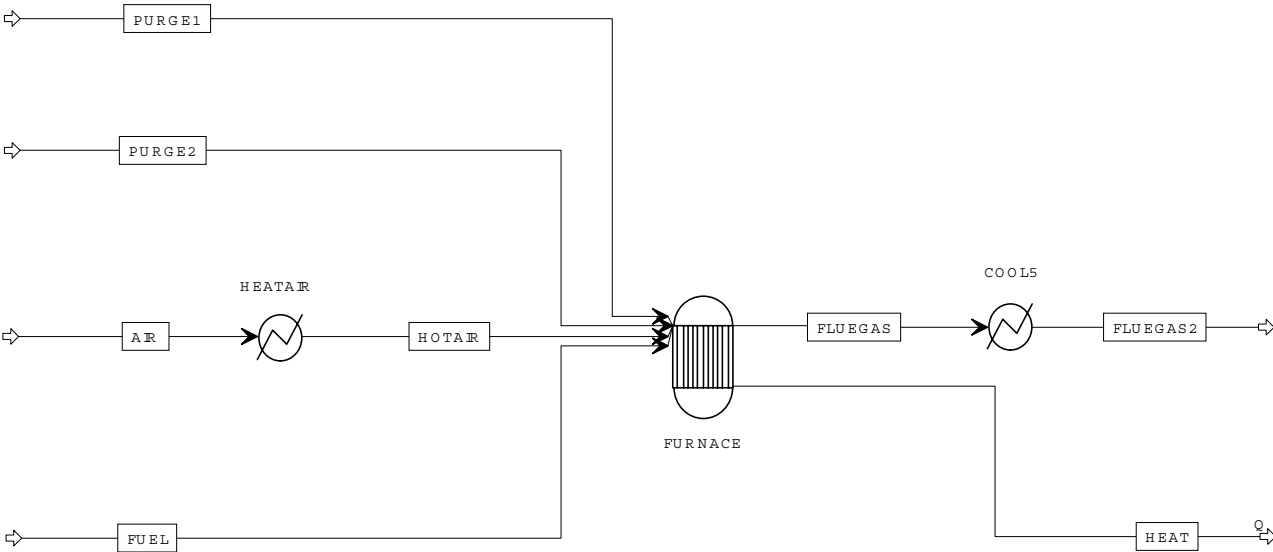


# APPENDIX B: CONVENTIONAL PROCESS: FLOWSHEETS

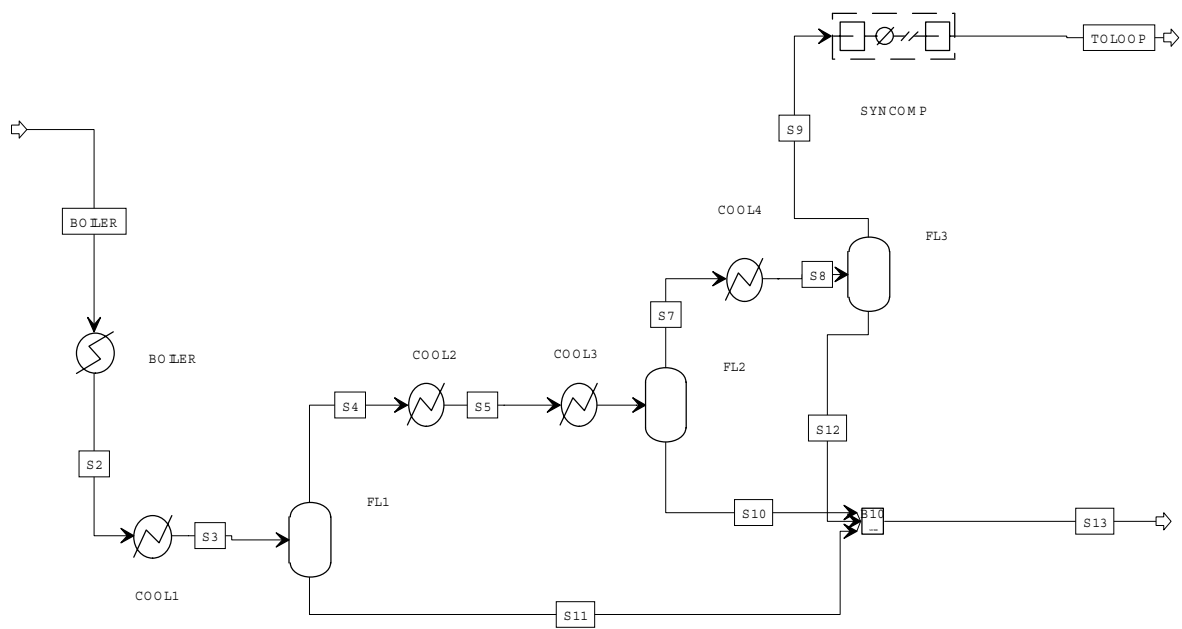
## Section 1: Reforming (without furnace)



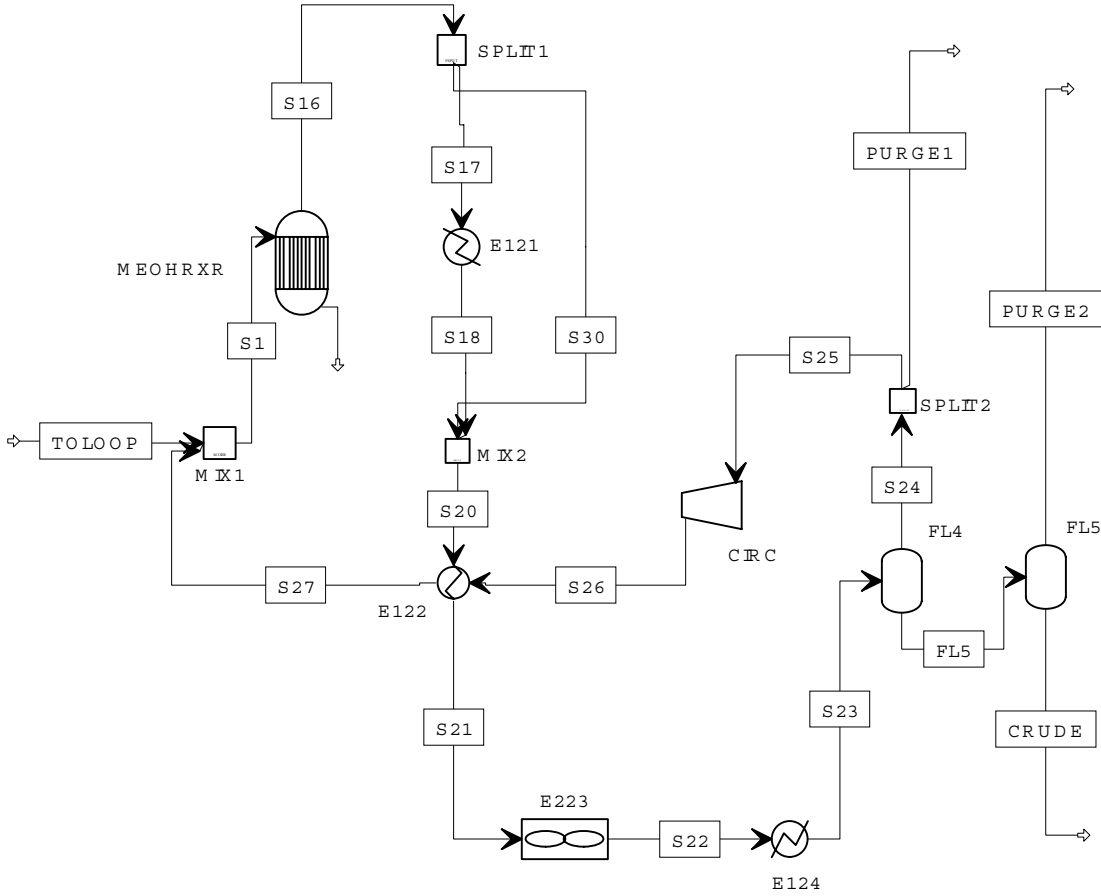
Section 1A: Reforming furnace



## Section 2: Heat recovery

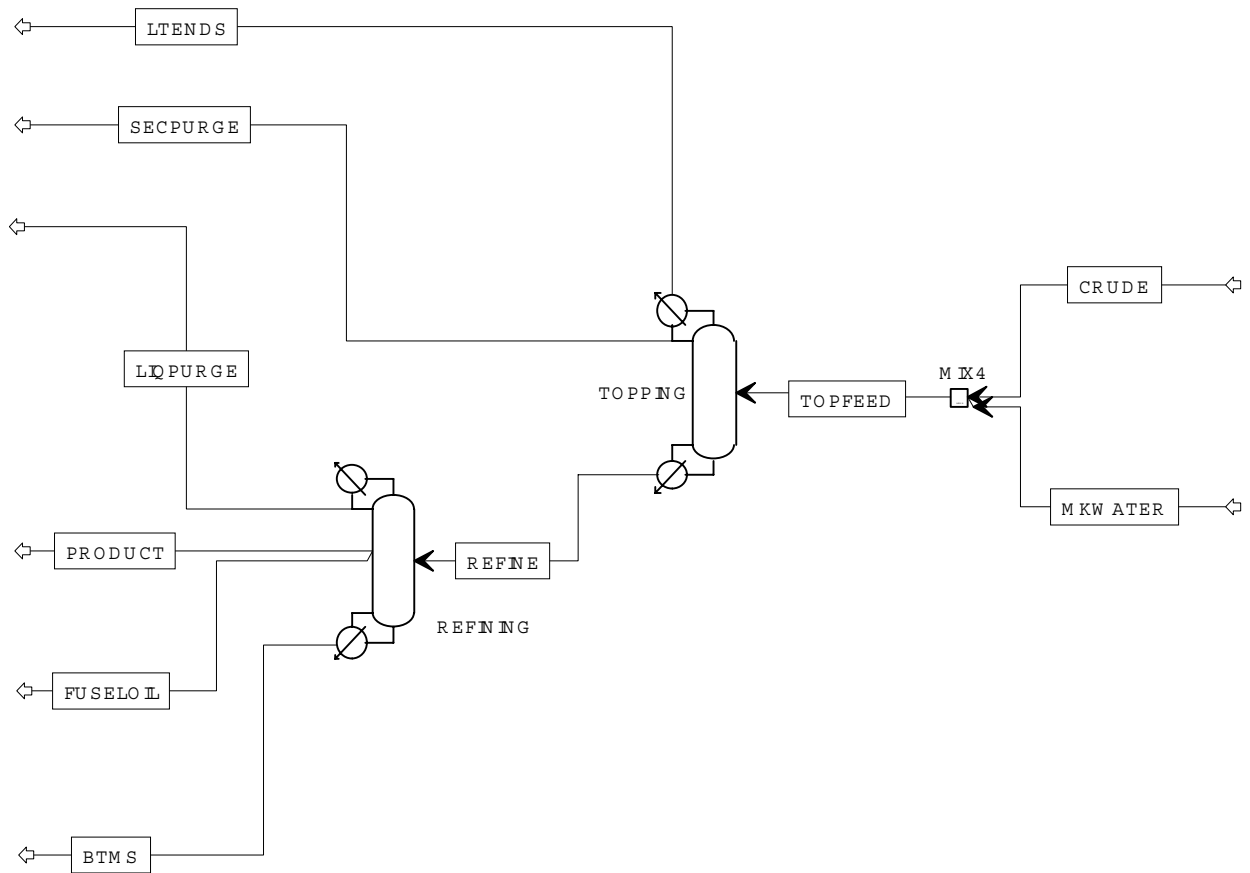


Section 3: Methanol synthesis





## Section 4: Distillation





## APPENDIX C: CONVENTIONAL PROCESS: MODELLING OF THE WATER RECYCLE LOOP

Section 1 of the process flowsheet (the reformer section) contains two input water streams (CIRCH<sub>2</sub>O and NEWH<sub>2</sub>O) and one output water stream (S15). In reality the stream S15 is recycled back to CIRCH<sub>2</sub>O, but this recycle loop has not been modelled in Aspen Plus. This was because addition of another recycle loop to such a flowsheet (which already contains several recycle loops) would lead to severe computational (convergence) problems for the Aspen Plus model. Instead of a rigorous Aspen Plus calculation, an approximate procedure was used whereby the flow of NEWH<sub>2</sub>O (the pure water make-up stream) was adjusted manually so that the mass flows of CIRCH<sub>2</sub>O and S15 were equal. This procedure leads to a mismatch in the compositions, because whereas CIRCH<sub>2</sub>O is assumed in the Aspen Plus model to be a pure water stream, S15 is calculated by the model to contain small quantities of dissolved gases (CH<sub>4</sub>, CO<sub>2</sub>, ...).

(In reality some of this gas might be deliberately flashed off before recycling the water, but this possibility has not been further considered here.) A more rigorous approach, including recycling of the dissolved gases, would introduce small changes in the entire flowsheet, with the overall result of a slightly higher methanol production. However since such changes would be at the level of less than 1%, they are of no practical consequence, and the approximate procedure used here is considered to be adequate.

In the exergy analysis, the exergies of the above-mentioned streams are included in the exergy balance, in order to ensure a consistent calculation of the internal exergy losses. However the exergy of stream S15 is not counted as an external exergy loss, because in reality this exergy is recycled.



# APPENDIX D: CONVENTIONAL PROCESS: HEAT AND MATERIAL BALANCES

## Section 1 Reforming (without furnace)

Heat and Material Balance Table

Stream ID	Stream Description	Stream Type	INATGAS	COMPNG	CO2	KNOCKOUT	COMPCOX	4	CHRCHO	RECYCHO	NEWCHO	S28	S19	S15	SATGAS	MIKIPST	I2	REFFEED	POILER
Temperature	C		26.0	49.0	43.0	1408	1408		195.0	147.8	20.0	148.0	147.9	195.0	190.6	225.9	203.6		
Pressure	BAR		21.700	27.500	1.400	27.500	27.500		27.500	27.500	27.500	27.500	27.500	27.500	27.500	27.500	26.000	26.000	18.000
Volume Flow	KMOL/HR		1.000	1.000	0.992	1.000	1.000		0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000	0.997	1.000	1.000
Mass Flow	KG/HR		1785.598	1785.598	391.843	2377.441	2377.441		22758.488	20548.755	2201.131	2201.131	22749.886	22749.886	4851.145	2512.700	7099.845	7099.845	10238.150
Volume Flow	CUM/HR		29552.000	29552.000	24823.000	54775.000	54775.000		410000.000	370345.799	39654.000	39654.000	409992.729	409992.729	94493.201	46267.000	139696.201	139696.201	139696.201
Enthalpy	MMKCAL/HR		1944.521	1655.238	10954.414	2996.603	2996.603		507.011	428.210	39.721	45.837	474.047	474.047	507.301	3578.504	9991.769	18758.224	58536.190
Mass Flow	KMOL/HR		-32.882	-32.541	-51.524	-83.907	-83.907		-1468.013	-1561.929	-151.465	-145.903	-1507.833	-1485.225	-207.990	-141.777	-349.767	-322.673	-214.211
Mass Flow	CH4		10.535	10.535	547.682	547.682		6.249	6.249	6.249	6.249	6.249	6.249	6.249	551.918	551.918	551.918	551.918	752.122
Mass Flow	H2O		1703.282	1703.282	1.125	1704.407	1704.407		6.184	6.184	6.184	6.184	6.184	6.184	1698.222	1698.222	1698.222	1698.222	239.677
Mass Flow	H2				35.866	35.866		20335.981	20335.981	2201.131	2201.131	2201.131	22737.112	22737.112	2258.343	2512.700	4771.044	4771.044	2991.687
Mass Flow	CO				5.563	5.563		0.005	0.005	0.005	0.005	0.005	0.005	0.005	5.559	5.559	5.559	5.559	4872.674
Mass Flow	N2			1.428	1.428	1.657	1.657		0.003	0.003	0.003	0.003	0.003	0.003	3.083	3.083	3.083	3.083	178.949
Mass Flow	C2H6		69.817	69.817	69.817	69.817		0.333	0.333	0.333	0.333	0.333	0.333	69.484	69.484	69.484	69.484	0.007	
Mass Flow	C3H8		0.536	0.536	0.536	0.536		0.001	0.001	0.001	0.001	0.001	0.001	0.535	0.535	0.535	0.535	trace	
Mass Flow	O2																		trace
Mass Flow	CH3OH																		trace
Mass Flow	ACETONE																		trace
Mass Flow	N-BUT-01																		0.001
Mass Flow	DIMETH-01																		trace
Mass Flow	TOTEN	KW	406271.455	496607.869	-59172.327	-56661.242	350006.627	-1.8743E+5	-27131.474	-20665.129	-21.260E+5	-20665.129	-21.260E+5	-1.8631E+5	354517.724	5228.938	359746.682	391256.614	494699.741
Mass Flow	CHEMEX	KW	473038.858	472028.858	3691.233	3691.233	423770.452	5689.615	500.283	500.283	500.283	500.283	7284.752	7284.752	424788.771	628.175	423416.987	423416.987	490075.956
Mass Flow	RYSEX	KW	3704.907	3996.867	174.780	2105.881	5762.103	1929.473	36.401	1054.017	10908.462	10908.462	10908.462	10908.462	16955.566	12551.809	29305.279	46238.751	70904.505
Mass Flow	MIXEX	KW	-255.835	-255.000	-118.857	-125.729	-1244.504	> -0.001	> -0.001	> -0.001	> -0.001	> -0.001	> -0.001	> -0.001	-3185.356	< 0.001	-4056.412	-4156.255	-3856.979
Mass Flow	TOTEX	KW	424547.830	423720.705	3747.155	5971.385	430888.051	252919.087	386.683	1604.300	181827.685	1604.300	181827.685	26832.492	438558.920	13179.984	450965.834	467259.484	552113.482

Section 1A: Reforming furnace

Heat and Material Balance Table

Stream ID	AIR	HOTAIR	FUEL	PURGE1	PURGE2	FLUEGAS	FLUEGAS2
Temperature	20.0	366.0	26.0	45.0	45.6	900.0	150.0
Pressure	1,000	1,000	21,700	75,600	5,000	1,000	1,000
Vapor Frac	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Mole Flow	8318,776	8318,776	436,565	650,914	77,604	9322,048	9322,048
Mass Flow	240000,000	240000,000	7003,700	8488,719	2477,376	257969,795	257969,795
Volume Flow	202637,575	442208,431	477,435	224,776	403,656	909465,652	327778,994
Enthalpy	-0,306	20,201	-7,808	-12,110	-4,718	-112,895	-170,607
Mole Flow							
CO2				77,796	42,178	841,941	841,941
CH4			436,565	232,807	25,068		
H2O				0,453	0,530	1733,072	1733,072
H2				316,253	3,477	< 0,001	< 0,001
CO				15,162	0,350	< 0,001	< 0,001
N2	6571,833	6571,833		2,829	0,134	6574,796	6574,796
C2H6				0,287	0,090		
C3H8				< 0,001	< 0,001		
O2	1746,943	1746,943				172,239	172,239
CH3OH				5,258	5,712	trace	trace
ACETONE				0,008	0,008		
N-BUT-01				0,002	0,001		
DIMET-01				0,059	0,056		
TOTEN	KW	23492,899	97255,857	66989,667	2389,237	-13963,825	-81081,090
CHEMEX	KW	3240,857	100640,252	77198,973	7476,113	7064,610	7064,610
PHYSEX	KW	-72,497	907,588	1885,754	84,620	45760,480	5436,055
MIXEX	KW	-2944,071	0,000	-469,323	-59,051	-5453,451	-5448,656
TOTEX	KW	224,289	101547,840	78615,404	7501,682	47371,639	7052,008

Section 2: Heat recovery

Heat and Material Balance Table

Stream ID	BOILER	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	TOLOOP
Temperature	C	859.6	166.0	136.0	104.0	85.0	84.9	40.0	39.9	84.9	136.0	39.9	106.0	40.0
Pressure	BAR	18,000	18,000	18,000	17,900	17,800	17,700	17,600	17,400	17,700	18,000	17,400	17,400	82,500
Vapor Frac		1,000	0.864	1,000	0.876	0.846	1,000	0.972	1,000	0.000	0.000	0.000	< 0.001	0.997
Mole Flow	KMOL/HR	10258.150	10258.150	8867.936	8867.936	8867.936	7503.025	7503.025	7294.458	1364.911	1390.215	208.567	2963.693	7294.458
Mass Flow	KG/HR	139696.201	139696.201	114648.938	114648.938	114648.938	90058.173	90058.173	86300.644	24590.765	25047.263	3757.530	53395.557	86300.644
Volume Flow	CUM/HR	53836.190	20649.512	16746.703	13663.469	12625.871	12668.749	10834.415	10953.023	26.338	28.507	3.838	58.602	2349.190
Enthalpy	MMKCAL/HR	-214.211	-273.952	-289.591	-210.196	-214.381	-122.181	-126.891	-112.619	-92.200	-92.493	-14.272	-198.965	-113.041
Mole Flow	KMOL/HR													
CO2		752.122	752.122	752.014	752.014	752.014	751.947	751.947	751.942	0.067	0.108	0.006	0.180	751.942
CH4		259.627	259.627	259.617	259.617	259.617	259.613	259.613	259.612	0.004	0.011	< 0.001	0.015	259.612
H2O		2991.687	2991.687	1601.645	1601.645	1601.645	236.823	236.823	28.263	1364.822	1390.042	208.561	2963.425	28.263
H2		4872.674	4872.674	4872.629	4872.629	4872.629	4872.614	4872.614	4872.613	0.015	0.044	0.001	0.060	4872.613
CO		1378.949	1378.949	1378.940	1378.940	1378.940	1378.937	1378.937	1378.937	0.003	0.010	< 0.001	0.012	1378.937
N2		3.083	3.083	3.083	3.083	3.083	3.083	3.083	3.083	trace	< 0.001	trace	< 0.001	3.083
C2H6		0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	trace	trace	trace	trace	0.007
C3H8		trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
O2		trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
CH3OH		0.001	0.001	0.001	0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
ACETONE		trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
N-BUT-01		trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
DIMET-01		trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
TOTEN	KW	494699.741	425222.441	407034.515	405254.591	400387.870	415211.971	409734.014	412212.081	-14824.135	-13453.249	-2478.079	-30755.463	411721.901
CHEMEX	KW	490075.956	490075.956	490075.956	489721.834	489722.024	489377.906	489378.030	488935.664	343.796	354.285	52.290	750.369	488935.664
PHYSEX	KW	70904.505	29190.016	22649.858	16837.722	15362.476	15156.470	13913.566	14264.474	178.615	547.389	3.734	661.038	21798.338
MIXEX	KW	-8866.979	-8642.075	-7357.999	-5863.606	-5343.682	-5345.243	-4776.253	-4777.704	-0.223	-0.353	-0.019	-0.608	-4449.701
TOTEX	KW	552113.482	510623.897	505367.814	500695.949	499740.818	499189.133	498515.342	498422.434	522.188	901.322	56.004	1410.799	506284.301

Section 3: Methanol synthesis

Heat and Material Balance Table

Stream ID	TOLOOP	S1	S16	S17	S18	S30	S20	S21	S22	S23	S24	S25	S26	S27	PURGE1	FLS	PURGE2	CRUDE
Temperature		40.0	240.0	240.0	130.0	240.0	168.3	123.0	60.0	45.0	45.0	45.0	45.0	55.5	120.0	45.0	45.0	45.6
Pressure		82.500	82.500	82.500	81.000	82.500	81.000	81.000	77.300	75.600	75.600	75.600	75.600	83.000	83.000	75.600	75.600	5.000
Vapor Flow		0.997	1.000	1.000	1.000	1.000	1.000	0.992	0.907	0.900	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000
Mole Flow		7294.458	21590.149	26987.686	26987.686	5397.537	26987.686	26987.686	26987.686	24287.828	23635.914	23635.914	23635.914	23637.569	23637.569	650.914	2699.858	71.604
Mass Flow		86300.644	394568.903	315655.123	315655.123	78913.781	394568.903	394568.903	394568.903	316743.253	308254.534	308254.534	308254.534	308288.259	308288.259	8488.719	77825.650	2477.376
Volume Flow		2349.190	11844.168	11274.922	9298.427	2818.730	12186.451	10722.519	8776.209	8485.461	8387.148	8162.372	7717.726	9404.711	9404.711	224.776	98.214	403.656
Enthalpy		-113.041	-537.602	-434.020	-432.779	-108.505	-561.284	-574.542	-608.569	-614.089	-451.849	-439.740	-437.819	-424.561	-424.561	-12.110	-4.718	-157.522
Mole Flow		751.942	2374.580	2374.580	2374.580	593.645	2374.580	2374.580	2374.580	2968.225	2968.225	2968.225	2968.225	2825.047	2825.047	65.382	42.178	23.204
CH4		259.612	8713.638	6970.910	6970.910	1744.728	8713.638	8713.638	8713.638	8713.638	8886.837	8454.029	8454.029	8454.029	8454.029	232.807	26.801	25.068
H2O		28.263	44.707	525.356	525.356	131.339	656.695	656.695	656.695	656.695	16.897	16.444	16.444	16.444	16.444	0.453	639.798	0.530
H2		4872.413	16356.891	9443.170	9443.170	2360.793	11803.963	11803.963	11803.963	11803.963	11800.466	11484.214	11484.214	11484.214	316.253	3.497	3.477	0.019
CO		1378.537	1929.532	566.100	566.100	113.220	566.100	566.100	566.100	566.100	565.746	550.584	550.584	550.584	0.354	0.354	0.350	0.004
N2		3.083	105.705	84.564	84.564	21.141	105.705	105.705	105.705	105.705	102.738	102.622	102.622	102.622	2.829	0.134	0.134	0.004
C2H6		0.007	10.826	8.561	8.561	2.165	10.826	10.826	10.826	10.826	10.710	10.423	10.423	10.819	0.287	0.115	0.090	0.025
C3H8		trace	0.013	0.010	0.013	0.003	0.013	0.013	0.013	0.013	0.013	0.012	0.013	0.013	< 0.001	< 0.001	< 0.001	< 0.001
O2		< 0.001	190.932	1726.922	1726.922	481.730	2158.652	2158.652	2158.652	2158.652	196.190	190.932	190.932	190.932	5.238	1962.463	5.712	1956.751
CH3OH		trace	0.293	0.475	0.475	0.119	0.593	0.593	0.593	0.593	0.301	0.293	0.293	0.293	0.008	0.292	0.008	0.284
ACETONE		0.056	0.856	0.685	0.685	0.171	0.856	0.856	0.856	0.856	0.057	0.056	0.056	0.056	0.002	0.798	0.001	0.797
N-BUT-01		trace	2.219	1.936	1.936	0.484	2.419	2.419	2.419	2.419	2.419	2.419	2.419	2.419	0.059	0.220	0.056	0.164
DIMET-01		411721.901	286270E+6	239247E+6	231979E+6	584946.796	290292E+6	288750E+6	284793E+6	284151E+6	249926E+6	24363E+6	243507E+6	243507E+6	66989.667	341891.927	2389.237	339502.710
TOTEN		488935.664	329250E+6	2.62593E+6	2.62593E+6	656482.489	3.28241E+6	3.28241E+6	3.28241E+6	3.28241E+6	2.80336E+6	2.80336E+6	2.80336E+6	2.80336E+6	71798.973	398335.530	7476.113	398857.927
CHEMEX		21796.338	94276.261	10949.600	798.978	18209.932	83648.228	79210.167	68564.393	67298.861	70363.298	68478.204	70061.171	72915.890	1885.754	517.191	84.620	106.900
PHYSEX		-4449.701	-23513.960	-20214.862	-16171.890	-17105.933	-4042.972	-2125.889	-2125.889	-18484.096	-17512.047	-17042.724	-16947.051	-17152.370	-469.323	-972.056	-59.051	-851.785
MIXEX		506284.301	3.46326E+6	2.68280E+6	2.67444E+6	670649.448	3.34474E+6	3.34038E+6	3.33215E+6	3.33123E+6	2.93341E+6	2.85480E+6	2.85667E+6	2.85920E+6	78615.404	397880.665	7501.682	399113.042
TOTEX																		



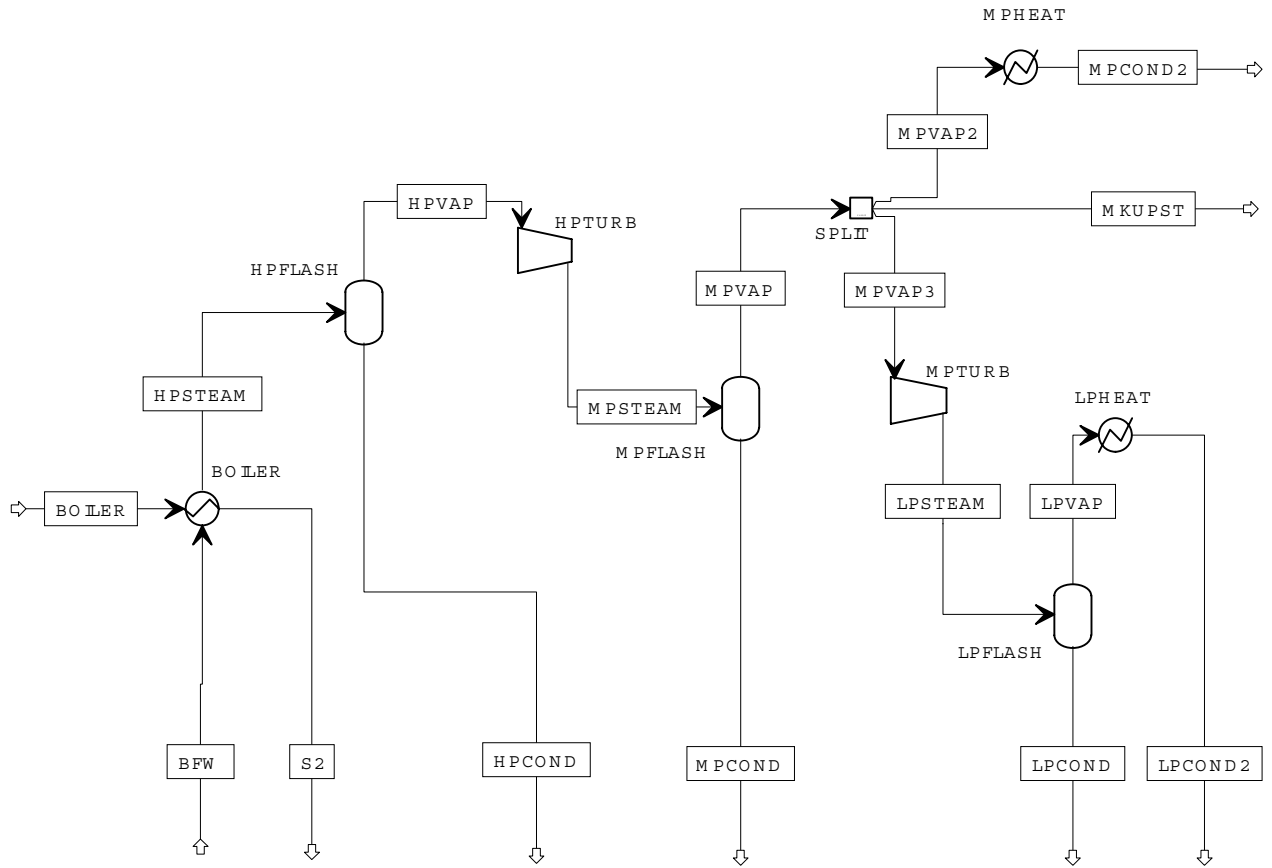
Section 4: Distillation

Heat and Material Balance Table												
Stream ID		CRUDE	MK WATER	TOPFEED	LTENDS	SECPURGE	REFINE	LIQPURGE	FUSELOIL	BTMS	PRODUCT	
Temperature	C	45,6	40,0	43,2	43,7	43,7	86,3	74,9	86,1	118,7	75,1	
Pressure	BAR	5,000	5,000	5,000	1,500	1,500	1,800	1,500	1,910	1,970	1,515	
Vapor Frac		0,000	0,000	0,001	1,000	0,000	0,000	0,000	0,000	0,000	0,000	
Mole Flow	KMOL/HR	2622,254	555,084	3177,339	35,254	0,356	3141,729	0,031	19,700	1192,997	1929,000	
Mass Flow	KG/HR	75348,276	10000,000	85348,276	1388,485	11,516	83948,275	1,000	558,766	21579,182	61809,327	
Volume Flow	CUM/HR	94,684	10,215	118,930	611,704	0,015	110,423	0,001	0,750	24,089	84,120	
Enthalpy	MMKCAL/HR	-157,522	-37,986	-195,508	-2,700	-0,020	-189,286	-0,002	-1,151	-79,337	-107,384	
Mole Flow	KMOL/HR											
CO2		23,204		23,204	23,201	0,002	trace					
CH4		1,734		1,734	1,734	< 0,001	trace					
H2O		639,268	555,084	1194,353	trace	trace	1194,353	trace	5,176	1189,176	trace	
H2		0,019		0,019	0,019	trace	trace					
CO		0,004		0,004	0,004	trace	trace					
N2		0,004		0,004	0,004	trace	trace					
C2H6		0,025		0,025	0,025	trace	trace					
C3H8		< 0,001		< 0,001	< 0,001	trace	trace					
O2												
CH3OH		1956,751		1956,751	9,821	0,351	1946,579	0,031	14,520	3,027	1929,000	
ACETONE		0,284		0,284	0,281	0,003	trace					
N-BUT-01		0,797		0,797	trace	trace	0,797		0,003	0,794		
DIMET-01		0,164		0,164	0,164	< 0,001	trace					
TOTEN	KW	339502,710	-6596,726	332905,875	-87,544	63,507	337002,622	5,582	2549,058	-11086,877	345031,158	
CHEMEX	KW	390857,927	138,771	390991,016	2704,386	71,278	388202,377	6,210	2892,941	1485,807	383817,420	
PHYSEX	KW	106,900	5,889	104,901	15,863	0,007	506,896	0,006	4,472	341,639	358,793	
MIXEX	KW	-851,785	> -0,001	-1128,019	-20,676	-0,019	-1057,377	> -0,001	-6,239	-15,946	> -0,001	
TOTEX	KW	390113,042	144,660	389967,899	2699,573	71,266	387651,896	6,215	2891,174	1811,500	384176,213	

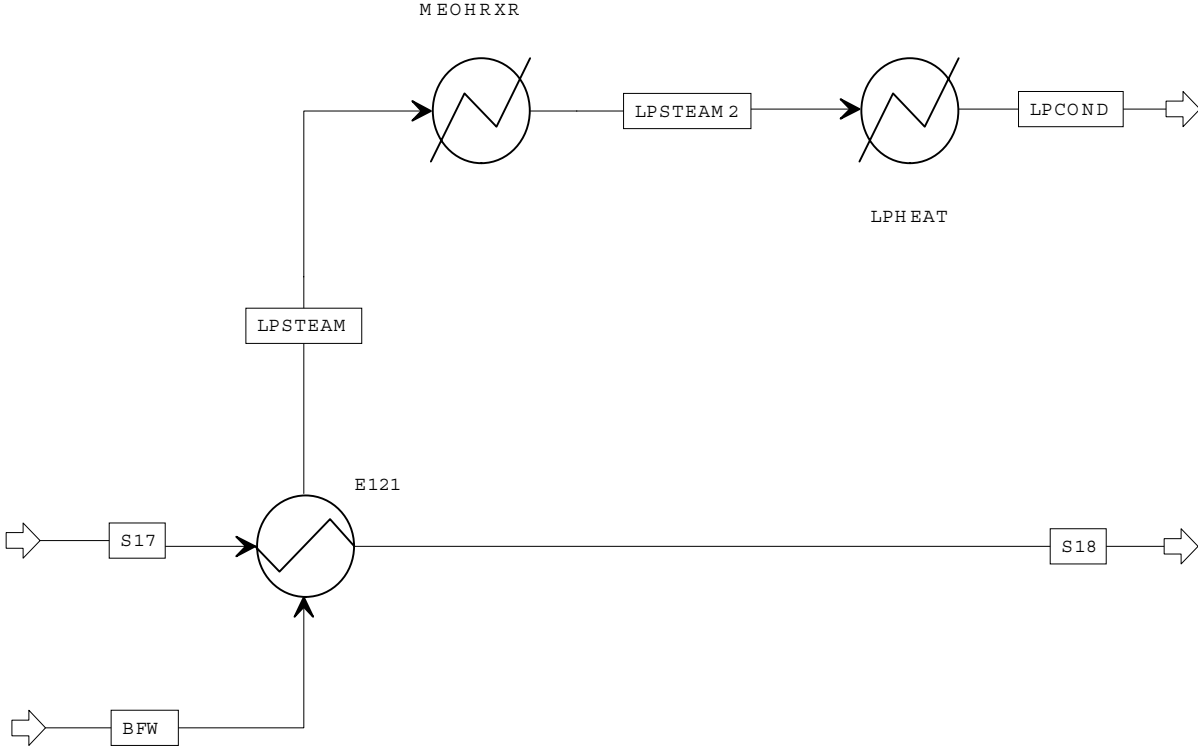


# APPENDIX E: CONVENTIONAL PROCESS: STEAM SYSTEM FLOWSHEETS

## Section 5: Steam system part 1



Section 5: Steam system part 2



# APPENDIX F: CONVENTIONAL PROCESS: STEAM SYSTEM HEAT AND MATERIAL BALANCES

## Section 5: Steam system part 1

Heat and Material Balance Table

Stream ID	BFW	BOILER	HFCOND	HFSTEAM	HPVAP	LFCOND2	LFSTEAM	LPVAP	MKUPST	MFCOND	MPCOND2	MFSTEAM	MPVAP	MPVA2	MPVA3	\$2
Temperature			310.1	310.1	310.1	140.1	140.1	140.1	225.9	225.9	200.0	225.9	225.9	225.9	225.9	166.0
Pressure	20.0	859.6	100,000	100,000	100,000	3,500	3,500	3,500	26,000	26,000	26,000	26,000	26,000	26,000	26,000	18,000
Vapor Frac	0.000	1.000	0.000	0.995	0.995	0.000	0.928	1.000	1.000	0.000	0.000	0.894	1.000	1.000	1.000	1.000
Mole Flow	88000.000	139096.201	23.869	4884.742	4860.873	56.019	717.542	717.542	2512.700	516.343	1058.268	4860.873	4344.530	1058.268	773.561	10238.153
Mass Flow	88.148	53837.908	430.011	88000.000	87569.989	1009.205	12926.719	12926.719	45267.000	9302.005	19065.000	87569.989	78267.924	19065.000	13935.924	139696.201
Volume Flow			0.683	1654.024	1633.341	1.155	14.421	6882.022	3578.880	12.113	23.763	6200.097	6187.984	1507.809	1101.796	20649.518
Enthalpy			-1.488	-276.241	-274.753	-3.723	-47.975	-44.534	-141.777	-33.356	-68.984	-275.493	-245.137	-59.712	-43.648	-273.952
Mole Flow																
CH2		752.121														752.121
CH4		259.606														259.606
H2O	4884.742	2991.697	23.869	4884.742	4860.873	56.019	717.542	717.542	2512.700	516.343	1058.268	4860.873	4344.530	1058.268	773.561	2991.697
H2		4872.677														4872.677
CO		1378.951														1378.951
N2		3.083														3.083
CH6		0.007														0.007
CH8		trace														trace
O2		0.001														0.001
CH10H		trace														trace
ACETONE		trace														trace
N-BUT-01		trace														trace
DIMET-01		trace														trace
TOTEN	KW	-6004.010	494703.756	-114.878	9440.162	-536.891	-7215.280	578.883	1115.774	5228.891	-8380.842	5205.913	9940.901	2202.240	1609.760	42522.983
CHEMEX	KW	1221.186	400076.013	5.967	1221.186	14.005	179.385	193.390	179.385	628.175	129.086	264.567	1215.218	1086.132	193.390	490076.013
PHYSEX	KW	288.932	70007.566	56.760	27721.477	23.057	207.245	2544.070	2221.012	12551.782	602.790	956.708	23205.176	21702.386	3864.199	291900.019
MIXEX	KW	> 0.001	-8865.983	< 0.001	> -0.001	0.000	0.000	0.000	0.000	< 0.001	< 0.001	< 0.001	< 0.001	0.000	0.000	-8642.074
TOTEX	KW	1510.118	592116.996	62.727	28942.663	37.062	386.630	2737.460	2700.398	13179.957	1221.275	23220.394	22788.519	5550.973	4057.589	510623.588

Section 6: Steam system part 2

Heat and Material Balance Table									
Stream ID		BFW	LPCOND	LPSTEAM	LPSTEAM2	S17	S18		
Temperature	C	20,0	120,0	140,1	140,1	240,0	150,0		
Pressure	BAR	3,500	3,500	3,500	3,500	82,500	82,500		
Vapor Frac		0,000	0,000	0,735	0,992	1,000	1,000		
Mole Flow	KMOL/HR	1998,304	1998,304	1998,304	1998,304	21590,149	21590,149		
Mass Flow	KG/HR	36000,000	36000,000	36000,000	36000,000	315655,133	315655,133		
Volume Flow	CUM/HR	36,061	40,161	14098,560	19017,455	11274,922	9129,375		
Enthalpy	MMKCAL/HR	-137,528	-133,606	-118,726	-113,802	-434,020	-452,822		
Mole Flow	KMOL/HR								
CO2						2374,580	2374,580		
CH4						6970,909	6970,909		
H2O		1998,304	1998,304	1998,304	1998,304	525,356	525,356		
H2						9443,171	9443,171		
CO						452,880	452,880		
N2						84,564	84,564		
C2H6						8,661	8,661		
C3H8						0,010	0,010		
O2									
CH3OH						1726,923	1726,923		
ACETONE						0,475	0,475		
N-BUT-01						0,685	0,685		
DIMET-01						1,936	1,936		
TOTEN	KW	-24654,250	-20093,907	-2787,705	2938,240	2,33979E+6	2,31792E+6		
CHEMEX	KW	499,576	499,576	499,576	499,576	2,62593E+6	2,62593E+6		
PHYSEX	KW	4,842	577,163	5379,288	6973,750	72839,728	65837,713		
MIXEX	KW	< 0,001	0,000	> -0,001	0,000	-16171,889	-17075,920		
TOTEX	KW	504,417	1076,739	5878,864	7473,326	2,68260E+6	2,67469E+6		

## APPENDIX G: CONVENTIONAL PROCESS: HEAT INTEGRATION OF SECTION 1

There are four heaters in section 1 (reforming):

- make-up water heater,
- recycle water heater,
- air heater,
- feed heater.

The heating requirements can be partly met by use of heat recovered by the flue gas cooler, however this is not sufficient and must be supplemented by MP and LP steam from the steam system. The way this heat integration has been done is summarised in the Table.

Heat integration of section 1

		Flue gas cooler 900 – 150 °C	MP steam 226 – 200 °C	LP steam 140 – 120 °C
Make-up water heater	20 - 86,8 °C			3326
Make-up water heater	86,8 - 148 °C		3142	
Recycle water heater	148 - 195 °C	18651	7641	
Air heater	20 - 120 °C			6892
Air heater	120 - 366 °C	16957		
Feed heater	204 - 560 °C	31509		
<b>TOTALS (kW)</b>		<b>67117</b>	<b>10783</b>	<b>10218</b>

The design philosophy behind this integration takes into account the temperature levels of the various heat sources/sinks, as follows. Since the flue gas cooler provides heat at the highest temperature level, this heat should be used at the highest possible level (feed heater, air heater, recycle water heater). However the needs of the air heater below 120 °C can be more efficiently met by use of LP steam. On this basis the needs of the feed heater and air heater are completely met, however the needs of the recycle water heater are only partly met. This shortfall must be supplied by MP steam. The needs of the make-up water heater can be supplied by a mixture of MP and LP steam (N.B. The transition temperature of 86.8 °C applied here has been determined by the availability of MP steam from the steam system, otherwise 120 °C would have been a more logical choice – in other words we are using a higher MP/LP steam ratio than really required for this heater).

This straightforward design approach avoids pinch points and results in a feasible, practical and reasonably efficient design. A more optimum design could probably be made by use of a rigorous pinch analysis, however this is beyond the scope of the current work.





## APPENDIX H: CONVENTIONAL PROCESS: CALCULATION OF ELECTRICITY AND STEAM IMPORTS

Electricity balance			kW
Required	sect.1	CO2 compressor	2511
	sect.1	NG compressor	396
	sect.2	syngas compressor	13378
	sect.3	recycle compressor	2255
	sect.4		0
TOTAL			18540
Generated	sect.5	HP turbine	4349
	sect.5	MP turbine	1031
	sect.6		0
TOTAL			5380
IMPORT			13160

LP steam balance			Enthalpy
			kW
Required	sect.1	heaters	10218
	sect.2		0
	sect.3		0
	sect.4	refining reboiler	39821
TOTAL			50039
Generated	sect.5	to sect. 1	8331
	sect.6	to sect. 1	1887
	sect.6	to sect. 4	21145
TOTAL			31363
IMPORT			18676



## APPENDIX I: CONVENTIONAL PROCESS: EXERGY ANALYSIS

Section 1: Reforming							
	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference App.,Stream no.
<b>STREAMS IN</b>							
Natural gas	BL	29952	26	21,7		425478	NATGAS
Carbon dioxide	BL	24823	43	1,4		3747	CO2
Make up water	BL	39654	20	27,5		587	NEWH2O
Make up steam	from MP steam (sect.5)	45267	226	26		13180	MKUPST
Air	BL to furnace	240000	20	1		224	AIR
Fuel (natural gas)	BL to furnace	7004	26	21,7		101548	FUEL
Fuel	recycle from section 3	8489	45	75,6		78615	PURGE1
Fuel	recycle from section 3	2477	46	5		7502	PURGE2
Water recycle	from S15	410000	195	27,5		25219	CIRCH2O
<b>STREAMS OUT</b>							
Syngas	to Section 2	139696	860	18		552113	BOILER
Fluegas	from furnace to atmosphere	257970	150	1		7052	FLUEGAS2
Condensate		0				0	KNOCKOUT
Water recycle	to CIRCH2O	410000				26835	S15
<b>HEAT IN</b>							
Make up water heater	from LP/MP steam		20 - 148		6468	1018	HEATNH2O
Recycle water heater	from MP steam/flue gas		148 -195		26292	8653	HEATH2O
Air heater	from LP steam/flue gas		20 - 366		23849	7885	HEATAIR
Feed heater	from flue gas		204- 560		31509	16854	FEEDHTR
<b>HEAT OUT</b>							
Flue gas cooler	to heaters		900- 150		67117	40320	COOL5
<b>ELECTRICITY IN</b>							
	to CO2 compressor				2511	2511	COMPCO2
	to NG compressor				396	396	CH4COMP
<b>ELECTRICITY OUT</b>							
					0	0	
<b>NET FLOWS (IN-OUT)</b>		0				67097	calc.
<b>EXERGY LOSSES</b>							
Internal						67097	
External	fluegas to atmosphere					7052	
Total						74149	

### Notes:

- \* Steam import is 10218 kW LP steam, 10783 kW MP steam, 21001 kW total
- \* The external water recycle, stream out S15, stream in CIRCH2O, is not rigorously modelled (see App. C)
- \* The furnace-reformer duty is 126138 kW
- \* Exergies of heat flows in/out of units are calculated from:
  - Exergy of heat flow in = exergy (material flow out) - exergy (material flow w in)
  - Exergy of heat flow out = exergy (material flow in) - exergy (material flow out)

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Section 2: Heat recovery

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	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference Unit/Stream
STREAMS IN							
Syngas	from sect. 5 (BOILER)	139696	166	18		510624	S2
STREAMS OUT							
Syngas	to section 3	86301	40	82.5		506284	TOLOOP
Condensate	to waste water treatment	53396	106	17		1411	S13
HEAT IN					0	0	
HEAT OUT							
Cooler	to sect.4 (refining)		166 - 136		18188	5256	COOL1
Cooler	to sect. 4 (topping)		136 - 104		15233	3771	COOL2
Cooler	to CW		104 - 85		4867	955	COOL3
Cooler	to CW		85 - 40		5478	674	COOL4
Syngas compressor	to CW		?		13868	5516	SYNCOMP
ELECTRICITY IN					13378	13378	SYNCOMP
ELECTRICITY OUT					0	0	
NET FLOWS (IN-OUT)		-1				135	calc.
EXERGY LOSSES							
Internal	flash vessels					135	
External	condensate, CW					8556	
Total						8691	

---

Notes:

- \* The boiler is included in section 5 (steam system)
- \* Exergies of heat flows in/out of units are calculated from:
  - Exergy of heat flow in = exergy (material flow out) - exergy (material flow in)
  - Exergy of heat flow out = exergy (material flow in) - exergy (material flow out)
- \* All exergy losses in the 2 coolers and the compressor have been attributed to external losses with CW. In fact some of these losses are internal losses.

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Section 3: Synthesis loop

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	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference Unit/Stream
STREAMS IN							
Syngas	from section 2	86301	40	82,5		506284	TOLOOP
process stream return	from section 6 (E121)	315655	150	82,5		2674690	S18
STREAMS OUT							
process stream	to section 6 (E121)	315655	240	82,5		2682600	S17
Crude methanol	to section 4	75348	46	5		390113	CRUDE
Fuel gas purge	to section 1 (furnace)	8489	45	76		78615	PURGE1
Fuel gas purge	to section 1 (furnace)	2477	46	5		7502	PURGE2
HEAT IN					0		
HEAT OUT							
Synthesis reactor	to steam system		240		5726	2399	MEOHRXR
Air cooler	lost to air		123 - 60		39573	8230	E223
Cooler	to CW		60 - 45		6420	920	E124
ELECTRICITY IN	recycle compressor				2255	2255	CIRC
ELECTRICITY OUT					0	0	
NET FLOW (IN-OUT)		-13			-68494	12850	calc.
EXERGY LOSSES							
Internal						12850	
External						9150	losses with air and CW
Total						22000	

---

Notes:

- \* The heat exchanger E121 is included in section 6
- \* The exergy of the heat stream from the synthesis reactor has been calculated with the Carnot factor at 240 degC
- \* Exergies of heat flows in/out of all other units are calculated from:
  - Exergy of heat flow in = exergy (material flow out) - exergy (material flow in)
  - Exergy of heat flow out = exergy (material flow in) - exergy (material flow out)
- \* All exergy loss from the 2 coolers has been attributed to external losses with air and CW. In fact some of the loss is internal.

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Section 4: Distillation

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	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference Unit/Stream
STREAMS IN							
Crude methanol	from section 3	75348	46	5		390113	CRUDE
Make-up water	BL	10000	40	5		145	MKWATER
STREAMS OUT							
Light ends (CO <sub>2</sub> , methanol)	to furnace?	1388	44	1		2700	LTENDS
Secondary purge		12	44	1		71	SECPURGE
Liquid purge		1	75	1		6	LIQPURGE
Fusel oil		559	86	1		2891	FUSELOIL
Bottoms (water)	to river	21579	119	2		1812	BTMS
Product		61809	75	2		384176	PRODUCT
HEAT IN							
Topping reboiler	from sect.2 (COOL2)		86		15235	2588	TOPPING
Refining reboiler	from sect.2 (COOL1)		119		18188	4360	REFINING
Refining reboiler	from LP steam (sect.6 + import)		119		39821	9545	
HEAT OUT							
Topping condenser	to CW		< 44		11162	2133	TOPPING
Refining condenser	to CW		< 75		56367	12672	REFINING
ELECTRICITY IN							
					0		
ELECTRICITY OUT							
					0		
NET FLOW (IN-OUT)							
		0				290	calc.
EXERGY LOSSES							
Internal						290	
External	purges, bottoms, CW					16694	
Total						16984	

Notes:

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- \* The exergies of the heat streams to the reboilers are calculated by use of Carnot factors at the operating temperatures
- \* The exergies of the heat streams from the condensers are calculated by exergy balances on the distillation columns; this implies that all exergy losses from the distillation columns have been attributed to external losses with CW from the condensers. In fact some of these losses are internal losses.
- \* Light ends and fusel oil have been considered as useful by-products and do not contribute to the external exergy losses

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Section 5: Steam system part 1

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	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference Unit/Stream
STREAMS IN							
BFW	BL	88000	20	100		1510	BFW
process stream	from section 2 to BOILER	139696	860	18		552116	BOILER
STREAMS OUT							
HP flash condensate	BL	430	310	100		63	HPCOND
MP flash condensate	BL	9302	226	26		732	MPCOND
MP condensate	BL	19065	200	26		1221	MPCOND2
LP flash condensate	BL	1009	140	3,5		37	LPCOND
LP condensate	BL	12927	120	3,5		387	LPCOND2
Make up steam	to section 1	45267	226	26		13180	MKUPST
process stream	from BOILER to section 2	139696	166	18		510624	S2
HEAT IN					0	0	
HEAT OUT		to sect.1 (MP steam heat)		226 - 200	10783	4330	MPHEATER
		to sect.1 (LP steam heat)		140 - 120	8331	2314	LPHEATER
ELECTRICITY IN					0		
ELECTRICITY OUT		HP turbine			4349	4349	HPTURB
		MP turbine			1031	1031	MPTURB
NET FLOWS (IN-OUT)		0			-1	15358	
EXERGY LOSSES:							
Internal						15358	
External		condensates to BL				2440	
Total						17798	

Notes:

\* This section includes the heat exchanger BOILER

\* Exergies of heat flows in/out of units are calculated from:

Exergy of heat flow in = exergy (material flow out) - exergy (material flow in)

Exergy of heat flow out = exergy (material flow in) - exergy (material flow out)

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Section 6: Steam system part 2

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	Flow from/to	Flow kg/h	Temp. deg.C	Pres bar	Enthalpy kW	Exergy kW	Reference Unit/Stream
STREAMS IN							
BFW	BL	36000	20	3,5		504	BFW
process stream	from section 3 to E121	315655	240	82,5		2682600	S17
STREAMS OUT							
Condensate	BL	36000	120	3,5		1077	LPCOND
process stream	from E121 to section 3	315655	150	82,5		2674690	S18
HEAT IN							
	from synthesis reactor		140		5726	1594	MEOHRXR
HEAT OUT							
	to sect. 1 (LP steam heat)		140 - 120		1887	524	LPHEAT
	to sect. 4 (LP steam heat)		140 - 120		21145	5873	LPHEAT
ELECTRICITY IN							
					0	0	
ELECTRICITY OUT							
					0	0	
NET flows (IN - OUT)							
		0				2534	calc.
EXERGY LOSSES:							
Internal	losses in E121					2534	
External	condensate to BL					1077	
Total						3611	

## Notes:

\* This section includes the heat exchanger E121

\* Exergies of heat flows in/out of units are calculated from:

Exergy of heat flow in = exergy (material flow out) - exergy (material flow in)

Exergy of heat flow out = exergy (material flow in) - exergy (material flow out)

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Interface A: Section 1 (reforming): external flue-gas heat recycle and interface  
with Sections 5 and 6 (steam systems)

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Flow from/to	Temp. deg.C	Enthalpy kW	Exergy kW	Reference App.,Stream no.
HEAT IN				
from sect. 1 (flue gas cooler)	900 - 150	67117	40320	COOL5
from section 5 (MP steam)	226 - 200	10783	4330	MPHEATER
from section 5 (LP steam)	140 - 120	8331	2314	LPHEATER
from section 6 (LP steam)	140 - 120	1887	524	LPHEAT
HEAT OUT				
To sect. 1 (make up water heater)	20 - 148	6468	1018	HEATNH2O
To sect. 1 (recycle water heater)	148 -195	26292	8653	HEATH2O
To sect. 1 (air heater)	20 - 366	23849	7885	HEATAIR
To sect. 1 (feed heater)	204 - 560	31509	16854	FEEDHTR
NET FLOWS (IN-OUT)		0	13078	
EXERGY LOSSES				
Internal			13078	
External				
Total			13078	

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Interface B: Interface between Section 3 (synthesis loop) and Section 6 (steam system)

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Flow from/to	Temp. deg.C	Enthalpy kW	Exergy kW	Reference App.,Stream no.
HEAT IN				
From sect. 3 (synthesis reactor)	240	5726	2399	MEOHRXR
HEAT OUT				
to section 6 (LP steam generation)	140	5726	1594	MEOHRXR
NET FLOWS (IN-OUT)		0	805	
EXERGY LOSSES				
Internal			805	
External				
Total			805	

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Interface C: Section 4 (distillation): interface with Section 2 (heat recovery),  
Section 6 (steam system), and BL

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Flow from/to	Temp. deg.C	Enthalpy kW	Exergy kW	Reference App.,Stream no.
<b>HEAT IN</b>				
from sect. 2 cooler	166 - 136	18188	5256	COOL1
from sect. 2 cooler	136 - 104	15233	3771	COOL2
from sect. 6 (LP steam)	140 - 120	21145	5873	LPHEAT
from BL (import steam)	140 - 120	18676	5187	
<b>HEAT OUT</b>				
to sect. 4 (topping reboiler)	86	15235	2588	TOPPING
to sect. 4 (refining reboiler)	119	18188	4360	REFINING
to sect. 4 (refining reboiler)	119	39821	9545	
<b>NET FLOWS (IN-OUT)</b>		-2	3594	
<b>EXERGY LOSSES</b>				
Internal			3594	
External				
Total			3594	

**Note:**

The exergy of the import steam is calculated assuming the same exergy/enthalpy ratio as the LP steam from section 6

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