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Flexible operation of steam power plants by integration of a power to methanol plant

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Für meinen Freund

Christian

Kurzfassung

In dieser Arbeit wird ein neuartiges Drei-Vektoren-Kraftwerksmodell für die Sektorenkopplung beschrieben, das auf 1. einem Dampfkraftwerk zur Stromerzeugung, 2. der Wärmeerzeugung in Form von Dampf und schließlich 3. der Methanolerzeugung unter Ausnutzung des höheren Heizwertes (H_O) des verwendeten Brennstoffs basiert. In dieser Arbeit wird beschrieben, wie die Rauchgaskondensation in Verbindung mit Hochtemperatur-Wärmepumpen die Brennstoffausnutzung verbessert, während die Integration einer Power-to-Methanol-Anlage, bestehend aus Wasserelektrolyse, einer Anlage zur Kohlendioxidabscheidung und einer Methanol-Erzeugungsanlage, die die Stromerzeugung mit der chemischen Produktion koppelt.

Es wird gezeigt, dass eine solche Anlage in der Lage ist, mit hoher Flexibilität bei zunehmend schwankendem Bedarf an erneuerbarer Stromerzeugung zu arbeiten, um Strom, Wärme und Methanol über einen weiten Bereich zuverlässig bereitzustellen. In dieser technisch-wirtschaftlichen Analyse wird ein vollständiger Betriebszyklus von einem Jahr unter Verwendung von Wind- und Solarstrom aus erneuerbaren Energien in Deutschland als Modell auf der Grundlage realer Daten dargestellt. Der Betrieb der Anlage wird auf seinen Kohlenstoff-Fußabdruck für die Methanolerzeugung durch Power-to-Methanol (PtX) in dieser Drei-Vektoren-Anlage analysiert. Dies wird mit anderen bestehenden kohlenstoffarmen Methanol-Erzeugungsoptionen und deren Kohlenstoff-Fußabdruck verglichen.

Abstract

This thesis describes a novel three-vector plant model for sector coupling based on 1.steam power plant producing electric power, 2. heat as steam, and finally 3. as methanol production by exploiting the higher heating value (HHV) of the fuel used. This thesis describes how flue gas condensation working in conjunction with high temperature heat pumps improves fuel utilization, while integration of a power to methanol plant consisting of water electrolysis, carbon capture unit and methanol generation couples power generation to chemical production.

Such a plant will be shown to have to capability to operate with high flexibly over increasingly fluctuating renewable electricity generation demands to provide electric power, heat and methanol production reliably over a wide range. This techno-economic analysis presents a full cycle of one year of operation, using wind and solar renewable generation using Germany as the model based on real data. The operation of the plant is analysed for its carbon footprint for methanol generation by power to methanol (PtX) in this three-vector generation plant. This is compared with other existing low-carbon methanol generation options and their carbon footprint.

Danksagungen

Natürlich wäre die Arbeit ohne die Unterstützung zahlreicher Menschen nicht möglich gewesen. Diesen gilt hier mein besonderer Dank. Die wären zuerst meine Lebensgefährtin, die mich im Vorhaben unterstützt hat, und meine Mutter , die mich immer ein wenig angetrieben hat. Dann mein Doktorvater Prof. Kakaras, der mich bei Schwierigkeiten gut unterstützt hat, sowie mein Arbeitskollegen Dr. habil Bergins, der mir bei Frage immer ein guter Diskussionspartner war. Mein Freund Marcus Brinkmann hat mich bei den FEM-Berechnungen beraten und mit seiner Software unterstützt, wofür ich gleichfalls zu danken habe. Ebenso muss ich mich bei Richard Espeseth dem Mehrheitseigentümer der Firma HydrogenPro bedanken, da er mich mit Interviews zur Elektrolysetechnik tatkräftig unterstützt hat um hier ein realistisches Bild zu zeichnen. „Last but not least" danke ich meinem Kollegen aus den USA, Tim Gardner, dass er mich beim Finden der richtigen Sprache unterstützt hat.

Acknowledgements

This work would not have been possible without the support of numerous people. I would like to express my special thanks to them. First of all Alice, my live-companion, who constantly supported and encouraged me through the entire the project, and my mother, who gave me a little push once in a while. Next I would like to thanks my doctoral supervisor Prof. Kakaras, who supported me when I had difficulties, and my colleague Dr. Habil Bergins, who was always a good discussion partner when I had questions. My friend Marcus Brinkmann advised me on the FEM calculations and supported me with his software. I have to also thank Richard Espeseth, the majority owner of the company HydrogenPro, who actively supported me with interviews on electrolysis technology in order to draw a realistic picture here. Last but not least, I would like to thank my colleague from the USA, Tim Gardner, for helping me find the right language.

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List of Abbreviations

AACE	Association of Advancement in Cost Engineering
AC	Alternating Current
AEL	Alkaline Electrolysis
AEM	Anion Exchange Membrane Electrolysis
BM	Biomass
BS	Base Scenario
C	Carbon
CAK	Chlor-Alkali Electrolysis
CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
CF	Carbon Footprint
CHP	Combined Heat and Power
COP	Coefficient of Performance
CRI	Carbon Recycling International Ltd.
DC	Direct Current
DRI	Direct Reduced Iron
EDV	Emission Default Value
EEX	European Energy Exchange platform
el	Electric
ETS	Emission Trading System
EU	European Union
FEM	Finite Element Method
F-Gas	Fluorides Green House Gases
FM	Finnish Method
GHG	Green House Gas
GWP	Global Warming Potential
H	Hydrogen
HHV	Higher Heating Value
IGBT	Insulated Gate Bipolar Transistor
IOGP	International association of Oil and Gas Producers
IPCC	Intergovernmental Panel on Climate Change
ISO	International Standard Organisation
KM-CDR	Kansei Mitsubishi Carbon Dioxide Recovery
KOH	Potassium Hydroxide
LCOE	Levelized Cost of Electricity
LHV	Lower Heating Value
MEA	Mono Ethanol Amine
MW	Megawatt
MWh	Megawatt hour
nEHS	National Emission Trading System of Germany
O	Oxygen
ODP	Ozon Depletion Potential
OPEX	Operational Expenditure
PEM	Proton Exchange Membrane Electrolysis
PV	Photo Voltaic
R #	Refrigerant #
RED II	Renewable Energy Directive of the EU in 2nd revision
SMR	Steam Methane Reforming
SOEC	Solid Oxide Exchange Cell Electrolysis
TCC	Tube Cooled Converter
th	thermal
WtE	Waste to Energy

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Preamble

Today´s well established knowledge about man-made climate change, proven by the scientific world [1], leads economic and political policy makers to a new way of thinking in all sectors of energy generation. International targets to limit global warming to 1.5°C have been developed using pre-industrialisation temperatures as the baseline reference. Renewable sources are gaining importance in the entire global energy sector. This new policy is being considered for both electric power generation, as well as heat and mobility.

The issue of climate change was already known and first published by the U.S. Environmental Protection Agency in February 1978 in a report dealing with coal liquefaction [2].

On page 66 of this EPA report was stated,

"Another development is a report by National Academy of Sciences (NAS) which warns that continued use of fossil fuels as primary energy source for more than 20-30 more years could result in increasing atmospheric levels of carbon dioxide. The greenhouse effect and associated global temperature increase and resulting climate changes could, according to NAS be both "significant and damaging". The findings, although not conclusive, demonstrate the need for positively identifying the long-range effects of using fossil fuels to provide energy needs. The impacts on coal utilization for energy, including coal liquefaction, are obvious."

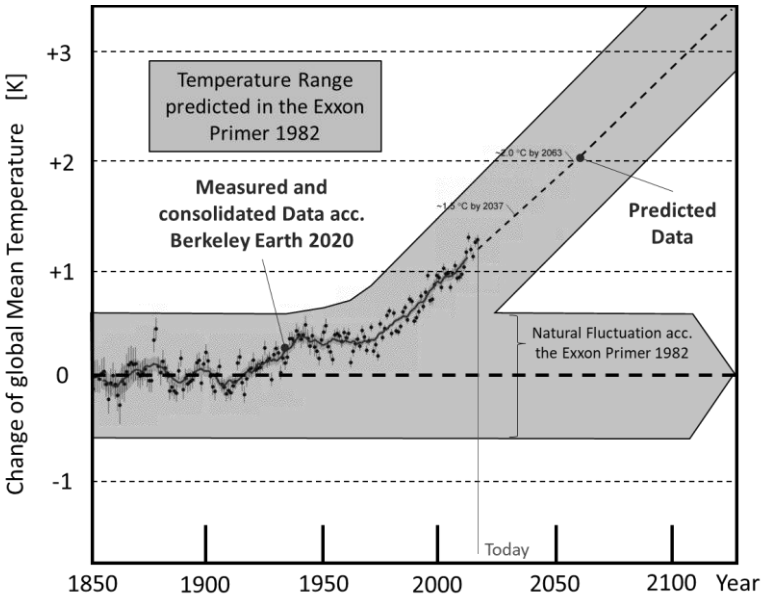

Figure 0-1: World average Mean Temperature taken from Exxon Primer 1982 [6] and Today [1]

But even as early as 1978 as mentioned above, the influence of carbon dioxide was not new to the research environment. In1968 it was stated that active climate influence can be used as a weapon by the U.S. or other governments [3]. This shows that even in 1978 the analysis was already based on long term scientific work running for more than a decade. In 1979 this materialised in a large scientific report [4], which was based on former works which developed the JASON Climate Model [5] in the JASON

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[1] http://berkeleyearth.org/global-temperature-report-for-2020/

defence advisory group in the USA. In 1982 it was also circulated and proved within oil majors such as Exxon Mobil with its “Exxon Primer” [6] and in 1983 it was summarised in a large overview report [7] the main examples of impacts we observe today.

Comparing the findings discussed in reports and works mentioned above it is shown that the prediction of the 1979 model shows very much the findings of today´s current research, and the prediction of the concentration on carbon dioxide and the accompanying temperature rise. This is also clearly expressed in Figure 0-1, showing that today’s reality has met a 40-year-old prediction. This concept has been clearly known and understood by scientists and governments and has been part of the international climate discussion and could have been acted on for quite some time,

A broad international consensus had settled on a solution: a global treaty to curb carbon emissions. The idea began to coalesce as early as February 1979, at the first World Climate Conference in Geneva, when scientists from 50 nations agreed unanimously that it was “urgently necessary” to act. Four months later, at the Group of 7 meeting in Tokyo, the leaders of the world’s seven wealthiest nations signed a statement resolving to reduce carbon emissions. Ten years later, the first major diplomatic meeting to approve the framework for a binding treaty was called in the Netherlands. Delegates from more than 60 nations attended, with the goal of establishing a global summit meeting to be held about a year later. Among scientists and world leaders, the sentiment was unanimous: Action had to be taken, and the United States would need to lead [2].

2016 the Paris agreement was signed by 196 parties and the GHG reduction target of the EU is set to 55% until 2030. Today many governments are on their way to react to climate change and to exit from coal for power generation, in addition to other measures being taken by industry, agriculture, space heating and the mobility sector. For example, Germany introduced their coal exit strategy 2019 [8] and their climate protection package [9]. This comes from the consensus that fossil fuels must be abandoned by 2050 or before, and that natural gas has a lower environmental impact compared to coal. This is the political view, but on the basis of science the issue is more complex, and corrective measures are still not succeeding as a recent analysis shows [10]. Usually in the emission counting systems only direct emissions of the fuels are counted, where obvious natural gas has an obvious advantage over crude oil, hard coal and lignite as energy carrier, The emissions of mining and production as well as transportation must be considered in the scientific comparison. All this will have impacts to the future use of the fuel-based power plants, as well on the use of special steam power plants.

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[2] https://www.nytimes.com/interactive/2018/08/01/magazine/climate-change-losing-earth.html#main, Author: Nathaniel Rich**,** online document for the political surrounding of the time 1979 to 1989

1 Introduction

1.1 Current Status

The current situation in the energy and power generation sector is a complex setting. Nevertheless today´s need for minimisation of green-house gas emissions, primarily carbon dioxide, as well as combustion related nitrogen oxides and hydro-carbons, establishes boundary conditions for the power generation sector. The ultimate goal is to reduce system losses, while utilising as much renewable energy as possible using all forms of renewable generation.

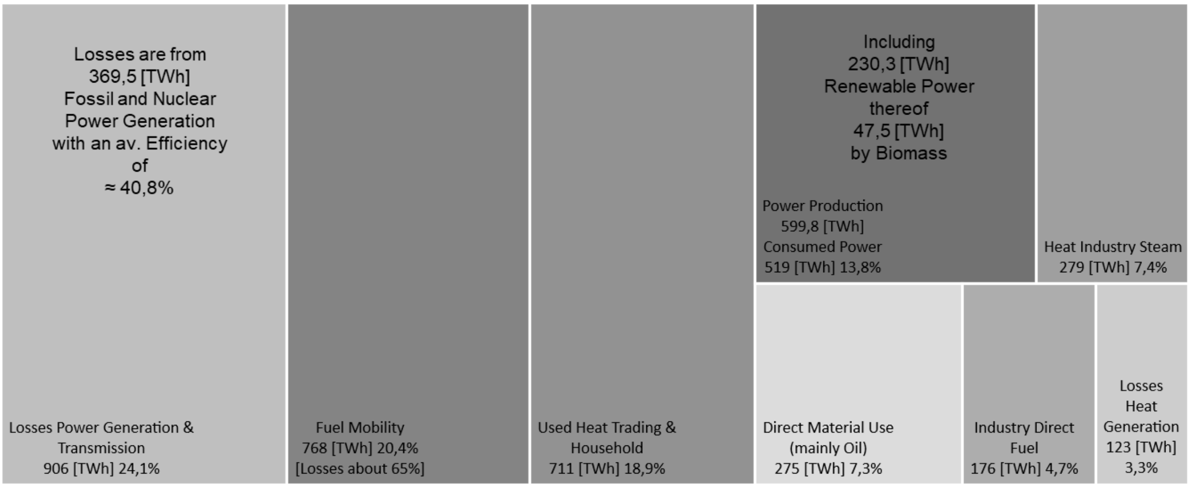

Figure 1-1: 2017 Primary Energy Utilisation in Germany of 3,756 [TWh] incl. 320 [TWh] biomass according AG Energiebilanzen e.V. [3]

Figure 1-1 clearly shows that the main utilisation of primary energy in incurred via losses for the power generation and transmission system. Capturing and utilizing this energy that would have otherwise been losses can significantly contribute to GHG savings.

1.1.1 Sector coupling

Sector coupling today is a word with a diffuse meaning in its use. To the author it means the coupling of all power generation to other non-electricity generation systems to develop an integrated single system [11,12,13]. The fluctuating renewable energy sources have to be coupled to today´s continually operated industries, transport, mobility, and finally to household consumers. An example of sector coupling is the operation of power plants in combined heat and power operation (CHP), delivering heat to thousands of households, while generating power for the electricity generation sector. All of this has to be pursued not only on a national but an international basis. Sector coupling is not well-established today, but this concept will certainly play a greater role in our future economy, politics, and society.

The European Union is working on this field [14] and oil majors are moving to become carbon neutral by 2050 [15]. But it is not a fast-moving game due to the fact that increased investment in innovation needs to be started to allow sufficient time for developing the new solutions needed for multiple sectors and processes, many of which have long investment cycles.

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[3] https://www.ag-energiebilanzen.de/

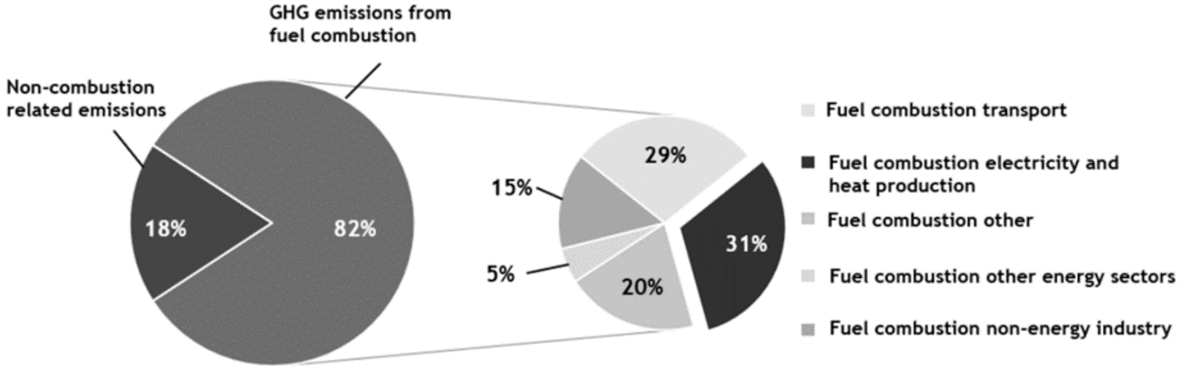

Figure 1-2: Share of fuel combustion in overall EU GHG emissions in 2016 [14]

The share of the combustion of fuels is the major share of greenhouse gas (GHG) emissions, which is illustrated by Figure 1-2. Thereof the fuel combustion for power generation is not the major share. Reviewing this it makes it obvious that sector coupling is needed for the future low or zero carbon power generation sector, but it will lead as well to an electrification of processes.

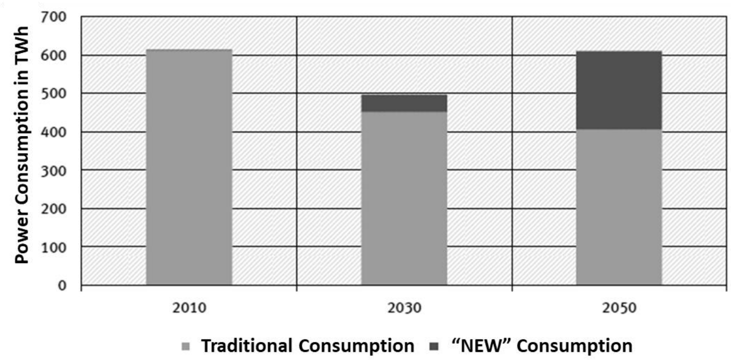

Figure 1-3: Example for a prediction scenario for power consumption in Germany [UBA, 13]

There are several ways to solve this issue. 32,5% energy consumption reduction, acc. to the draft of the directive on energy efficiency, is the main target of the EU. Any resource used must be used to its best and highest efficiency to avoid unnecessary emissions. The above mentioned CHP use is exactly targeting this area. But it is also necessary to leave the greatest amount of fossil fuels in ground as possible. The source of fuels replacement shall be renewable energy sources such as biomass, wind, solar, geothermal and hydro power. These are mainly fluctuating sources, due to the high share in wind and solar in the active on line portfolio, while others are restricted in amount or locations.

This moving of the energy from its generation to its consumption with a time-gap is storage, which is in long term the best possible method to convert renewable electric power to a storable fuel. This makes it obvious that high efforts are taken today to solve this issue, which is expressed in hydrogen strategies or roadmaps around the world.

1.1.2 Hydrogen roadmap

The European Commission has published its hydrogen strategy in 2020 [16] and its member states as Germany followed the example [17]. Other organisations and the industry also previously published hydrogen roadmaps or similar papers [18]. One can state it is a worldwide movement in politics.

The aim of these hydrogen roadmaps is to give a policy basis to the *increased investment in innovation needs to be started to allow sufficient time for developing the new solutions*, mentioned while the sector coupling. The strategy and roadmaps are currently flanked by large funding programs, which can be best reviewed in the Hydrogen Public Funding Compass[4] and EU directives as the renewable energy directive, which is also later mentioned.

These hydrogen strategies and roadmaps shall not be seen as purely for hydrogen. It is also included in these strategies to generate other chemicals from hydrogen, but it is obvious that the electric generation of energy carriers is seen as “the” important building block, which is missing today.

The reason for this hydrogen integration is the presence of the today´s fluctuating renewable electricity sources as on- and off-shore wind or photo voltaic systems [19] and thus it’s directly the target of this thesis.

1.2 Thesis Structure and target formulation

While operating a CHP plant, which needs to deliver its heat continuously (e.g. to a chemical park) the electricity demand in the grid might fluctuate in such a way that the electricity produced is unneeded at times, and therefore over-produced at certain instances in time. This is for the reason that CHP generation, which is today very often by steam power plants, cannot serve very low electric load simultaneously with high heat production.

A good way to utilise the electricity oversupply is redirecting this energy to another sector, such as the mobility or chemical production sector, producing a valuable product such as methanol.

To reach this we must first analyse single processes as building blocks, and the possibilities to combine these to be able to discuss the consequences in the implementation regarding the economics and environmental impacts. These building blocks are steam power plant, high temperature heat pump, hydrogen electrolysis, carbon capture, methanol generation from carbon dioxide and hydrogen and the necessary balance of plant systems such as water treatment.. This is described in chapter 2 incl. its cost and process parameters.

This building blocks need to be combined to the overall plant, which is described in chapter 3, which includes also the analysis how such a plant can be arranged on a real site of a steam power plant. This thesis may also illustrate that retrofits are also possible, in additional to grass roots plant designs.

After this site analysis the possible operating modes of such a plant are reviewed and described in detail in chapter 4 to have the overview about the operational limits. This is also with a focus on potential retrofit of an existing plant, which is not best state of the art, but some decades in existing operation, and has been running well for its purpose.

This full process overview makes it possible to analyse the carbon footprint of produced methanol and to compare this carbon footprint versus other production options. In chapter 5 this is not only in comparison to today´s state of the art fossil methanol production routes, but as well compared to other

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[4] https://ec.europa.eu/growth/industry/strategy/hydrogen/funding-guide_en

methanol generation via other low carbon generation by “blue” hydrogen or hydrogen generated by methane pyrolysis. Other carbon sources as the flue gas of a steam power plant are discussed here.

In chapter 6 the plant is discussed under techno-economic conditions and analysed in its cost and revenues in a full year. This is analysed with the boundary that the three-vector steam plant is operated corresponding with a wind/solar mix generation and shall balance this to a set baseload electric generation.

Finally, the results are summarised and concluded in chapter 7 of the thesis, and an outlook on the necessary future works is given by the author.

The target is to show that it is possible to operate a retrofitted steam power plant corresponding to renewable electric generation to reach a baseload production of electricity, heat and methanol, and which the described plant operating at load following renewable power generation source via wind and solar.

1.3 Novel aspects for the integration of the methanol production process to steam power plants

The integration of methanol production in a steam power plant is not a novel idea and has been previously investigated extensively. The author has submitted a patent application which was later granted in 2017 as a co-inventor [20]. In other existing thesis’s this concept was analysed more in detail [21,22]. In this work the basic principles have been analysed and this thesis is based on the suggested necessary future works of this author. In previous work methanol generation was integrated, but its flexibility and efficiency were not optimised. Both authors suggested to investigate more in-depth implementation of the power to methanol plant in such a steam power plant, which is the subject of this thesis.

In this thesis, the following novel aspects have been investigated:

1. The combination of a steam power plant, a high temperature heat pump and a power to methanol plant for flexible operation in the electric power grid, to reach the higher heating value use of the fired fuel in its load following production of electric power in depended from methanol and heat production
2. By using this new configuration it is possible to produce such methanol from natural gas lower in its carbon footprint compared to the best available technology natural gas derived methanol
3. A cost reduction option for the main system building block, the hydrogen electrolysis, by automated manufacturing and optional design changes
4. To find a retrofitting option for a certain rage of steam power plant is CHP operation in chemical parks, which is essential for the operation of some chemical sites
5. Using the mentioned granted patents in combination with another granted patent for high temperature heat pumps [38]

These novel aspects provide the opportunity to rethink the co-generation of several products while co-integrating with steam power plants in CHP operation.

2 Basic technology building blocks

This chapter is describing the various building blocks necessary to integrate a methanol production in a steam power plant. The technologies are explained and where necessary technology choices are justified by stringent technical arguments.

2.1 Steam power plant with heat balance for combined heat and power steam power plant

Steam power plants are a proven technology for power generation but also in combined heat and power generation [23]. Over the time the efficiencies have been significantly improved and so today´s state of the art are maximum electric efficiencies up to 45-46% in electricity only operation and based on the lower heating value of the fuel for hard coal. In electricity only operation for lignite fuel it is up to 43%. Using natural gas only the efficiencies can be slightly higher, which would result in efficiencies of approx. 48% based on the lower heating value (LHV).

Beside the maximisation of the fuel utilisation, in such coal fired power plant it is also possible to run a steam power plant on a multi-fuel mode. The firing technology gives the option to run on coal (hard coal or lignite), but also on solid biomass as wood pellets or with a co-firing of a gaseous or liquid fuel like natural gas or fuel oil [24]. Natural gas or fuel oil of course can be replaced by biogas or liquid biofuels. The technology is giving here the full options on the available and economic suitable fuels.

Special new tests also utilise ammonia as a fuel for the steam power plants. Here test have been executed in Japan [25] and showed that the use of ammonia up to 20% is easily possible. Higher ratios of co-combustion are under investigation. This gives the option of the direct use of a fuel, which can be produced by renewable electricity, causing no direct carbon emissions at the power plant.

Steam power plants running in CHP can be already today maximised in their fuel utilisation to fuel efficiencies higher than 90% based on their lower heating value, but this is only possible in the optimum point for such CHP operation. A good example for such a power plant is the power plant Avedoere in Copenhagen in Denmark [26]. This power plant unit 2 is operated on hard coal, wood pellets and natural gas, while it is operated at always maximum CHP mode for the district heating of Copenhagen. Through a secondary straw boiler steam is also imported to the main water steam cycle. In addition, also 2 gas turbines are integrated in the operation as so-called toping cycle turbines, which are of course only operated on natural gas in Avedoere, but are also optional thinkable fired on bio-gas or renewable liquid fuel [27].

For the later discussion of the topic of the implementation of a methanol production in a CHP steam power plant it is best to create an example, which is close to a real-world problem. Therefor the author set-up the following scenario.

2.1.1 Process of steam power plant for combined heat and power steam power plant

The in Figure 2-1 shown power plant is assumed to be from an older generation with moderate steam conditions and is operated in a chemical park in combined heat and power mode with an extraction of high pressure (HP), medium pressure (MP) and low-pressure steam. Over the year the HP and MP steam extractions are constant, due to its direct use for process feeds. The LP steam extraction is varying over the year, due to the reason that the heating needs are changing with the seasons. The example is also based on some literature for assistance [28].

Of course it also could be chosen an example of a CHP power plant operated for district heating as the mentioned Avedoere power plant, but due to the reason that such an implementation is in its technical challenges comparable it was decided for a process steam CHP unit. Such kind of coal fired steam power plant can be assumed as implemented in various chemical parks or refineries in Europe and Germany.

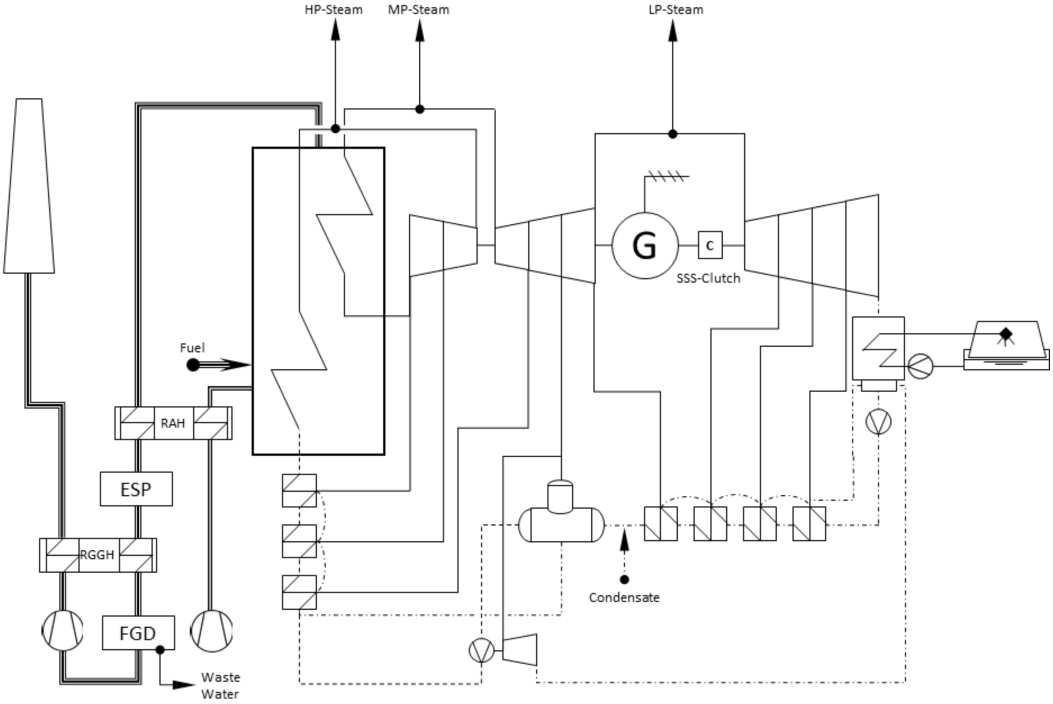


Figure 2-1: Process Flow Diagram of a CHP steam power plant today fired by Coal

Table 2-1: Process Data from Heat Balance for CHP Power Plant with no LP Steam Extraction

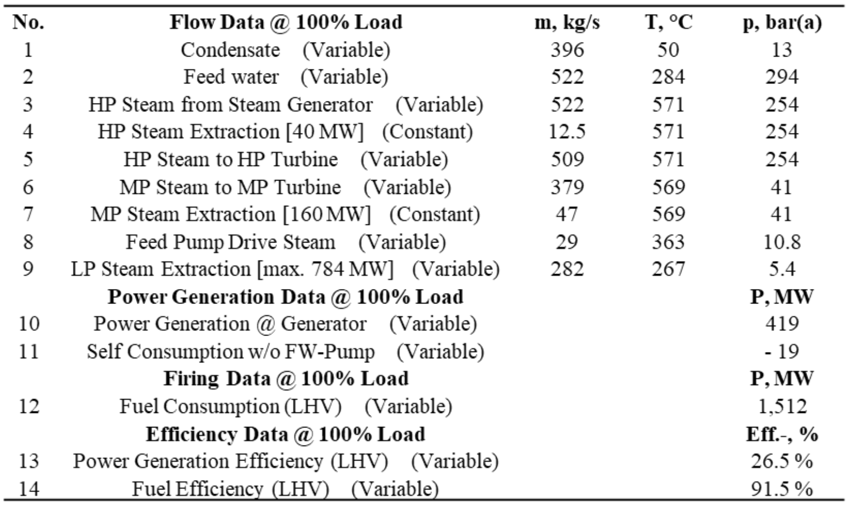
No.	Flow Data @ 100% Load		m, kg/s	T, °C	p, bar(a)
1	Condensate	(Variable)	396	50	13
2	Feed water	(Variable)	522	284	294
3	HP Steam from Steam Generator	(Variable)	522	571	254
4	HP Steam Extraction [40 MW]	(Constant)	12.5	571	254
5	HP Steam to HP Turbine	(Variable)	509	571	254
6	MP Steam to MP Turbine	(Variable)	379	569	41
7	MP Steam Extraction [160 MW]	(Constant)	47	569	41
8	Feed Pump Drive Steam	(Variable)	29	363	10.8
9	LP Steam Extraction [set 0 MW]	(Variable)	0	267	5.4
	Power Generation Data @ 100% Load				**P, MW**
10	Power Generation @ Generator	(Variable)			532
11	Self Consumption w/o FW-Pump	(Variable)			- 19
	Firing Data @ 100% Load				**P, MW**
12	Fuel Consumption (LHV)	(Variable)			1,512
	Efficiency Data @ 100% Load				**Eff.-, %**
13	Power Generation Efficiency (LHV)	(Variable)			33.9 %
14	Fuel Efficiency (LHV)	(Variable)			47.2 %

Table 2-1 is showing brief the operation parameters for the power plant without any low-pressure steam extraction.

The only special part here is the use of a low-pressure turbine, which is coupled with a state-of-the-art Synchro-Self-Shifting clutch (sss-clutch) to the generator to decouple it, when it is not needed. This usually would need a retrofit of the power plant, because this is not a standard application. This is recognised by the author and in the later parts also included in the retrofit cost for the power plant with all the necessary installations needed for the full retrofit with the methanol production facilities.

Table 2-2 is showing brief the operation parameters for the power plant with full low-pressure steam extraction and maximum heat supply.

Table 2-2 Process Data from Heat Balance for CHP Power Plant with full LP Steam Extraction



No.	Flow Data @ 100% Load	m, kg/s	T, °C	p, bar(a)
1	Condensate (Variable)	396	50	13
2	Feed water (Variable)	522	284	294
3	HP Steam from Steam Generator (Variable)	522	571	254
4	HP Steam Extraction [40 MW] (Constant)	12.5	571	254
5	HP Steam to HP Turbine (Variable)	509	571	254
6	MP Steam to MP Turbine (Variable)	379	569	41
7	MP Steam Extraction [160 MW] (Constant)	47	569	41
8	Feed Pump Drive Steam (Variable)	29	363	10.8
9	LP Steam Extraction [max. 784 MW] (Variable)	282	267	5.4
	Power Generation Data @ 100% Load			**P, MW**
10	Power Generation @ Generator (Variable)			419
11	Self Consumption w/o FW-Pump (Variable)			- 19
	Firing Data @ 100% Load			**P, MW**
12	Fuel Consumption (LHV) (Variable)			1,512
	Efficiency Data @ 100% Load			**Eff.-, %**
13	Power Generation Efficiency (LHV) (Variable)			26.5 %
14	Fuel Efficiency (LHV) (Variable)			91.5 %

From the data generated it is possible to draw the operation diagram, which is shown in Figure 2-2. It is showing the iso-firing lines from 100 – 30% firing and the related net electric and net thermal generation.

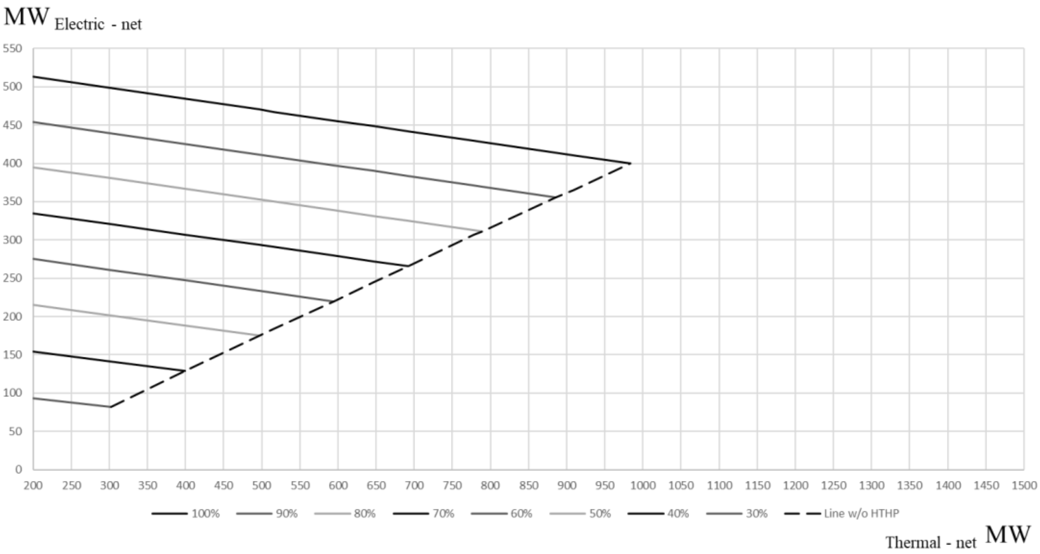


Figure 2-2: Operation Diagram of the Steam Power Plant with Electric & Thermal Production

The common minimum thermal need of the chemical park in summer is approx. 680 MW total, while the spring and autumn average load is at 880 MW thermal. The winter peak thermal load is at 1,080 MW thermal needs and cannot be fully covered by this power plant. Here usual also peak load boilers are taken in operation. The lowest load line in the diagram, shown as dashed line is giving for the operational points approx. total fuel efficiencies of 91% ± 1%, but the flexibility of the operation is very limited and the operation is driven by the thermal needs of the chemical park only. This operation is in future not suitable for the operation together with high fluctuating renewable energy electricity sources.

2.1.2 Arrangement planning of a steam power plant with combined heat and power

For the arrangement planning it was necessary to identify a typical long time operated site to analyse, if it is possible to integrate such a plant to an existing site, because this is the most interesting exercise. A completely new build on a green field is always possible. To fulfil this task the author has chosen the site of the 1500 MW thermal power plant Heyden, but this shall be only an example for a possible and it is clearly stated here, that there is not the intention to change this site by the operator. I fact the Heyden site was closed on the 1st of January 2021. At the same time the author is using the in chapter 1 discussed process for the power plant. It is a 100% virtual example.

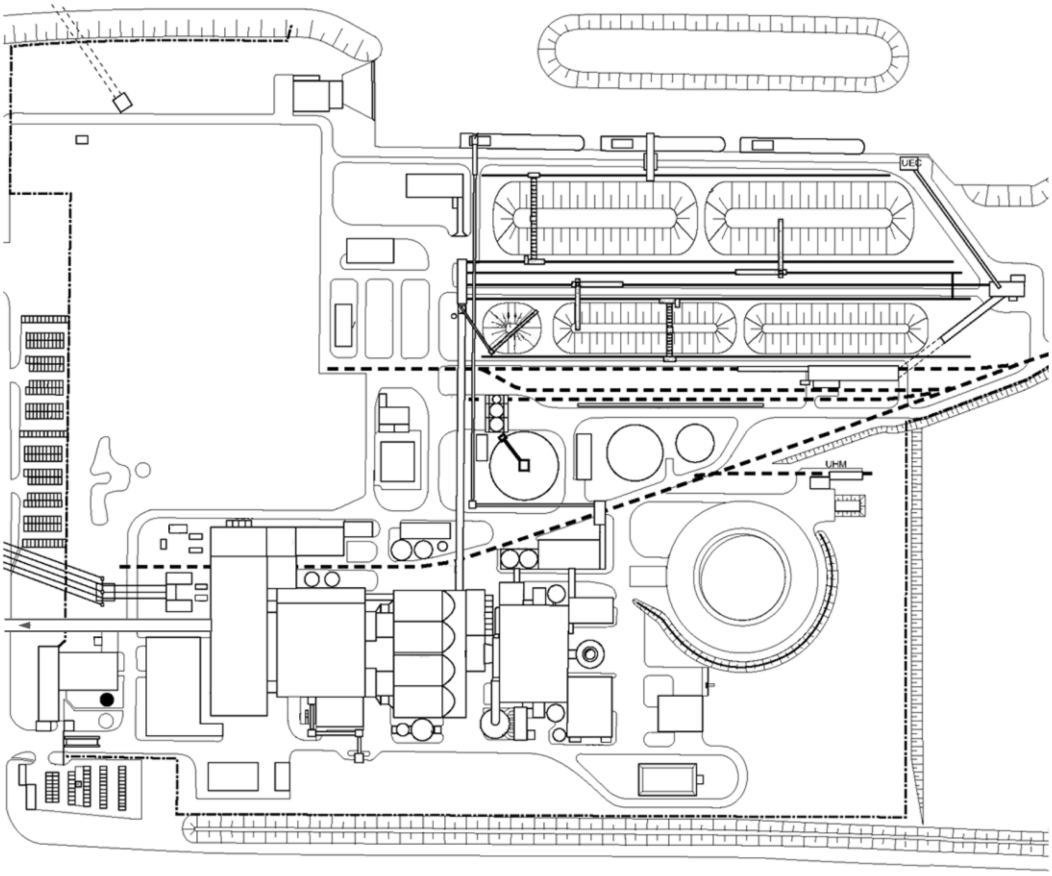


Figure 2-3: Layout plan of the power plant Heyden without changes[5] used as example basis

To retrofit the power plant, it is first necessary to bring the power plant in a condition as close as to its new build status again to extend its lifetime again. For this a full revamp of the boiler and all other equipment is necessary. The turbine needs to be exchanged with a turbine with decouplable low pressure turbine as it is necessary for the new CHP plant operation. For this it is considered that about 48% of

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[5] https://docplayer.org/43149184-11-unternehmen-mit-aktivem-wasserwegeanschluss.html

the today´s new build cost will be necessary. Also, for the implementation of the heat pump area, it is necessary to make major changes on the flue gas cleaning equipment and to add an additional second gas scrubber with a cooling cycle feeding the heat pump system, which is considered as additional cost.

2.1.3 Next decade fuels for steam power plants in CHP operation

Taking all this fuel options in the running decade it is not expectable that for CHP operation other fuels as solid biomass and natural gas can replace today´s mainly used solid fuel hard coal and lignite. Already this fuel switch will have a significant impact, but not only on the GHG emissions, but also on the cost [29,30]. Today´s fuel cost must be based on the direct fuel supply cost and in addition the carbon emission cost for the fuel acc. to the ETS trade cost for carbon emissions [6], which aims to achieve a reduction of carbon emission of 55% by the end of the decade until 2030. This will lead to an increase of the carbon emission cost in the year to come. This will also be discussed later in this thesis with the total fuel cost of the future, but it must be understood that these predictions are even using scientific methods is only giving tendencies and is not predicting the full truth.

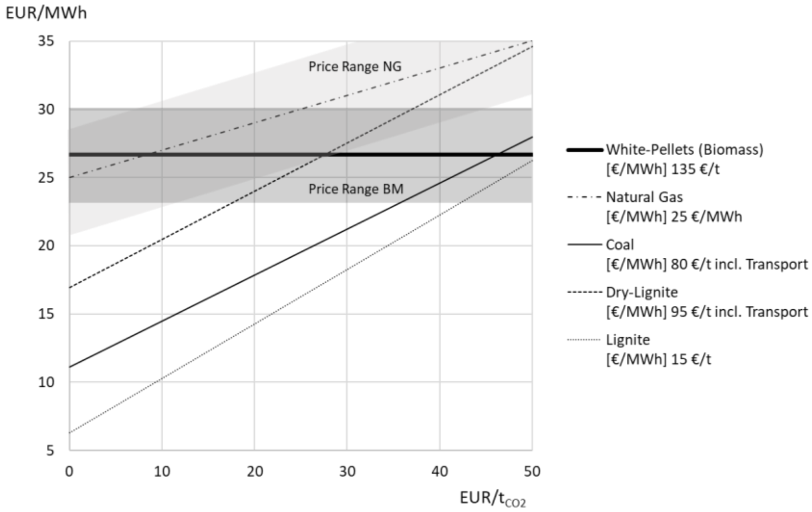

Figure 2-4: Overview of Fuel Cost incl. Carbon Emission Cost from the ETS Trade

Figure 2-4 is giving a first overview of today´s mainly used fuels for power and heat generation. The given numbers must be seen as an average and all these lines are of course varying with the actual trade price of the named fuel. As mentioned above the coal fuels are phasing out in countries as Germany anyhow and are also only an option for countries not phasing out coal.

This leads to the analysis that in the running decade natural gas and solid biomass will be the competing fuels in countries like Germany, where also the nuclear phase out was decided [31].

The history of carbon pricing acc. the EU ETS can be found public and is shown here in Figure 2-5. It is obvious that this development has a long-time low-price history 2012 to 2017. This was the result from policies with too much free certificates. Carbon pricing is pure policy and scientific carbon price prediction are not possible.

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[6] https://ec.europa.eu/clima/sites/clima/files/factsheet_ets_en.pdf

This shows, that the policy measures taken for the carbon price development are resulting in an average price increase until February 2021, but fluctuation are still to be expected.

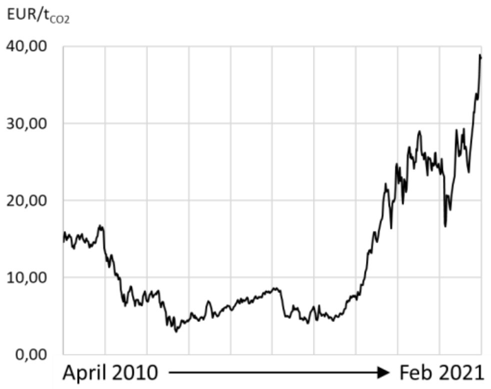

Figure 2-5: History of ETS Carbon Trade Prices [7]

The given white-pellets shall be seen here as the example for solid biomass only. It can be expected that the competition in this market will also lead to more competing sources for solid biomass fuels. This also can be found in the literature dealing with the biomass potential of e.g. Germany [32,33]. But, of course, it must be recognized, that the use of solid biomass for the energy production is seen critical today [34]. Most of the reasons are obvious as e.g. the debate in the food or fuel discussion, but there are also other impacts as e.g. the duration of the disposition of carbon dioxide in the atmosphere by biomass firing. It results that biomass has to follow sustainability regulations as those decided by the EU [35]. One shall not expect that the total available biomass will increase to a bottomless source. As a more conservative estimate it can be assumed as follows.

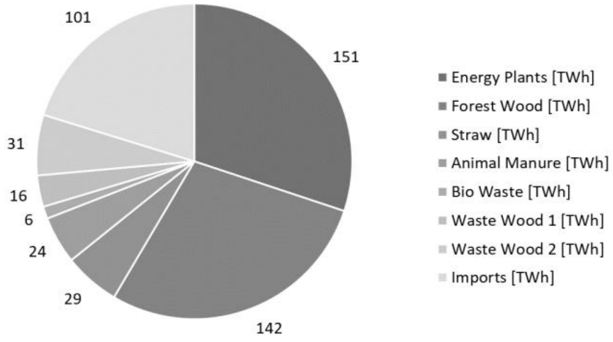

Figure 2-6: Potential for solid Biomass in Germany 2020 to 2030, 500 TWh/Year + 56% to 2017 [32]

The comparison of Figure 2-6 and Figure 1-1 shows, that biomass cannot be the silver bullet and it needs to be used very efficient to give its best use to an power generation sector of the future. It will not have the potential to avoid the use of fossil fuels and it will be used in the combination with natural gas.

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[7] https://ember-climate.org/data/carbon-price-viewer

Natural gas itself will face its own challenges, as natural gas must be seen not only with its GHG emission from its combustion but also with its emissions caused by its mining and transport. Especial its methane emissions are there of a special interest [36].

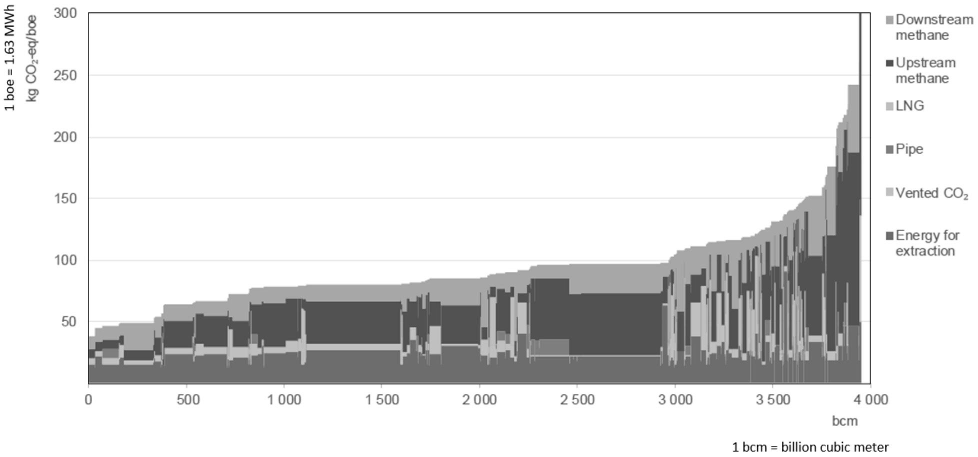

Figure 2-7: Impact on the Mining and Transport on the Carbon Emissions of Natural Gas for various international sources of Natural gas in addition to combustion emissions (DE 201 kg$_{CO2}$/MWh) [36]

The values in Figure 2-7 have a variation between 25 – 185 kg of carbon emissions per MWh of natural gas, which have to be seen as an addition to the combustion emission. In the opinion of the author these will be taken into account more strictly in the future and will be added to the combustion emissions of 202 kg of carbon emissions per MWh.

2.2 High temperature heat pump systems

A heat pump for process steam generation is in principle a series connection of two heat pumps. Upstream classical heat pump process and downstream a vapor compression with water injection for intermediate vapor cooling as shown in Figure 2-8 [37,38,39].

The heat pump process can be run with all known refrigerants (e.g. R134a, R717, R1234ze(E), R744, R600, R600a, etc.) [40][8] . Vapor compression is using water (R718). The refrigerant is selected according to performance optimization, environmental analysis and the hazard potential determination, whereby in the industrial environment the environmental analysis is weighted more heavily than the hazard potential determination than in the case of heat pumps in private use, since here maintenance can be ensured by specialists. The hazard classification is based on the common standard and weighted according to flammable to non-flammable and toxic to non-toxic. Two criteria are decisive for the environmental analysis. One is the potential of the refrigerant to deplete the ozone layer - the Ozone Depletion Potential (ODP).The other is the potential of the refrigerant to warm the climate - the Global Warming Potential (GWP), which is given as a multiple of the GWP of CO2. The F-Gas Regulation regulates here what is allowed for use and what is not [41]. The ODP here must be 0 for industrial heat pumps, although values greater than 1 are also permissible for the GWP here. As an example, R134a

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[8] https://www.bitzer-refrigerantreport.com/fileadmin/user_upload/A-501-20.pdf

has a GWP of 1,430. In comparison, of course, R744 (CO2) has a GWP of 1, illustrating that larger amounts of conventional refrigerants are a climate hazard. R717 (NH3), like R718 (water), as an inorganic refrigerant has a GWP of 0, so their use is advantageous from a sustainable climate protection perspective. R1234ze(E) as a designer liquid has a GWP of 7 and R600a (isobutane) as a hydrocarbon has a GWP of 3, so both are many times smaller than that of R134a.

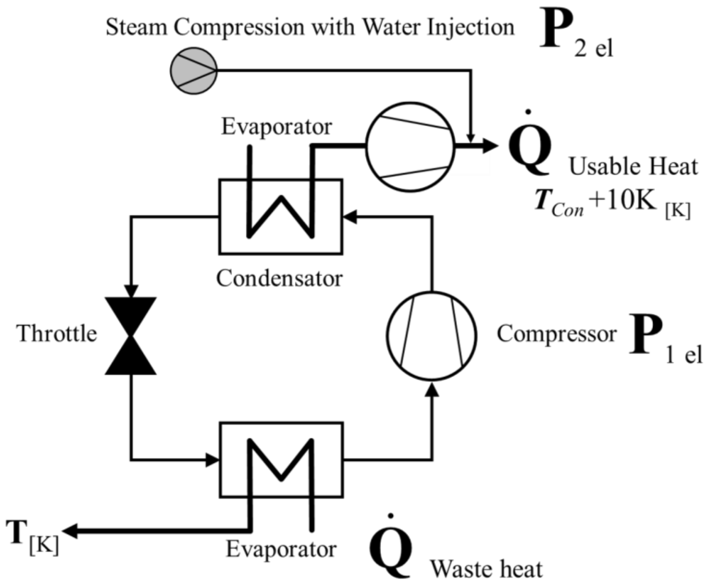


Figure 2-8: Principle flow sheet of a steam generation heat pump

The safety classification is different for all of them. R134a is classified as A1 as non-flammable and non-toxic, as is R744. NH3 is classified B2 as toxic and flammable. R1234ze(E) is rated A2L as non-toxic and flame retardant. R600a is classified as A3 as non-toxic but highly flammable. The flammability of R600a is comparable to that of natural gas. It can therefore be safely controlled in an industrial environment and is significantly less expensive than, for example, R1234ze(E) as a designer fluid. In addition, R600a has a higher volumetric heat capacity, which has a positive effect on compressor costs. Therefore, in an overall analysis, the authors concluded that R600a would be the refrigerant of choice in the industrial environment.

For illustration purposes, an example process is now shown here. Figure 2-9 describes the process in more detail and figure 2-10 shows a 3D view of the heat pump system. As can be seen in the process schematic, the refrigerant and vapor compression stages are combined on an integral gear compressor, which makes the machine a compact unit.

It may be necessary to put up to four compressor shafts in one gearbox or to split the design between two gearboxes in series. The sealing media of the compressors are oil for the R600a compression stages and water for the vapor compression stages. In this case, the housing is designed to be pressure surge resistant since it is flooded with the refrigerant.

The system shown in figures before has a coefficient of performance (COP) of 2.05. The COP gives the thermal energy produced per electric energy input and is used for system comparison.

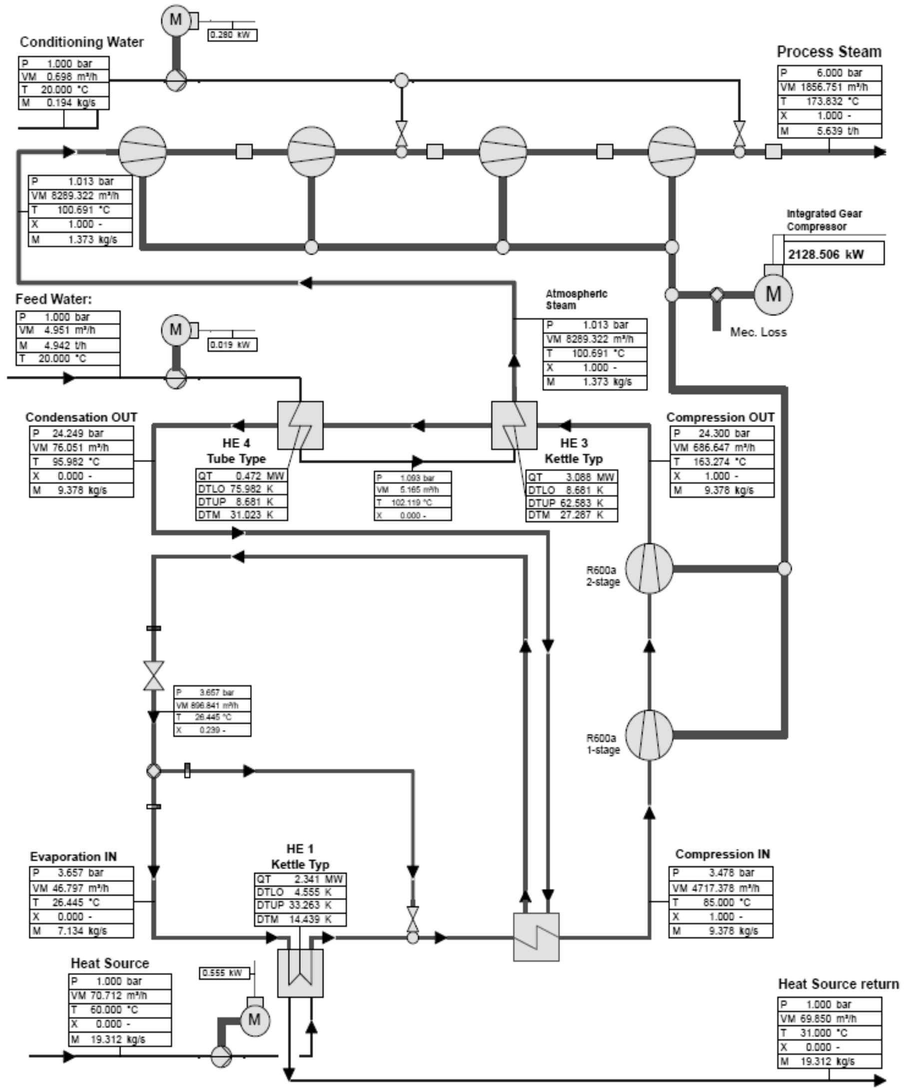


Figure 2-9: Example process of a high temperature heat pump calculated with Ebsilon

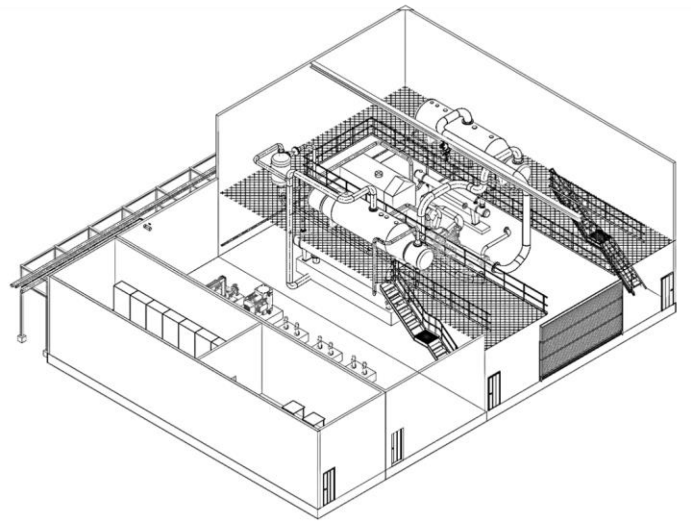


Figure 2-10: 3D-view on a high temperature heat pump system

The Carnot COP here would be < 3.38 resulting in a Carnot grade of > 60%. The calculations are only valid for R600a. Here, the final vapor temperature is always the corresponding condensing temperature plus 15 Kelvin. Likewise, variations of this process with R600a for the steam generation case can be recalculated¸ using the developed approximation formula.

$$COP = \left(\left(a\,{T_R}^2 + b\,T_R + c\right) \cdot d\,{P_{St}}^e + f_1 \ln(P_{St}) + g\right)^{-1} \cdot (t\,T_{Con} + u) \cdot \eta$$

Equation 2-1: Approximation of the COP of a high temperature heat pump

Parameters

$a = -7 \times 10^{-6}$

$b = -0{,}0033$

$c = 0{,}4616$

$d = 1{,}0095$

$e = -0{,}0800$

$f_1 = 0{,}0887$

$g = 0{,}0077$

$t = -0{,}0015$

$u = 1{,}0310$

$\eta = 0{,}9750$

Variables

$T_R \triangleq Return\ Temperature\ HP\ [°C]$

$T_{Con} \triangleq a)\ Kondensattemp.Dampf\ [°C]$

$P_{St} \triangleq Steam\ Pressure$ [bar(a)]

Such heat pump system can be used to optimise power plant processes as well as any wate heat producing process as e.g. electrolysis, carbon capture systems or else. We shall pick this up again.

2.3 State of the art of the power to methanol process

The state of the art of the power to methanol process can be seen already as commercially available [42]. The meta-study of the international renewable energy agency mentions commercial operated plants as e.g. the plant of the company CRI in Iceland (Figure 2-11), which is already in operation since 2011.

Commercially available does not mean necessarily mean 100% mature large-scale technology, but the technology readiness level acc. to EU regulations is to be assumed at TRL 8-9. The reason for this is that the up-scaling is still a matter, which is currently tackled by the newest developments of commercial projects. Currently officially about a dozen of commercial projects are reported in the study and also 10 pilot and demonstration plants of smaller scale are reported.

The implementation of the power to methanol process needs three main technologies: Hydrogen Electrolysis, Carbon Capture and Methanol Generation. These technologies have to be combined, optimised by heat integration and water treatment for their individual site incl. the waste treatment of the process.

In this sub-chapter is discussing this topic incl. necessary technology choices to be taken for the implementation of the power to methanol process in the example CHP power plant process. The mass balances used in this thesis one can find in chapter 3. The full implementation to the steam power plant is described in the same chapter.

Figure 2-11: 4,000 t/year Methanol Production of CRI in Iceland (see also Chapter 2.3.1)

2.3.1 Data of some demonstration plants for the methanol process and discussion of efficiency

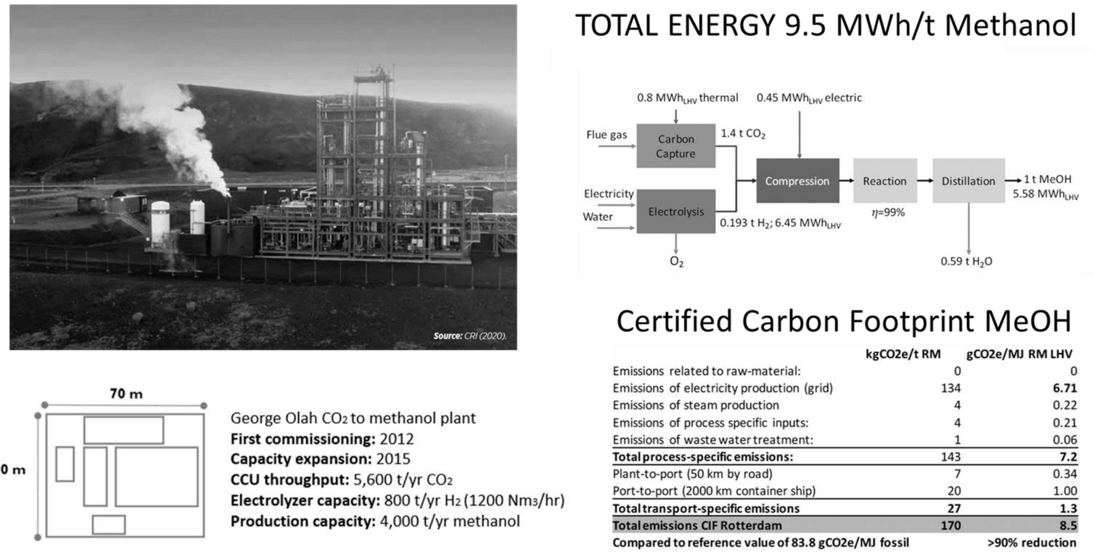
As mentioned before, several demonstration projects for methanol production have been executed before and the author tried to reach out to some operational data of such plant. Publications about details of the operational data is rare. In the following shall be mentioned some information of two plants. None of the today´s operated plants has today a heat utilisation by heat pumps in place.

2.3.1.1 Commercial George-Olah Plant in Iceland

The company Carbon Recycling International SA (CRI) is commercial operating a "green" methanol production in Iceland [43,44]. Due to its commercial character only a view operational data is published. The first difference compared to the here researched technique is the carbon dioxide source. The carbon source at the CRI site is the steam condenser of a geothermal power plant. Here wet and sulphur contaminated carbon dioxide is recovery from the process. Because of this the amine scrubbing in this system is not capturing CO_2, but is cleaning CO_2 from H_2S. This process is less energy consuming compared to carbon capture itself. The not verified reported energy consumption of the system is 9,5 MWh electricity per ton of methanol with a lower heating value of 5,53 MWh/t of an electricity utilisation of 58,2%.

The production of 4000 tons of methanol is realised in base load on an area of 3500 square meters with 143 kg of carbon dioxide equivalent emissions per ton of methanol or 7,2 g/MJ, which can be compared to the emission default value of the renewable energy directive of common fuel, which is 94,1 g/MJ. This is a reduction of more than 92%, but the carbon is from a debated source as it is coming from the geothermal source deep underground where it may have stayed otherwise.

The main take-away from this plant for this thesis is that the methanol generation from CO_2 and H_2 can be securely operated on a commercial basis and that it is possible to build a business case on the technology. That sounds not too much, but is for sure a relevant issue for every technology and so even if only a view data is available the value of this information is high and very important.



George Olah CO_2 to methanol plant
First commissioning: 2012
Capacity expansion: 2015
CCU throughput: 5,600 t/yr CO_2
Electrolyzer capacity: 800 t/yr H_2 (1200 Nm_3/hr)
Production capacity: 4,000 t/yr methanol

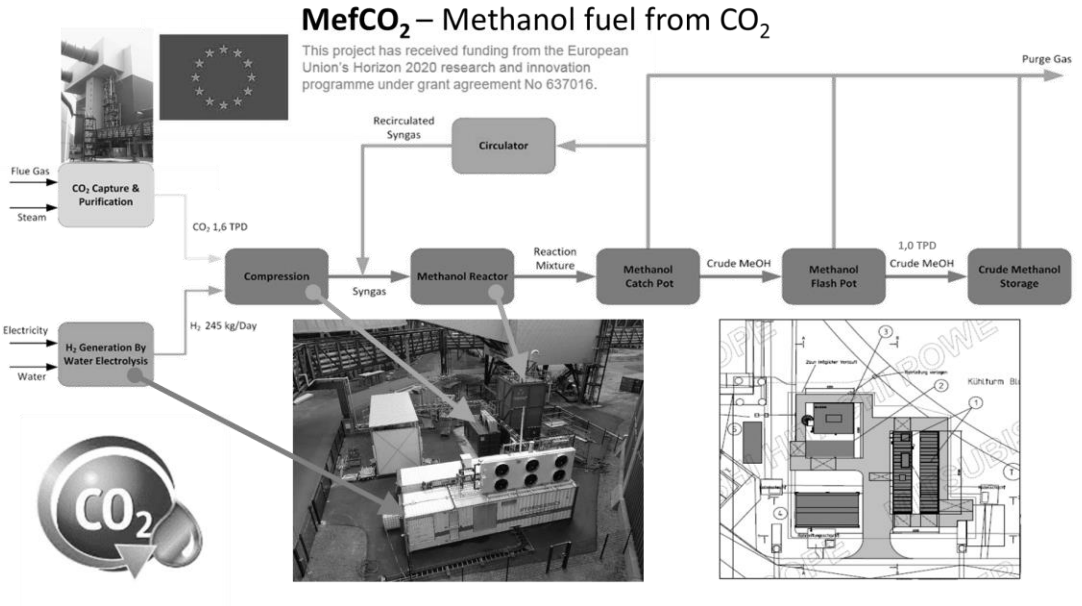
Certified Carbon Footprint MeOH

	kgCO2e/t RM	gCO2e/MJ RM LHV
Emissions related to raw-material:	0	0
Emissions of electricity production (grid)	134	**6.71**
Emissions of steam production	4	0.22
Emissions of process specific inputs:	4	0.21
Emissions of waste water treatment:	1	0.06
Total process-specific emissions:	143	**7.2**
Plant-to-port (50 km by road)	7	0.34
Port-to-port (2000 km container ship)	20	1.00
Total transport-specific emissions	**27**	**1.3**
Total emissions CIF Rotterdam	**170**	**8.5**
Compared to reference value of 83.8 gCO2e/MJ fossil		**>90% reduction**

Figure 2-12: Picture and reported key figures of the Gorge-Olah plant by CRI

2.3.1.2 Technology demonstration plant of MefCo2 project

The other plant, which shall be mentioned is the demonstrator of the research project MefCo2, which is a project funded by the EU under the HORIZON 2020 program [45]. The plant here is about 12 time smaller compared to the Gorge-Olah plant on an area of ca. 900 square meters and was not operated in a base load mode.


$MefCO_2$ – Methanol fuel from CO_2

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 637016.

Figure 2-13: Picture about main configuration of the MefCO2 demonstrator

The plant was integrated in a steam power plant and the carbon source was a slip stream carbon capture from a lignite power plant of RWE in Germany. The published data give no real view in the inside of the total reached efficiency of the demonstrator, but one information is as well obvious and important. The plant showed that a power to methanol unit can be operated load following to a steam power plant and for this thesis it is the important and main takeaway.

The research executed in the project also is giving other interesting insides of the methanol reactor process and possible options for future catalysts, which are verifying other process assumption taken in this thesis.

2.3.2 Hydrogen Generation

The generation of hydrogen is today broad discussed in several countries as the EU27, UK, Japan, USA but also others [46]. In this international discussion it is seen as one of the main energy vectors of the future. It is also not a new technology. Already 1929 the first large scale installation was taken in operation in [47]. It was installed by Norsk-Hydro at Rjukan ca. 200 km west of Oslo in Norway. It had a capacity of 27,900 Nm³/h at atmospheric pressure and an electrical consumption of 142 MW electrical power, which is corresponding to ≈ 5.1 kWh/Nm³ of hydrogen. This plant was operated until 1972 and the hydrogen was used for the production of fertilizers. In 1972 the last large-scale plant was taken in operation in Kwe-Kwe, 200 km west of Harare in Zimbabwe by the company Lurgi. It had a capacity of 21,000 Nm³/h at 30 bar(a) and an electrical consumption of 95 MW, which corresponds to an efficiency of ≈ 4.6 kWh/Nm³(AC). Both plants were based on the alkaline hydrogen electrolysis technology and the plant in Kwe-Kwe is with its efficiency not worth than today´s reported efficiencies of the competing technologies as e.g. the proton exchange membrane electrolysis (PEM) [48]. At this time the membranes were made from asbestos and in the case of the Kwe-Kwe plant it was consisting of 28 stacks with 750 Nm³/h and stack.

Source: Lurgi (1972)

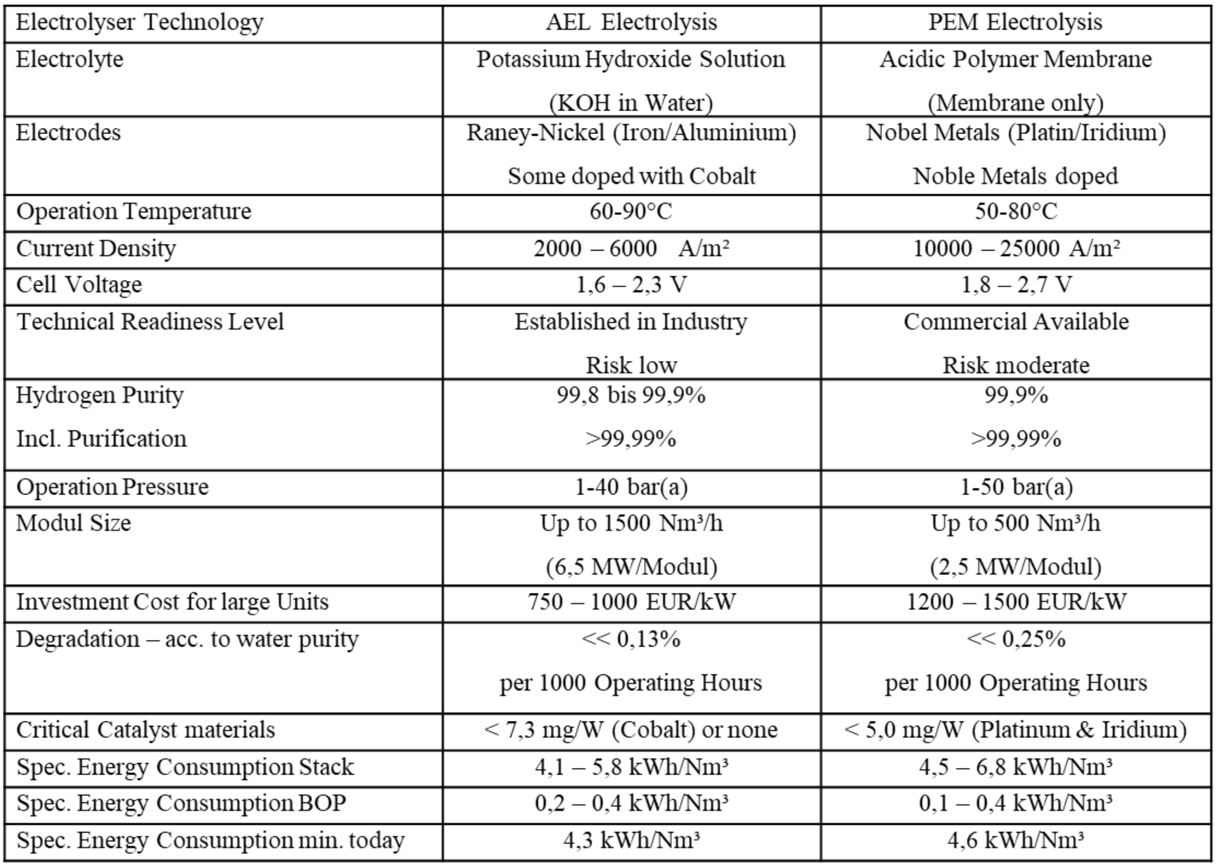
Figure 2-14: Kwe-Kwe Electrolyser Plant for 21,000 Nm³/h at 95 MW electrical consumption [48]

2.3.2.1 Comparison of hydrogen electrolysis processes and choice of technology

As the author already analysed in his publications there are today three discussed electrolyser technologies, which are recognised for the future large-scale use. This is the established alkaline electrolyser technology (AEL), the proton exchange membrane electrolysis (PEM) and the solid oxide electrolyser cell for hydrogen (SOEC) [49,50,51]. But there are also other emerging technologies which are the anion exchange membrane electrolyser (AEM) and the so called battolyser, what is simply an overcharged Edison-battery [52,53]. But those two technologies will not be taken in the comparison, due to the reason they are today and in the next decade not commercially available for large scale applications. As well the SOEC will not be taken into account here for the same reason. It will also not be commercially available in the running decade for large industrial applications.

Within the running decade the decision for large scale installation will be between AEL and PEM technology as also analysed by the author before [54]. This comparison from literature data and own analysis leads to the following table [55,56].

Table 2-3: Comparison of AEL & PEM Electrolyser Technology main technical Data [48]



Electrolyser Technology	AEL Electrolysis	PEM Electrolysis
Electrolyte	Potassium Hydroxide Solution (KOH in Water)	Acidic Polymer Membrane (Membrane only)
Electrodes	Raney-Nickel (Iron/Aluminium) Some doped with Cobalt	Nobel Metals (Platin/Iridium) Noble Metals doped
Operation Temperature	60-90°C	50-80°C
Current Density	2000 – 6000 A/m^2	10000 – 25000 A/m^2
Cell Voltage	1,6 – 2,3 V	1,8 – 2,7 V
Technical Readiness Level	Established in Industry Risk low	Commercial Available Risk moderate
Hydrogen Purity Incl. Purification	99,8 bis 99,9% >99,99%	99,9% >99,99%
Operation Pressure	1-40 bar(a)	1-50 bar(a)
Modul Size	Up to 1500 Nm^3/h (6,5 MW/Modul)	Up to 500 Nm^3/h (2,5 MW/Modul)
Investment Cost for large Units	750 – 1000 EUR/kW	1200 – 1500 EUR/kW
Degradation – acc. to water purity	<< 0,13% per 1000 Operating Hours	<< 0,25% per 1000 Operating Hours
Critical Catalyst materials	< 7,3 mg/W (Cobalt) or none	< 5,0 mg/W (Platinum & Iridium)
Spec. Energy Consumption Stack	4,1 – 5,8 kWh/Nm^3	4,5 – 6,8 kWh/Nm^3
Spec. Energy Consumption BOP	0,2 – 0,4 kWh/Nm^3	0,1 – 0,4 kWh/Nm^3
Spec. Energy Consumption min. today	4,3 kWh/Nm^3	4,6 kWh/Nm^3

Based on this table the author comes to the conclusion that for large industrial installation the AEL technology will be ahead of the PEM technology for such installations. PEM have several advantages in small scale installation for some MW installation, as e.g. for a hydrogen filling station for mobility use, and in general this technology will become competitive if some of its restrictions are solved. The today´s main restrictions are the higher investment at a lower efficiency, with at the same time fewer experience in the lifetime of a large-scale plant. In the further course we analyse more in depth the alkaline electrolyser technology and its future potential.

This analysis in also matching an expert analysis executed in 2017 by the Imperial College London [57]. The study comes to the conclusion that AEL will have at lower capital cost even in 2030 advantages in efficiency, lifetime.

2.3.2.2 Alkaline hydrogen electrolysis

For the alkaline hydrogen electrolyser, the shown flow diagram is giving the basics of the process. It is showing the generation of the direct current, the electrolyser stack and the gas separation system. The gas separation system is divided in two independent flow cycles for the hydrogen and the oxygen side.

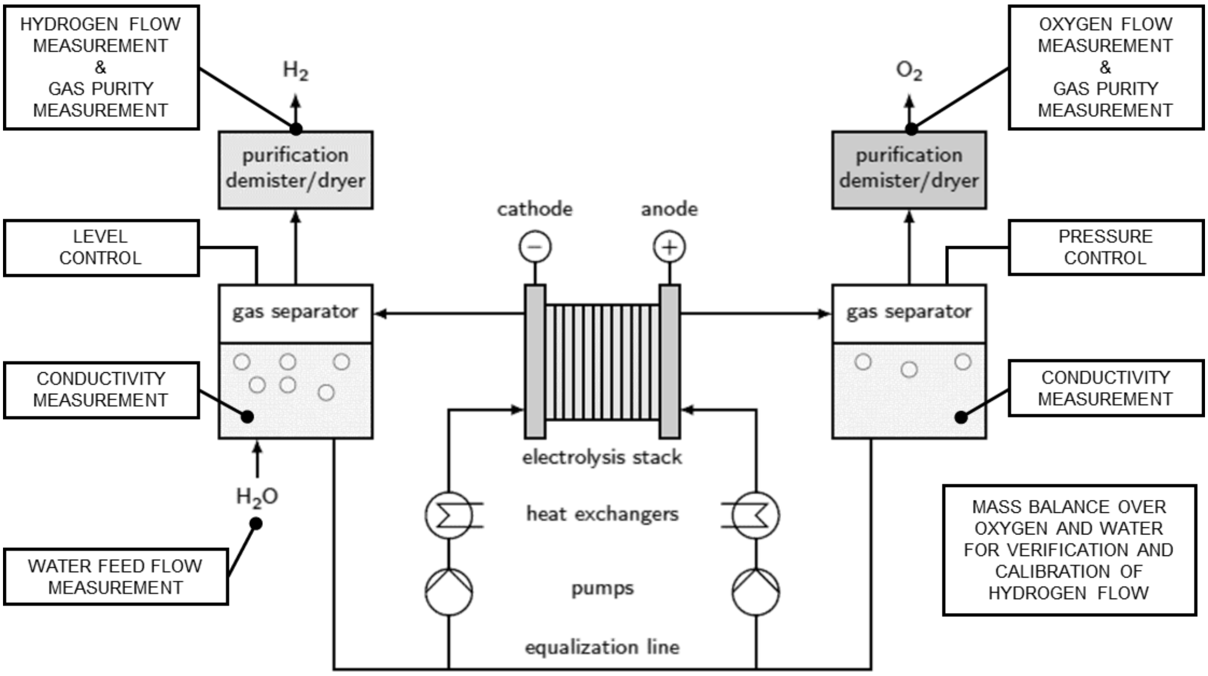


Figure 2-15: Simplified Process Flow Diagram of an Alkaline Hydrogen Electrolyser

Lye feed pumps circulated at a fixed rate the KOH lye through the system and transport a lye gas bubble mix from the electrolyser stack, which is under DC current, to the gas separator vessels. Here gas and liquid are separated and the gas is afterwards cooled by cooling water and via mist eliminators cleaned from droplets. The water recovered after the cooling stage is sometimes disposed to avoid the concentration of heavy water in the system [58] but at temperatures of 30-40°C enough slip stream removal of D_2O is considered. Only the hydrogen is purified via an oxidation reactor, where the always present oxygen contamination in the hydrogen is catalytically burned with the hydrogen forming pure water [59].

As mentioned before the AEL is an established technology since almost 100 years and its efficiency of the stack only can be easily calculated from the following equation [60,61].

$$E_{Electrolysis}\left[\frac{kWh}{Nm^3{}_{Hydrogen}}\right] = 2{,}39298 \times U_{Cell}\,[V] \times \frac{kAh}{Nm^3{}_{Hydrogen}}$$

Equation 2-2: Electrolyser Efficiency evaluated from Faraday´s Law with implemented constants

$$
\begin{aligned}
U_{Cell}[V] \;=\;\; & U_{Reversible}\,[V] + U_{KOH-Anode}\,[V] + U_{Bubble-O2}\,[V] + U_{\eta-Anode}\,[V] \\
& + U_{R-Anode}\,[V] + U_{R-Membrane}\,[V] + U_{R-Cathode}\,[V] \\
& + U_{\eta-Cathode}\,[V] + U_{Bubble-H2}\,[V] + U_{KOH-Cathode}\,[V] \\
& + U_{R-Bipolar-Plate}\,[V]
\end{aligned}
$$

$$
U_{Cell}\,[V] \;=\; U_{Leakage-Current}\,[V]
$$

Equation 2-3: Summation of single Voltage Drops over the Electrolyser cell

It says that with a known cell voltage (U_{cell}) of an electrolysis the efficiency is terminated by a constant factor. The cell-voltage (U_{cell}) is now a not linear function of the current density ($D_{current-DC}$) of the cell stack. It is depended on several variables of the cell stack itself (geometry, operating temperature & pressure) but also of the used materials of the electrodes, the potassium hydroxide solution concentration and the membrane resistance. The total kinetics of the reaction in the cell stack is a complex system. The cell voltage (U_{cell}) is so consisting of several single voltage losses according to the following equation.

Figure 2-16 is visualising the voltage drops over a today´s electrolyser cell, with a zero-gap configuration, which is according to the given literature common today [62].

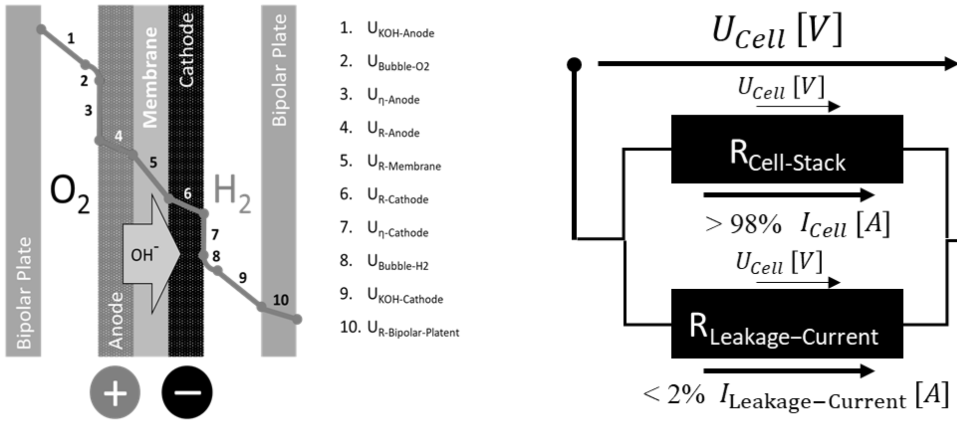


Figure 2-16: Single Voltage Drops over a single Electrolyser Cell additional to the reversible Cell Voltage and the parallel resistances of the stack for leakage and voltage drop

All the given single voltage losses have various factors, which will be described in the following and the information is mainly taken from the literature given under endnote [63].

0. $U_{Reversible}$ – Reversible voltage drop of the electrolyser cell

    a. The voltage drop is caused by the thermodynamics of the water splitting and is depended on
    b. the operating temperature, where higher temperatures will reduce the voltage drop
    c. and the operating pressure, where a higher pressure will raise the voltage drop

1. U $_{\text{KOH-Anode}}$ – Ohmic losses of the KOH lye

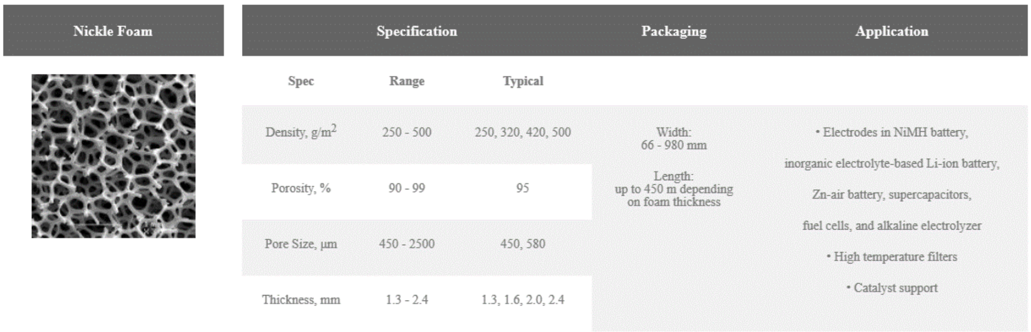
    a. This voltage drop is depended on the distance between bi-polar plate and the anode, where a lower distance will reduce the voltage drop limited by the needed space for the gas transport,
    b. the operating temperature, where here as well a higher temperature leads to a lower pressure drop
    c. and concentration of the KOH lye with an optimum point for each operating temperature (e.g. 30wt% @ 85°C)

2. U $_{\text{Bubble-O2}}$ – Ohmic Losses and overvoltage raise of oxygen bubbles in the KOH lye

    a. The gas bubbles in the KOH lye are causing the necessity for the ions to travel longer ways and this is raising the higher ohmic resistance of the KOH lye. This is reduced by higher operating pressure
    b. Also, the gas bubbles on the surface of the electrode are causing an area reduction of the electrode, what lead to an addition voltage drop. With raising pressure, the cover-factor of the oxygen bubbles on the surface is raising as well and here higher pressures lead to a higher voltage drop
    c. The loss can also be reduced by raising the forced flow of the KOH lye through the cell, which has to be optimised with the pressure loss in the recirculation system. Pressure drop is commonly 2-4 bar(a)

3. U $_{\eta\text{-Anode}}$ – Overvoltage of the Anode

    a. The overvoltage is depended on the material composition and the material surface. It can be influenced by the geometry by using metal foam (see figure 2-17), but also it can be influenced by chemical activation by electrochemical or chemical precipitation of metal oxides or the use of Raney-Metal. This is toady´s the MAIN research field for the material in AEL technology. The Anode is causing highest voltage drops in the total electrolyser cell.



Nickle Foam	Specification			Packaging	Application
	Spec	Range	Typical		
	Density, g/m^2	250 - 500	250, 320, 420, 500	Width: 66 - 980 mm Length: up to 450 m depending on foam thickness	• Electrodes in NiMH battery, inorganic electrolyte-based Li-ion battery, Zn-air battery, supercapacitors, fuel cells, and alkaline electrolyzer • High temperature filters • Catalyst support
	Porosity, %	90 - 99	95		
	Pore Size, µm	450 - 2500	450, 580		
	Thickness, mm	1.3 - 2.4	1.3, 1.6, 2.0, 2.4		

Figure 2-17: Example for Nickel Foam from Industry as Base Material[9]

    b. Beside the activation before operation there are also options of in situ activation of the anodes by deposing e.g. Fe_2O_3 on its surface [64]. In situ activation has the advantage that is can be also done in AEL operation

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[9] https://www.cnemcorp.com/metal-foams/

c. The overvoltage is also temperature depended and will be activated by higher temperatures, but is limited by the corrosion resistance of the design materials

d. Activated Anodes usually loose faster the performance compared to non-activated anodes. This must be taken in consideration in life-time calculations and give an advantage to in situ activation methods

e. Figure 2-18 shows the effect of electrode morphology on the ohmic resistance. The initial ohmic resistance of the cell with nickel foam as the electrodes is 2% lower than the next best of the expanded mesh, the coarse woven mesh has the lowest initial value. This is attributed to the reduced distance for ion conduction between the electrodes. The poor performance of the foam cell at high current densities is ascribed to thickness of the nickel foam, causing gas entrapment in the large quantity of pores [65].

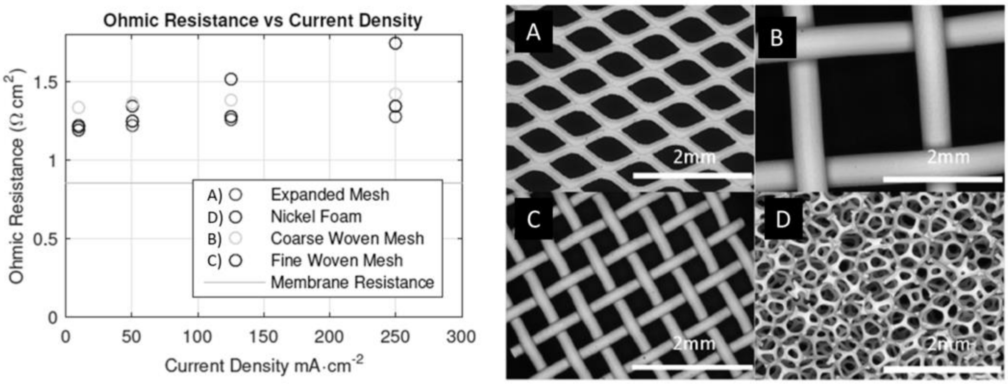


Figure 2-18: Effect of electrode morphology on the ohmic resistance with Ni electrodes [66]

In this work the various options of anode activation can only be briefly mentioned and is not possible to give a full overview of the options. For further investigation check the given literature. Examples of materials from literature:

4. U $_{R\text{-}Anode}$ – Ohmic resistance of the Anode

   a. The ohmic resistance of the Anode is today mainly reduced by the use of the mentioned electrode materials and the use of the zero-gap technology and are usually small

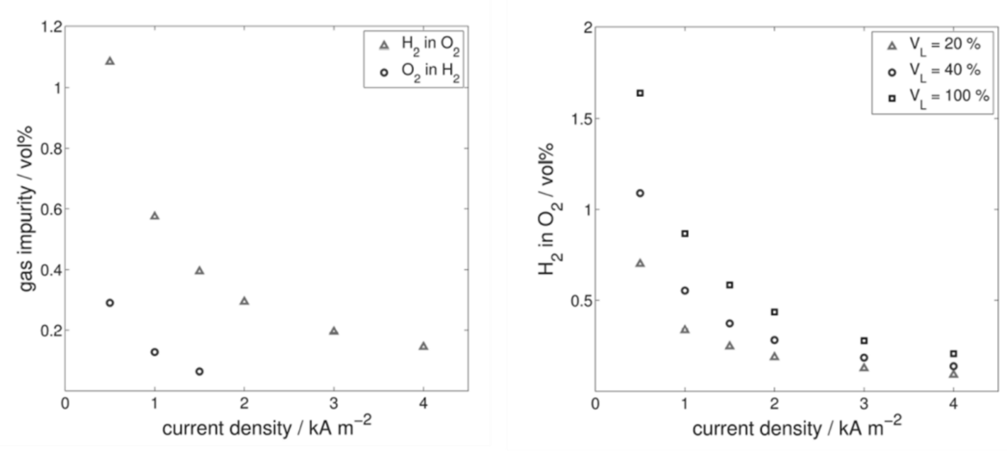
5. U $_{R\text{-}Membrane}$ – Resistance of the membrane of the electrolyser cell

   a. This voltage drop can be calculated according the equation

$$U_{R-Membrane}\,[V] = I\,[A]\ \times S\,[m^2]\ \times \frac{\rho_{KOH\ Lye}\ \times\ s_{Membrane}\ \times\ \tau}{\varepsilon}\,[\Omega/m^2]$$

Equation 2-4: For Membrane Resistance with I as Cell Current, S as active Cell Area, ρ as specific Resistance of KOH-Lye, s as Thickness of the Membrane, τ as Labyrinth-Factor and ε as Porosity

Here various materials deliver various options for the design. Beside low resistance it is also very important that the membrane is a good separator to avoid oxygen in the hydrogen and vis versa. The mechanical strength of the material is also important for the robustness of the electrolyser stack. Material examples are: Asbestos with organic binder, poly-tetra-flour-ethylene (PTFE), PTFE with TiO, poly-sulphone, poly-ethylene-sulphide, but also other polymers. See also [66]. Every membrane has also a limit of lowest operation current density.



Measurement with 30% KOH-Lye @ 80°C with the Membrane: Zirfon^{TM} Perl UTP 500 by AGFA with var. Flow Rates

Figure 2-19: Measurements of gas impurity from literature with var. flow rates [67]

At a certain lower limit of the current density the oxygen concentration in the hydrogen is reaching its safety limit, where a save operation is not possible. A common value for this is usually 1% of hydrogen in the produced Oxygen (50% of the explosion limit) [67].

6. $U_{R\text{-Cathode}}$ – Ohmic resistance of the Cathode

    a. The ohmic resistance of the Cathode is as for the Anode mainly reduced by the use of metal foams and the use of the zero-gap technology and are usually small

7. $U_{\eta\text{-Cathode}}$ – Overvoltage of the Cathode

    a. The overvoltage is as well depended on the material composition and the material surface. It can be influenced by the geometry and it can be influenced by chemical activation by electrochemical or chemical precipitation of metal oxides or the use of Raney-Metal
    b. Beside the activation before operation there are also options of in situ activation of the cathodes by deposing e.g. Co2O3, Ni-Co-Mo and Fe-Co-Mo on its surface [49]. In situ activation has the advantage that is can be also done in AEL operation
    c. The overvoltage is also temperature depended and will be activated by higher temperatures, but is limited by the corrosion resistance of the design materials
    d. The overvoltage is also reduced by reducing the KOH lye concentration
    e. The overvoltage of the cathode is usually only 50% of the anode

    In this work also the various options of cathode activation can only be briefly mentioned.

8. $U_{Bubble\text{-}H2}$ – Ohmic Losses and overvoltage raise hydrogen bubbles in the KOH lye

    a. The gas bubbles in the KOH lye are causing the necessity for the ions to travel longer ways and this is raising the higher ohmic resistance of the KOH lye. This is reduced by higher operating pressure
    b. The grip of gas bubbles on the surface of the electrode is bad, independent from the pressure. In comparison with the oxygen side the size of the bubbles is small and the bubble size in independent of the temperature and the KOH concentration
    c. The resistance is strongly reduced by a raise of the KOH concentration (until a maximum of conductivity between 25 and 30wt.%)
    d. The loss can also be reduced by raising the forced flow of the KOH lye through the cell, what has to optimised with the pressure loss in the recirculation system. Pressure drop is commonly 2-4 bar(a)

9. $U_{KOH\text{-}Cathode}$ – Ohmic losses of the KOH lye

    a. This voltage drop is dependent on the distance between bi-polar plate and the anode, where a lower distance will reduce the voltage drop limited by the needed space for the gas transport,
    b. the operating temperature, where here as well a higher temperature leads to a lower pressure drop
    c. and concentration of the KOH lye with an optimum point for each operating temperature (e.g. 30wt% @ 85°C)

10. $U_{R\text{-}Bipolar\text{-}Plate}$ – Ohmic losses of the bipolar plate

    a. This voltage drop is depended on the thickness of the bipolar plate and can be reduced by this. Usually the voltage drop is low, but a reduction by 0.5 mm on a large stack can have some impact to the total losses. It shall be part of any optimization

11. $U_{Leakage\text{-}Current}$ – Ohmic losses of leakage current over the cell

    a. This loss is depended on the design of the cell itself and can be minimised below 2% of the current losses of a stack. Further minimisation is still possible. It can be expressed by an efficiency factor of the stack e.g. η_{LC} = 98% for 2% leakage current of the entire stack and is a measured value. The voltage itself is equal to the cell voltage

The power consumption of a full AEL cell stack can be calculated by the following equation. It can be analysed that the current density ($D_{current}$) is part of the equation, but the cell voltage is also a function of the current density.

$$P_{DC-Stack}\,[\,kWh\,] = [\,Cells/Stack \times U_{Cell}\,(D_{Current}\ [A/m^2], T[°C], p[bar(a)],\ \chi_{KOH}[wt\%])\,[V] \times D_{Current}\ [A/m^2] \times S[m^2] \times 2{,}39298\,\frac{kAh}{Nm^3{}_{Hydrogen}}\,] \div \eta_{LC}$$

Equation 2-5: Calculation Formular to calculate the Stack Power of an AEL Stack, S = Active Area of Cell

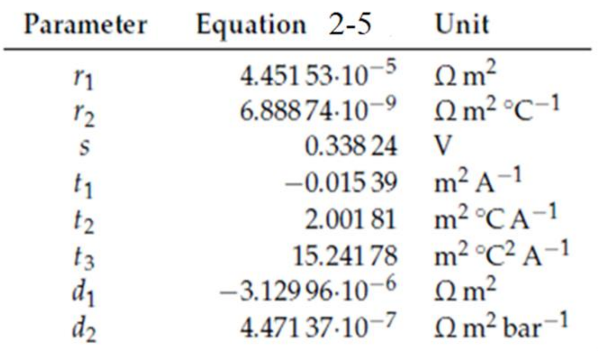
The needed function for the cell voltage (U_{cell}) over the current density ($D_{current}$) can only be given by the delivering company or must be taken from a test of a designed stack with defined temperature (T [°C]), pressure (p [bar(a)]) and KOH lye concentration (χ_{KOH} [wt%]). Here also the degradation of the cell is important and shall be given by the manufacturer as a function of the operating hours and total installation time. A full pre-calculation from theoretical values is usually not possible. This function as a derivate from supplier tests looks as follows [68,69,70,71], where the KOH lye concentration (χ_{KOH} [wt%]) is neglected due to the reason that the effect is suppressed in the concentration range from χ_{KOH} [wt%] 25 – 30 % of the lye. The main adjustable factor for various electrolyser types is s, which includes geometry, electrode materials and the membrane effects for the cell voltage. This equation is valid for temperatures from 10 to 110 °C and pressures from 5 to 40 bar(a).

$$U_{cell} = [(-0{,}0004333 - \frac{0{,}0002785}{30}) \times p + T + (1{,}2396017 + \frac{0{,}0771937}{30}) \times p\,] + [(r_1 + d_1) + r_2 \times T + d_2 \times p] \times D_{Current} + s \times log[(\,t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}) \times D_{Current} + 1]$$

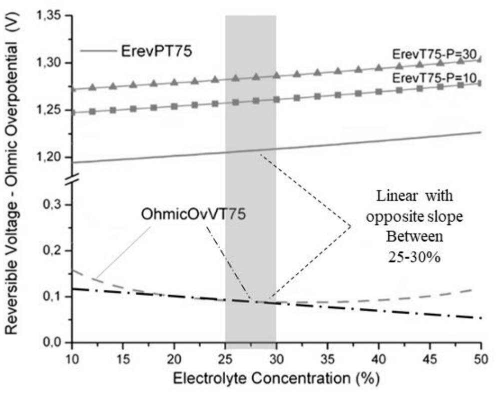
Equation 2-6: Calculation Formular for real Cell voltage U_{cell} [V] incl. parameters for p, T and Cell

Here the factors r_i describe the Temperature impact and factors d_i describe the pressure impact, while s and t_i describing the cell material, geometry and membrane materials. Here the main cell factor is the factor s, which´s variation can cover most effects.

Table 2-4: Parameters Equation 2-5 and Diagram showing Lye Concentration Independence Window



Parameter	Equation 2-5	Unit
r_1	$4.451\,53 \cdot 10^{-5}$	$\Omega\,m^2$
r_2	$6.888\,74 \cdot 10^{-9}$	$\Omega\,m^2\,°C^{-1}$
s	$0.338\,24$	V
t_1	$-0.015\,39$	$m^2\,A^{-1}$
t_2	$2.001\,81$	$m^2\,°C\,A^{-1}$
t_3	$15.241\,78$	$m^2\,°C^2\,A^{-1}$
d_1	$-3.129\,96 \cdot 10^{-6}$	$\Omega\,m^2$
d_2	$4.471\,37 \cdot 10^{-7}$	$\Omega\,m^2\,bar^{-1}$



The Electrolyser cells are put in a row to form the electrolyser stack (see Figure 2-20). The connection to the electric plus pole is usually done in the middle of the stack, while the liquid and gas connection are done at both ends of the stack at the electric minus pole. The reason for this is to avoid static charging of the gas separator unit. Electrodes are running from the minus to the plus pole and this measure is avoiding the mentioned static charging of the unit.

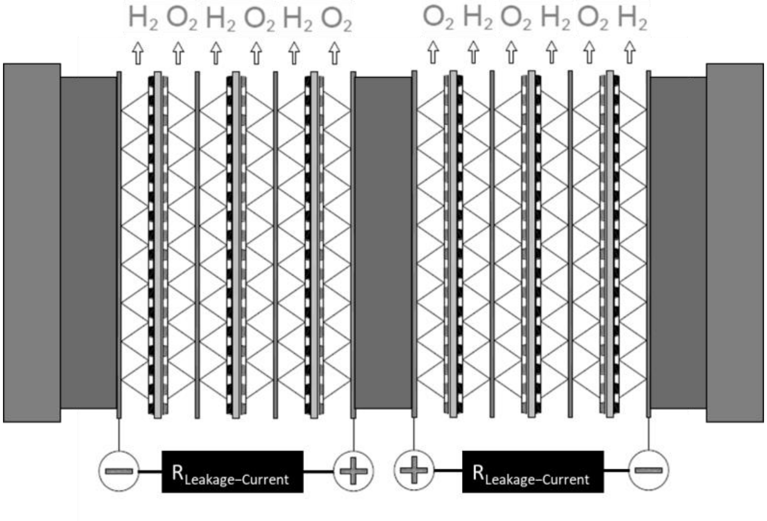


Figure 2-20: Electrolyser stack design for bipolar stack design with middle plate connection to plus pole

This topic will be raised again in chapter 2.4 when we discuss the electric part and the power electronics. Direct current generation is easier, if the voltage is high and the current is low. This design is working against this rule, because it is limiting the possible voltage by the number of cells, which are mechanical possible on a manufacturable and transportable stack. In the next chapter it is also a topic to overcome this issue.

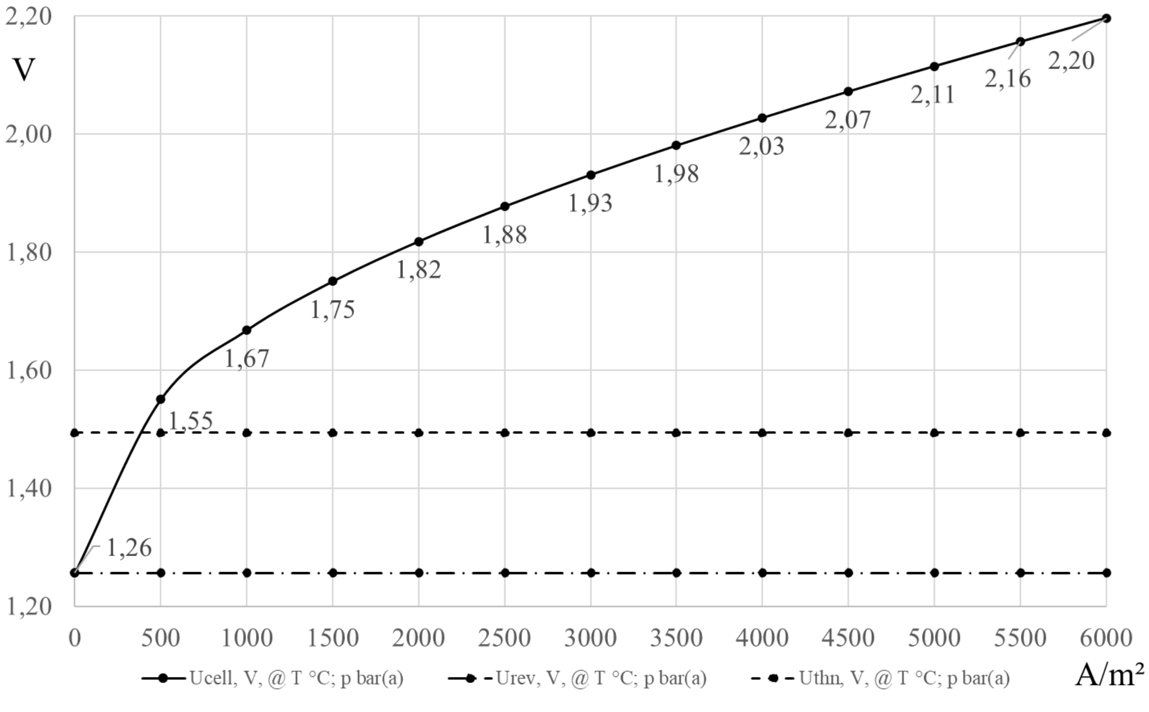


Figure 2-21: Cell Voltage over Current Density of one Manufacturer and from Literature [45]

From the literature and interviews with a manufacturer the following cell voltage function could be defined. It counts at 30 bar(a) internal pressure, 85 °C operating temperature and a lye concentration of 30 wt%. The cells are assumed to be safely operated above 1,000 A/m².

The interviewed manufacturer is today already operating its 2nd generation of its cell type and is currently introducing the 3rd generation of its cell type with activated anode and optimised geometry. The expected performance for the 3rd generation is already expected better what means for the calculation al lower factor s, which drops than by 33%.

Deactivation for the 2nd generation electrode is currently given with 1 % addition to factor s per 8000 operation hours. For the other data sets no degradation value can be given. A used safety margin of the supplies is usually also 0,01 [V] on the cell voltage.

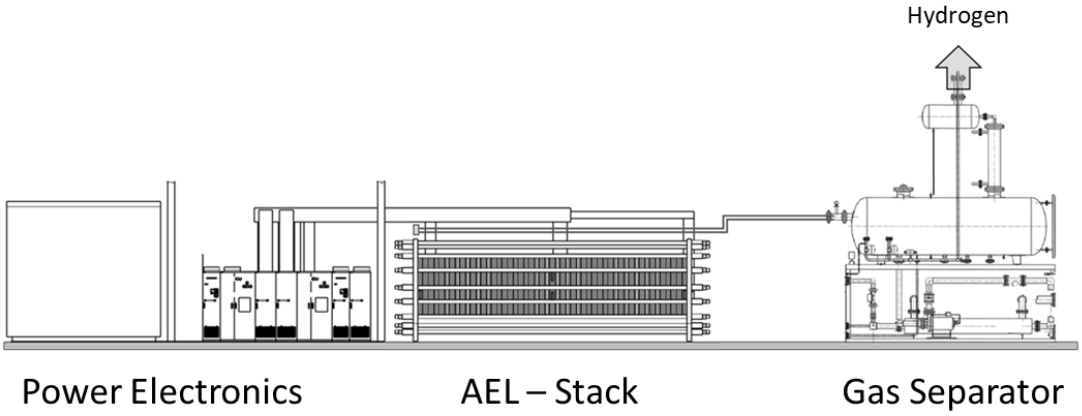
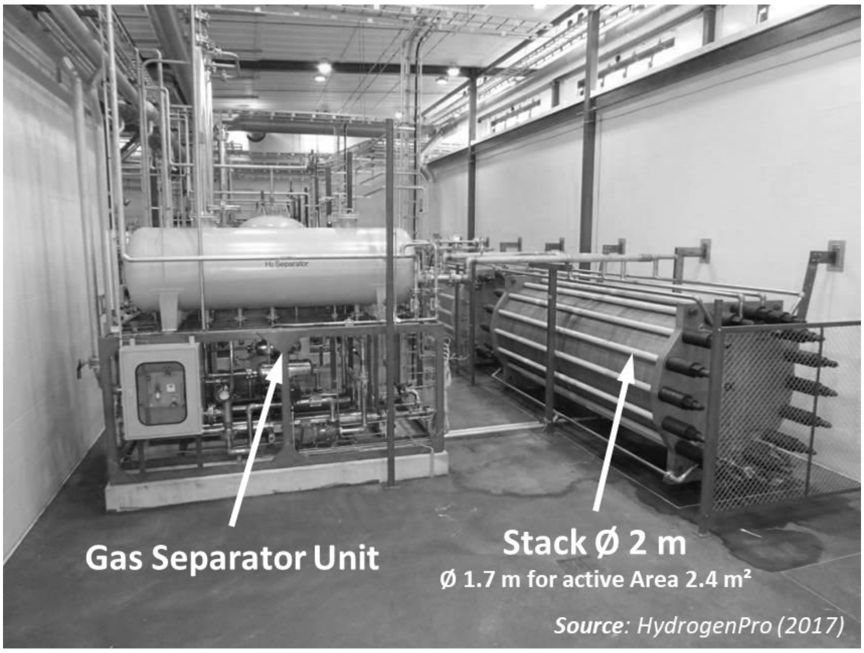


Figure 2-22: Picture of an Electrolyser Modul with Power Electronics and Gas Separator Unit



Source: HydrogenPro (2017)

Figure 2-23: Picture of an Installation of an Electrolyser System in Finland, 600 Nm³/h per Stack

Today (see also Figure 2-23) the pressurised AEL are, since 1972 by Lurgi designed the first time, in a cylindric form. Together with the production width of the membranes this is limiting the designable cell area in the construction. This is today limited by approx. 1.75 m active diameter. From interviews with four manufactures the given reason is the internal pressure of the cell stack, while the manufacturers are fully aware that this is limiting the possible cell area, by the limitations in the manufacture’s width of the membrane materials. This will be one of the topics to discuss in following chapter with the way forward in the electrolyser design.

2.3.2.3 Future design of alkaline hydrogen electrolysis electrodes

The design on today´s alkaline electrolyser systems is falling apart in three major systems. First the power electronics, which usually can be sourced also from a different supplier as the process system. Second the core part, the electrolyser stack, which is usually the core know-how of the specialised supplier and third the gas separation unit incl. the hydrogen and oxygen cleaning systems. If the operating parameters as temperature, pressure, lye concentration and flow rated through the stack are defined the gas separation and cleaning unit, consisting of separation vessels, piping, valves, heat exchangers, cooling system, pumps, hydrogen deoxidation, hydrogen drying, oxygen deoxidation and drying, LV electrical system and I&C, can in a general assumption be sources from many chemical companies.

The power electronics will be discussed in the following chapter. The gas separation in future needs to be optimised in its design. Here the used corrosion resistant parts have the need to be optimised by a cost to value system to minimise the material cost. The main location of corrosion is here the oxygen side, where the presence of oxygen together with KOH lye is the main corrosion driver. As also given in the literature already the addition of LiOH in the KOH can reduce the corrosion potential of the lye, while at the same time the overpotential on the anode side can be reduce. To discuss all options here is too lengthy for this work, but the reader can assume, that for the design of gas separation units also suppliers can serve, which are not necessarily specialised in electrolysis. Gas separation in a standard process in chemical and petro-chemical industry and this market pressure in the future will lead to cost reduction by a learning curve. The interviews with manufactures showed that this process is running already.

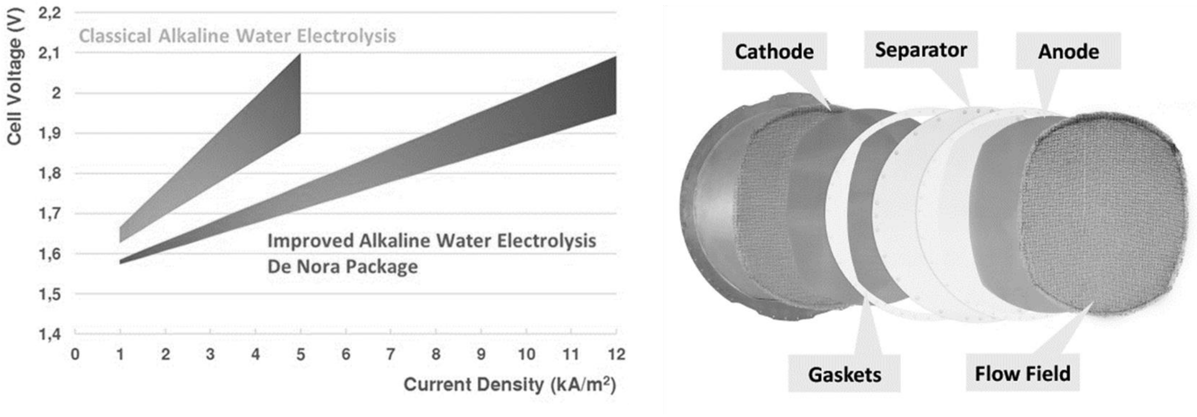


Figure 2-24: AEL performance advertisement of DeNora Electrodes with AGFA Membranes

From this short analysis it can be followed, that the main cost reduction and efficiency raise of the system must come from the reinvention of the stack design. The research of the past was mainly focused on the used electrode pair and the membrane. The geometry designs were focused on the positioning of the electrodes and the minimisation of the free flow gap.

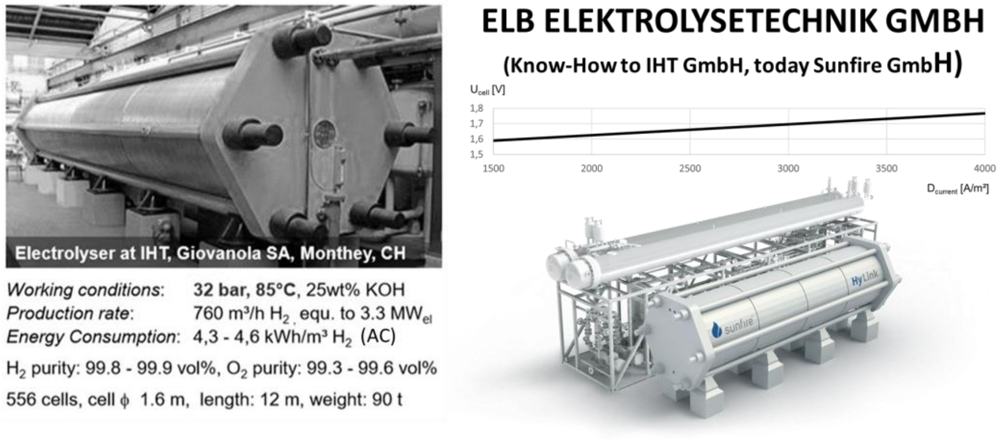


Figure 2-25: ELB Electrolyser System incl. best available process data for the System 2012

These efforts already lead to good success. The company DeNora claims in its advertisement[10] already for its high-performance system, using their own electrodes together with a membrane from AGFA[11]. These stack materials are already used by the electrolyser manufacturer McPhy, according to DeNora advertisement.

The given data are also corresponding to official number given by ELB Elektrolysetechnik GmbH already in 2012 [72]. Technology is today technology of Sunfire [12]. The activation technology use here was already developed by Lurgi as “DSK” activation based on Raney nickel power and carbonyl nickel power.

Both offered technologies promise DC consumptions of approximated 4,2 - 4.3 kWh/Nm³ of hydrogen at a current density of 4000 A/m² and shall be accepted as today´s best available technology.

2.3.2.4 Excursus on cost reduction possibilities for AEL stacks of rectangular design

Now a new focus now shall be on the geometry for up-scaling of the stack design to reach better economy of scale. This shall be discussed in the following.

The design of the cylindrical stacks, as mentioned before, is based on the engineer’s assumption, that this is necessary to withstand the internal pressures of the electrolyser stack as e.g. given here with 30 bar(a). This is taken into account that the structural ring of the bipolar plat is carrying all loads of the internal pressure. The gaskets between the cells are only withstanding the pressure due to the compression forces in the gasket itself.

Now we are looking in the formular of the deformation of such a structural ring. This is given by a differential equation for the radial deformation u(x) in polar coordinates as follows [73].

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[10] https://denora.com/products/applications/energy-storage/alkaline-water-electrolysis.html

[11] https://www.agfa.com/specialty-products/solutions/membranes/zirfon/

[12] https://www.sunfire.de/de/wasserstoff

$$E \times \frac{b \times h^3}{12} \times u''''(r) + (\frac{4 \times E \times h}{d^2} + \frac{2 \times E \times s}{\mathrm{d}})\, u(r) \;=\; p(r)$$

Equation 2-7: Differential Equation of the Model of a Ring Element with internal Slab

Here E is Young's Modul, h is the height of the beam element, b is the width of the beam element, d is the diameter of the structural ring, s is the thickness of the slab and p is the pressure. With this approach the differential equation of a cylinder under internal pressure including bending is set equal to the problem of a beam on an elastic support.

If we take the assumption that a slab (bipolar plate) welded in a rectangular frame (structural cell stack frame) is also an elastic support, we can arrange the equation for the deformation w(x) of the structural frame beams quite similar for each beam in the frame.

$$E \times \frac{b \times h^3}{12} \times w''''(x) + \frac{2 \times E \times s}{\mathrm{d}_{1,2}}\, w(x) \;=\; p(x)$$

Equation 2-8: Differential Equation of the Model of a Structural Frame Beam with internal Slab

Here E is again Young's Modul, h is the height of the beam element, b is the width of the beam element, $\mathrm{d}_{1,2}$ is the distance between to opposed beams, s is the thickness of the slab and p is the pressure.

Having the two equations in comparison we can assume that the mechanical behaviour is also somehow similar. This is checked by the following real dimension calculation by FEM (Software: RFEM by Company Dlubal, Version 5.214) of a possible cell stack frame with the following dimensions.

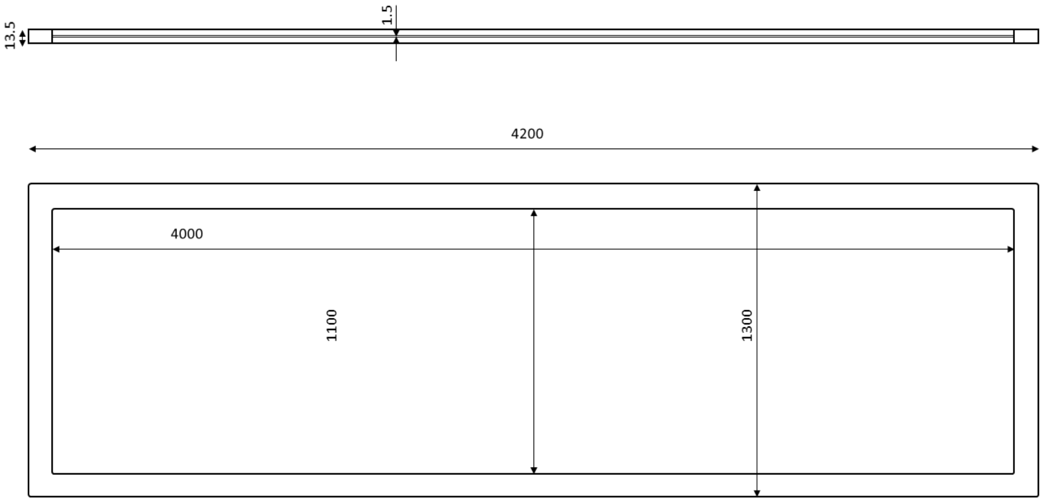


Figure 2-26: Model Geometry for Cell Stack Frame for next Generation AEL Stacks [mm]

The calculation was executed for an internal pressure of 30 bar(a) and for the line force on the beams also the additional area of the gaskets was taken into account with 2 mm. It was resulting in 45 N/mm as applied load to the frame as interpretation of the internal pressure. As material of the frame is P355 (carbon steel) chosen with a strength parameter of 230 N/mm² for dynamic loads and below 100°C. Figure 2-27 gives the results of the calculation of the bending moment, the normal force and the share forces of the beams in the frame.

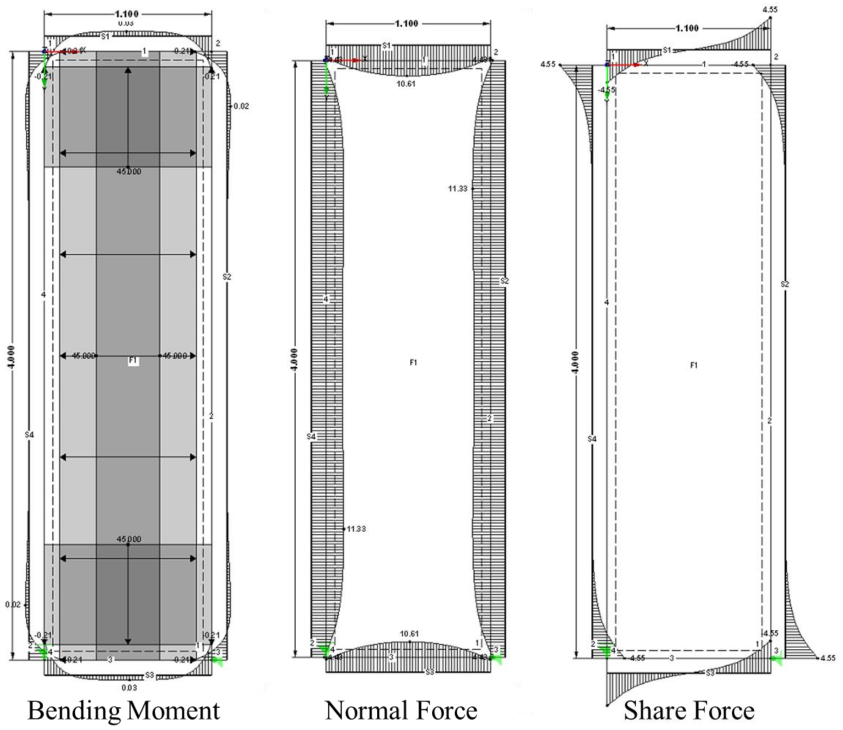
This results now in stresses in the beams of the frame, which are very low. The max. bending stress calculates down to 9.4 N/mm² the max. stress from normal forces calculates down to 4.2 N/mm² and the max. share stresses from the pressure load calculates down to 3.4 N/mm².

From the assumptions of the pressure, we can calculate down to a compression force. The assumption is that the force of the tie rods of the frame is min. three times as high as the force from the internal pressure of 13,500 kN (almost 1,350 t) and if we define the carrying gasket area is 90% this results in a compression stress of 42.5 N/mm² on the beam flank. This stress is reduced in operation by 14.1 N/mm² in operation to 28.4 N/mm². Both values also shall be fine for the gasket materials.

Even if all these stresses would occur in one point, what not applies, a max. equivalent stress is 52 N/mm² acc. to the von Mises theory. This would be a utilisation of material of less than 23%. Real for this problem assumed is about only 70% at the corners of the frame, where the normal force is at its minimum.

In the bipolar plate of 1.5 mm max. 33 N/mm² as equivalent stress are applied to the material, if the beam carries 0% of the load as it almost in the middle of the long beams, where the bipolar plate has to carry 100% of the applied line load and the pressure forced. This is as well uncritical.

This leads to the analysis that the rectangular design is not a technical problem from the view of the material strength. Even higher pressures shall be possible from that point of view.



Bending Moment
Max.   0.03 kNm
Min. - 0.21 kNm

Normal Force
Max. 11.33 kN
Min.   4.43 kN

Share Force
Max.   4.55 kN
Min. - 4.55 kN

Figure 2-27: Calculation Results from FEM-Analysis of Cell Stack Frame at 30 bar(a)

For the analysis of a cost reduction options we need to start with a today´s cost analysis of a state-of-the-art stack. The stack has an outer diameter of 2,000 mm and an active cell diameter of 1,750 mm (2.41 m² active area). The operating pressure is 30 bar(a) and the operating temperature is 85°C. It is consisting of 424 cells and has a total weight of ca. 65 tons of material without filling. The stack is connected to the electrical plus pole in the middle and has two minus poles at its ends. The stack efficiency is 4.375 kWh/Nm³ of produced hydrogen and the production rate is 835 Nm³/h of hydrogen.

Table 2-5: Cost estimate of a AEL stack based on interviews with manufacturers and own work

1960 A/m² AEL-Stack 835Nm³/h @ DC 4,375 kWh/Nm³ 30 bar(a)	Ring	Plate	Coatings	Anode	Cathode 2nd Generation	Gaskets	Membrane	Rods/Nuts	End-Plate	Connection	TOTAL
Weight [kg]	76,30	28,32	2,80	2,78	2,92	2,43	1,98	382,48	3797,87	1294,73	65428
Number [pc.]	424	424	432	424	424	848	424	8	2	3	1
Total Weight [t]	32,35	12,01	1,21	1,18	1,24	2,06	0,84	3,06	7,60	3,88	65,43
Cost [€/kg]	3,4	1,3	136,5	34,6	34,6	27,3	141,7	3,66	2,3	3,0	11,7
Cost [€/pc.]	260,6	35,8	382,0	96,3	101,1	66,3	281,2	1399,9	8647,1	3832,2	589867,3
Manufacturing Cost [€/Stack]	110.482 €	15.190 €	165.019 €	40.832 €	42.873 €	56.251 €	119.232 €	11.199 €	17.294 €	11.497 €	589.867 €
Assembly Cost [€/pc]	26,1	7,2	n.a.	28,9	30,3	50,1	184,2	774,1	2594,1	1149,7	174594,2
Assembly Cost [€/Stack]	11.048 €	3.038 €	n.a.	12.249 €	12.862 €	42.470 €	78.097 €	6.193 €	5.188 €	3.449 €	174.594 €
Cost [€/Stack*No]	121.530 €	18.228 €	165.019 €	53.081 €	55.735 €	98.721 €	197.328 €	17.392 €	22.482 €	14.946 €	764.462 €
Stack Price									Overhead	21%	924.998 €
	INPUT Manufacturer: 30 USD/m2 for the Ni foam (produced in China), 90 USD/m2 for the Chinese membrane									EUR/Nm³/h	1.108 €
Electrode Area [m²]	2,41									EUR/kW	253 €

This estimate is checked in an interview with a manufacturer and seen as a best estimate for this comparison. It is of course only in a preliminary cost classing, but is here a good working model for the research exercise.

With the 3rd generation electrodes (cathodes), the stack has the possibility to almost double its output (production rate 1660 Nm³/h), while only the Anode cost go up significantly. For this we in the first approach assume that the design still does not change, but it can be shown that the cost saving is already significant. The comparison costs are the €/kW installed, because the estimate is arranged with always the same stack efficiency.

Table 2-6: Cost Estimate of a AEL Stack incl. 3rd Generation Cathodes and double Gas Generation

4000 A/m² AEL-Stack 1660 Nm³/h @ DC 4,375 kWh/Nm³ 30 bar(a)	Ring	Plate	Coatings	Anode	Cathode 3rd Generation	Gaskets	Membrane	Rods/Nuts	End-Plate	Connection	TOTAL
Weight [kg]	76,30	28,32	2,80	2,78	2,92	2,43	1,98	382,48	3797,87	1294,73	65428
Number [pc.]	424	424	432	424	424	848	424	8	2	3	1
Total Weight [t]	32,35	12,01	1,21	1,18	1,24	2,06	0,84	3,06	7,60	3,88	65,43
Cost [€/kg]	3,4	1,3	136,5	34,6	194,1	27,3	141,7	3,66	2,3	3,0	14,7
Cost [€/pc.]	260,6	35,8	382,0	96,3	567,3	66,3	281,2	1399,9	8647,1	3832,2	787512,5
Manufacturing Cost [€/Stack]	110.482 €	15.190 €	165.019 €	40.832 €	240.518 €	56.251 €	119.232 €	11.199 €	17.294 €	11.497 €	787.512 €
Assembly Cost [€/pc]	26,1	7,2	n.a.	28,9	170,2	50,1	184,2	774,1	2594,1	1149,7	174594,2
Assembly Cost [€/Stack]	11.048 €	3.038 €	n.a.	12.249 €	12.862 €	42.470 €	78.097 €	6.193 €	5.188 €	3.449 €	174.594 €
Cost [€/Stack*No]	121.530 €	18.228 €	165.019 €	53.081 €	253.380 €	98.721 €	197.328 €	17.392 €	22.482 €	14.946 €	962.107 €
Stack Price									Overhead	21%	1.164.149 €
	INPUT Manufacturer: 30 USD/m2 for the Ni foam (produced in China), 90 USD/m2 for the Chinese membrane									EUR/Nm³/h	701 €
Electrode Area [m²]	2,41									EUR/kW	160 €

The calculation shows that the specific stack costs are reduced by ca. 37% compared to the stack with the 2nd generation cathodes.

Of course this manufacturing can be more automated. A developed automation scheme for the stack manufacturing is given in the attachments C/D to this thesis. This will lead to a significant cost reduction for its supply by cutting the manufacturing cost by more than 50%.

Table 2-7: Cost Estimate of a AEL Stack incl. 3rd Generation Cathodes and automated manufacturing

4000 A/m² AEL-Stack 1660 Nm³/h @ DC 4,375 kWh/Nm³ 30 bar(a)	Ring	Plate	Coatings	Anode	Cathode 3rd Generation	Gaskets	Membrane	Rods/Nuts	End-Plate	Connection	TOTAL
Weight [kg]	76,30	28,32	2,80	2,78	2,92	2,43	1,98	382,48	3797,87	1294,73	65428
Number [pc.]	424	424	432	424	424	848	424	8	2	3	1
Total Weight [t]	32,35	12,01	1,21	1,18	1,24	2,06	0,84	3,06	7,60	3,88	65,43
Cost [€/kg]	2,0	0,8	81,7	34,6	126,2	19,11	77,9	1,83	0,9	0,9	11,1
Cost [€/pc.]	153,8	22,8	228,7	96,3	368,7	46,4	154,6	699,9	3572,9	1108,4	491873,7
Manufacturing Cost [€/Stack]	65.215 €	9.683 €	98.809 €	40.832 €	156.337 €	39.376 €	65.551 €	5.599 €	7.146 €	3.325 €	491.874 €
Assembly Cost [€/pc]	15,4	4,6	n.a.	28,9	110,6	35,1	101,3	387,1	1071,9	332,5	99610,2
Assembly Cost [€/Stack]	6.521 €	1.937 €	n.a.	12.249 €	0 €	29.729 €	42.936 €	3.096 €	2.144 €	998 €	99.610 €
Cost [€/Stack*No]	71.736 €	11.620 €	98.809 €	53.081 €	156.337 €	69.105 €	108.487 €	8.696 €	9.290 €	4.323 €	591.484 €
Stack Price									Overhead	21%	715.695 €
	INPUT Manufacturer: 30 USD/m2 for the Ni foam (produced in China), 90 USD/m2 for the Chinese membrane									EUR/Nm³/h	431 €
Electrode Area [m²]	2,41									EUR/kW	99 €

We now apply the described larger and new rectangular stack design, where the active cell area is raised to 4.4 m² and the number of cells is 680 cells. All other operating data are the same for the comparison. Additional we change the cell connections to two, for electrical reasons. This will be discussed in the chapter of the DC generation. The total weight is than 120 t, which is assumed capable to be transported on road. This was analysed in an interview with a specialist for heavy road transport for the EU.

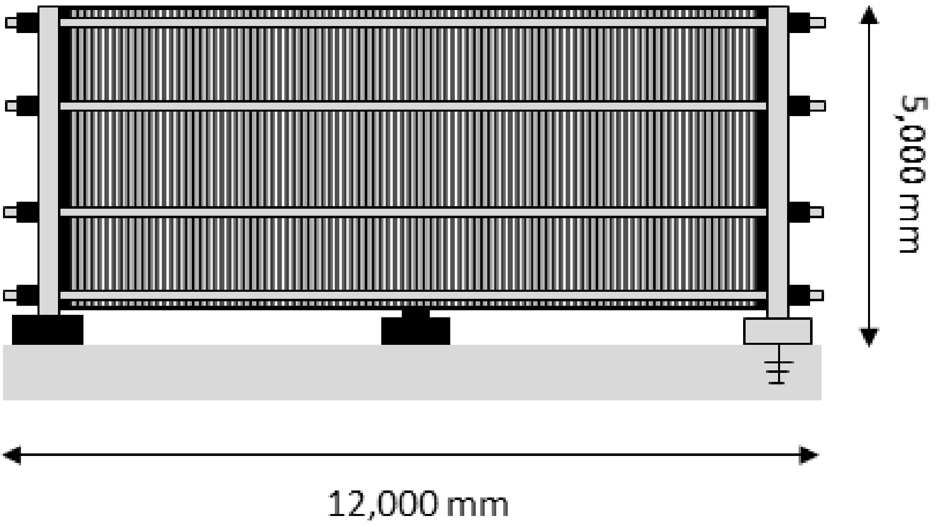


Figure 2-28: Outer Dimensions of the rectangular Cell Stack with Cell Frames described before

Table 2-8: Cost Estimate of the rectangular AEL Stack incl. 3rd Generation Cathodes high Output

4000 A/m² AEL-Stack 4985Nm³/h @ DC 4,375 kWh/Nm³ 30 bar(a)	Frame	Plate	Coatings	Anode	Cathode 3rd Generation	Gaskets	Membrane	Rods/Nuts	End-Plate	Connection	TOTAL
Weight [kg]	68,39	51,81	5,10	4,00	4,20	4,36	4,06	909,75	3404,26	2357,36	118281
Number [pc.]	680	680	684	680	680	1360	680	8	2	2	1
Total Weight [t]	46,50	35,23	3,49	2,72	2,86	5,92	2,76	7,28	6,81	4,71	118,28
Cost [€/kg]	2,4	0,9	101,3	34,6	194,1	27,3	111,3	3,66	1,6	2,1	16,7
Cost [€/pc.]	162,2	49,2	516,4	138,4	815,0	118,9	451,8	3329,7	5382,6	4845,5	1542344,6
Manufacturing Cost [€/Stack]	110.295 €	33.423 €	353.250 €	94.084 €	435.269 €	161.730 €	307.201 €	26.637 €	10.765 €	9.691 €	1.542.345 €
Assembly Cost [€/pc]	32,4	14,7	n.a.	41,5	244,5	89,8	295,9	1841,3	1614,8	1453,6	432726,1
Assembly Cost [€/Stack]	22.059 €	10.027 €	n.a.	28.225 €	28.225 €	122.106 €	201.217 €	14.731 €	3.230 €	2.907 €	432.726 €
Cost [€/Stack*No]	132.353 €	43.449 €	353.250 €	122.309 €	463.494 €	283.835 €	508.418 €	41.368 €	13.995 €	12.598 €	1.975.071 €
Stack Price									Overhead	21%	2.389.836 €
	INPUT Manufacturer: 30 USD/m2 for the Ni foam (produced in China), 90 USD/m2 for the Chinese membrane									EUR/Nm³/h	396 €
Electrode Area [m²]	4,4									EUR/kW	91 €

Table 2-9: Cost Estimate of the rectangular AEL Stack in automated Manufacturing

4000 A/m^2 AEL-Stack 4985Nm^3/h @ DC 4,375 kWh/Nm^3 30 bar(a)	Frame	Plate	Coatings	Anode	Cathode 3rd Generation	Gaskets	Membrane	Rods/Nuts	End-Plate	Connection	TOTAL
Weight [kg]	68,39	51,81	5,10	4,00	4,20	4,36	4,06	909,75	3404,26	2357,36	118281
Number [pc.]	680	680	684	680	680	1360	680	8	2	2	1
Total Weight [t]	46,50	35,23	3,49	2,72	2,86	5,92	2,76	7,28	6,81	4,71	118,28
Cost [€/kg]	2,0	0,8	81,7	34,6	126,2	19,11	77,9	1,83	0,9	0,9	11,1
Cost [€/pc.]	137,9	41,8	416,4	138,4	529,8	83,2	316,2	1664,8	3202,6	2018,1	1136030,4
Manufacturing Cost [€/Stack]	93.750 €	28.409 €	284.850 €	94.084 €	282.925 €	113.211 €	215.041 €	13.319 €	6.405 €	4.036 €	1.136.030 €
Assembly Cost [€/pc]	9,7	4,4	n.a.	12,5	73,4	26,9	88,8	920,7	807,4	726,8	175401,9
Assembly Cost [€/Stack]	6.618 €	3.008 €	n.a.	8.468 €	49.878 €	36.632 €	60.365 €	7.365 €	1.615 €	1.454 €	175.402 €
Cost [€/Stack*No]	100.368 €	31.417 €	284.850 €	102.552 €	332.803 €	149.842 €	275.406 €	20.684 €	8.020 €	5.490 €	1.311.432 €
Stack Price									Overhead	21%	1.586.833 €
	INPUT Manufacturer: 30 USD/m2 for the Ni foam (produced in China), 90 USD/m2 for the Chinese membrane									EUR/Nm^3/h	318 €
Electrode Area [m^2]	4,4									EUR/kW	73 €

Here can be shown that the cost reduction is again significant compared to the smaller round stack with 3rd generation electrodes. For this calculation it was not taken into account that in future the stack manufacturing needs to become 100% automated. Applying this assumption on the rectangular stack design it is assumed that the manufacturing cost can be reduced by 25% and the assembly cost can be reduced by 70%.

This reduces the cost again by 20%. This exercise is showing the significant opportunity for cost reduction by economy of scale, design optimisation and automation for alkaline electrolysers. Further costs of the electrolyser are discussed at the end of the chapter. Pleas recognise expressed costs at a cost class level of 3 according to the AACE cost classing system [74].

2.3.2.5 Direct current generation for alkaline hydrogen electrolysis

Large direct current (DC) generation is not only a topic for industrial hydrogen electrolyser systems. It is today widely used in the process industry. Today the application for hydrogen is actually rather small. Table 2-10 is giving here an overview [75].

Table 2-10: DC Rating for large industrial Applications [75]

Rectifier application	Current [kA]	Voltage (DC [V])
Chemical electrolysis	5 – 150	40 - 1000
Aluminium potline	10 – 300	< 1300
DC Arc Furnace	50 – 130	600 - 1150
Graphitizing Furnace	20 – 120	50 - 250
Zinc/Lead, etc electrolysis	5 – 100	100 - 1000
Copper refining	10 -50	40 - 350
Plasma Torch	1 – 10	500-1200

Today there are various options discussed for the DC generations systems of hydrogen electrolyser systems [76]. The target is here to get best efficiency for moderate cost in large scale. The main cost for a system come more from the needed current or the system, than from the needed voltage. The target of the system is to operate at highest possible voltage and with lowest possible current. But, beside the efficiency, it is also very important to keep the distortion of gird by a large installation as low as possible. Those distortions are coming from harmonics feed to the grid but also from an unacceptable low power-factor < 0,9.

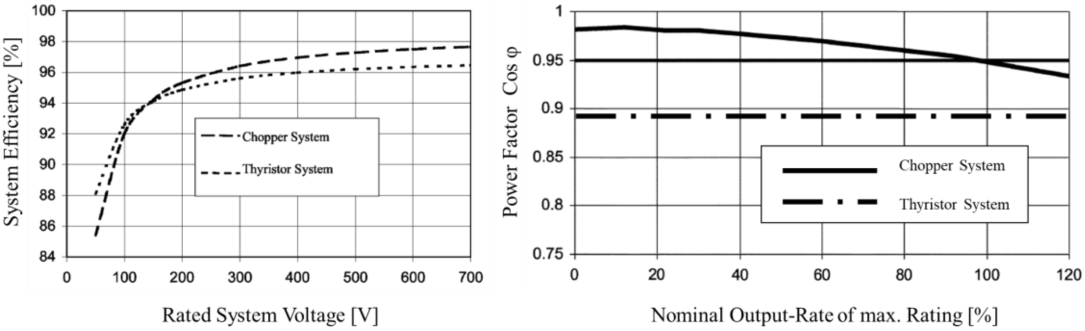
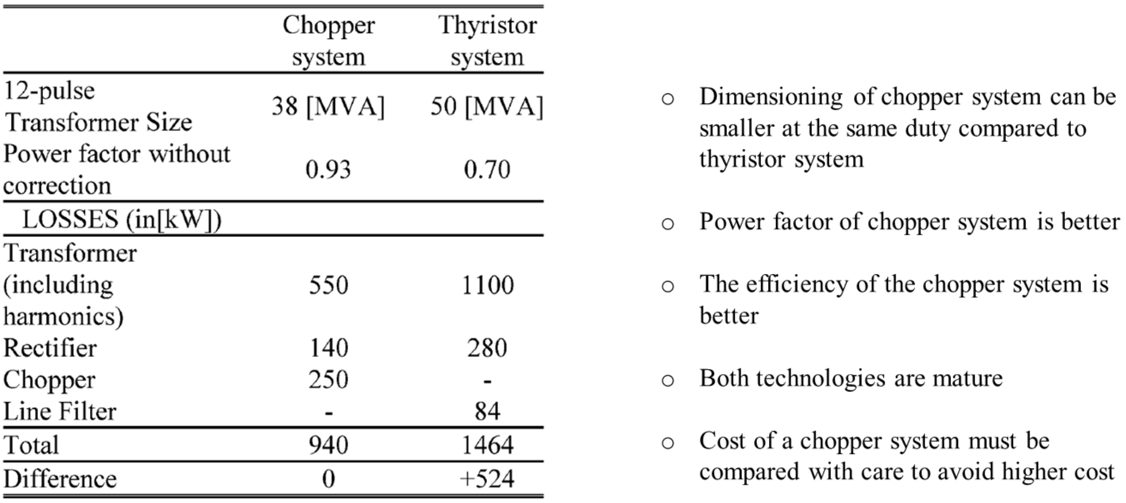


Figure 2-29: Showing left the Comparison of the System Efficiencies and right the Power Factor Comparison [75]

For such an installation basically today are two different system available. First there is the most common thyristor phase-controlled rectifiers with usual efficiencies >97% and without correction power factors below 0,9. This can be called the today´s standard for the application. Second there is the today more and more used chopper rectifiers using insulated-gate bipolar transistor (IGBT) technology. Such a rectifier is shown in the process flow of the alkaline electrolysis.

The reason for this choice was that the promised performance of such a system is avoiding the need for an additional system for correcting the power factor and a system for harmonic filtering. This technology already includes this and will also avoid payments for sourcing reactive power. Future upscaling of the stack design will than lead again to cost reductions also for these systems. From literature it can be shown that for large scale installation this technology has significant advantages.

Table 2-11: Comparison Table of two large-scale Systems[75]



	Chopper system	Thyristor system
12-pulse Transformer Size	38 [MVA]	50 [MVA]
Power factor without correction	0.93	0.70
LOSSES (in[kW])		
Transformer (including harmonics)	550	1100
Rectifier	140	280
Chopper	250	-
Line Filter	-	84
Total	940	1464
Difference	0	+524

- Dimensioning of chopper system can be smaller at the same duty compared to thyristor system
- Power factor of chopper system is better
- The efficiency of the chopper system is better
- Both technologies are mature
- Cost of a chopper system must be compared with care to avoid higher cost

The comparison shows that for large systems there are advantages for the chopper rectifier technique. This count especial for future systems where voltages will raise for the systems. Today the voltage of a rectifier is about 300 V at a power supply of about 5 MW. In future, e.g. for a large module of two stacks described here before rectangular with 680 cells which leads to a voltage of > 1,100 V and about 45 MW power supply. Here the gain of efficiency can be higher that 1%-point compared to the thyristor type rectifying system.

2.3.3 Carbon dioxide separation

The capture of carbon dioxide is as the electrolysis not a new technology [77,78]. First installation for gas cleaning purposes, were already installed in 1920 and were using amine scrubbing technology for natural gas sweetening. Today there is a wide spread of technology options and a good overview is here given by the International Standard organisation (ISO) in a technical report [79].

A review of all the technologies will not be executed, due to the reason that the review has been done for carbon capture from power plant flue gas already in the past by a lot of research [80,81,82]. Also cost reviews have been executed to a great depth [83].

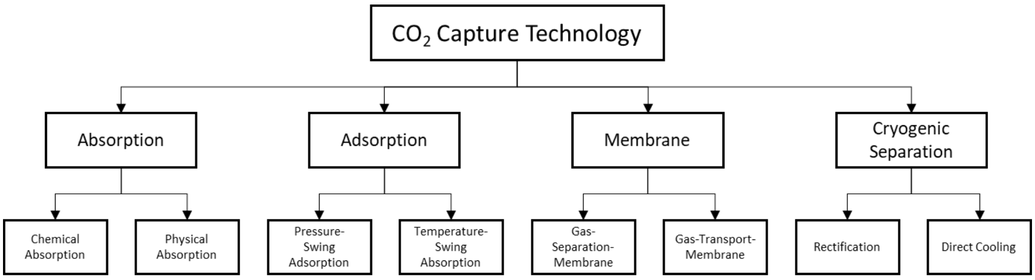


Figure 2-30: Overview over Technology Options for Carbon Capture acc. ISO

It was reduced to three technology groups. Pre-combustion capture, oxyfuel technology and post-combustion capture. The first two options can be neglected for the given case, because these technologies are for the treatment of 100% of the carbon dioxide of the power plant and not a slip stream only. We will concentrate on the options of the post combustion technology, which are easy to adopt for treated slip streams.

2.3.3.1 Comparison of post combustion carbon capture processes and technology choice

For power plants discussed post combustion carbon capture technologies are mainly chemical absorption processes. Physical absorption processes usually need either deep chilling or pressures above atmospheric pressure, which makes it difficult to implement it to a power plant process [84]. Membrane technologies are under research and neglected here, because an established and mature technology shall be used.

The chemical absorption process is based either on the use of amine scrubbing (see figure 2-31) or the use of potassium carbonate mainly also using promotors as amines or others [85]. The leading and established technologies are amine-based solutions [86]. The diagram given in Figure 2-31 is showing that for the commercially available technologies the amine based are the technologies of choice for flue gas applications. The mature availability of the used technique is the most important for the technology. Even before 1999 have been more than 20 plant operational. In this field are several companies present and many plants are in operation or planned [87]. The used amines are primary amines as mono ethanol amine (MEA), but also secondary, tertiary or hindered amines. MEA in the mix with 60-80% of water is the most known. The largest unit installed is in Texas USA with 4,760 t/day of carbon capture [68].

The companies active are mostly using their own developed solvents, where the solvent is not free available in the market. The companies advertise proved low thermal energy consumption of the solvents as e.g. Mitsubishi Heavy Industries together with KANSEI with their KS-1® solvent. They claim to have a heat use of 2,500 – 2,800 kJ/kg of captured carbon dioxide [88,89]. Compared the consumption of a MEA process is between 3,100 – 4,700 kJ/kg [90, 91] depending on the plant design.

In the literature there are several other companies with own solvents named as e.g. Shell with Cansolv® or BASF with OASE® beside others. If the choice goes to one of these solvents is chosen it is not necessary that the cost is lower. It must be analysed that total cost of ownership are lower, what concludes for solvent price, solvent consumption together with the energy consumption.

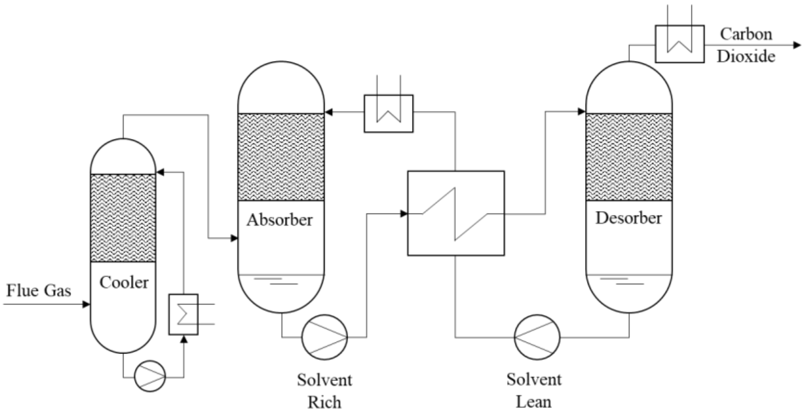


Figure 2-31: Principle flow sheet of a amine scrubbing system

As it is planned in this special case to use the cooling energy of the carbon capture plant together with heat pumps again for the usage, the thermal energy consumption cannot be considered as a loss. Therefore the solvent cost alone are more or less our decision criteria.

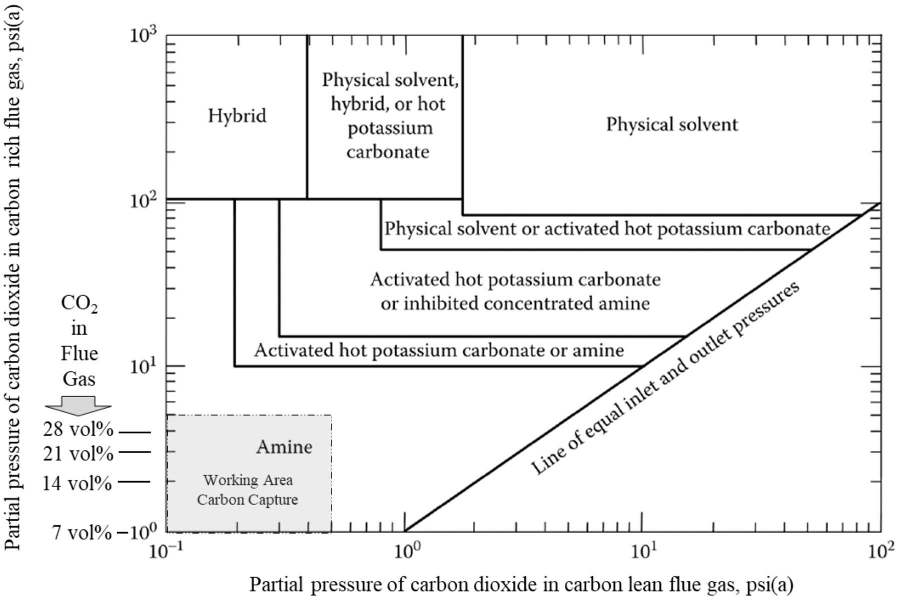


Figure 2-32: Chart for Selecting CO2 Removal Technologies Available Commercially [66]

From interviews with suppliers there was a finding that under this condition the cost comparison is usually in favour for the MEA solution in water. This also has the advantage that there are no restrictions in the sourcing of the solvent. The author decided for an amine-based carbon capture using a 35% MEA in water solution for the further work, with an desorber pressure of 1.2 bar(a) (123°C), lean loading of

0,25, rich loading of 0,5 and a resulting energy consumption of 3,600 kJ/kg of carbon dioxide acc. to literature [71]. In later works here more detailed comparisons and further optimisation can be made.

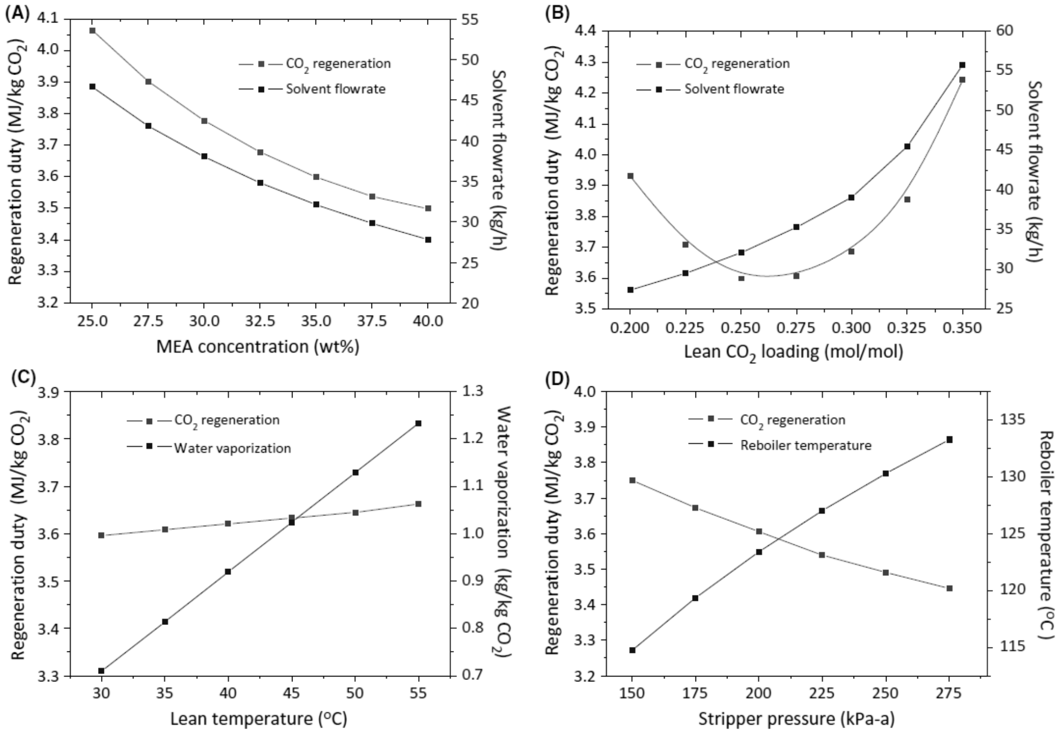


Figure 2-33: Effect of (A) MEA concentration, (B) lean CO2 loading, (C) Lean solvent temperature, (D) stripper top pressure on the regeneration energy based on single factor analysis [71]

In the present case for this research work it is the opinion of the author best to use an open-source technology on its average state-of-the-art performance level.

2.3.4 Short excursus for carbon capture and storage

In the further work the carbon capture is limited to a slip-stream capture, but of course it shall be mentioned that there is also in general the possibility to extend this carbon capture for additional carbon capture and storage.

The planned flue gas cooling prepares 100% of the flue gas to be treated with a carbon capture. This makes it possible for the installation to be really 100% capture ready [92], even if in the planned installation only a small slip stream (about 5%) of the flue gas is treated. This is important, due to the reason that new build power plants need to be capture ready by law. A large retrofit is in this context seen a new build. In the future it might be policy that the climate target is only reachable by additional carbon capture and even the generation of negative carbon emissions, which can be reached by carbon capture from biomass combustion [93]. Today there are already efforts, which are working towards this [94,95] and a retrofit is possible at any time. This makes such an installation resilient for future policy developments and can further secure the security of the investment necessary.

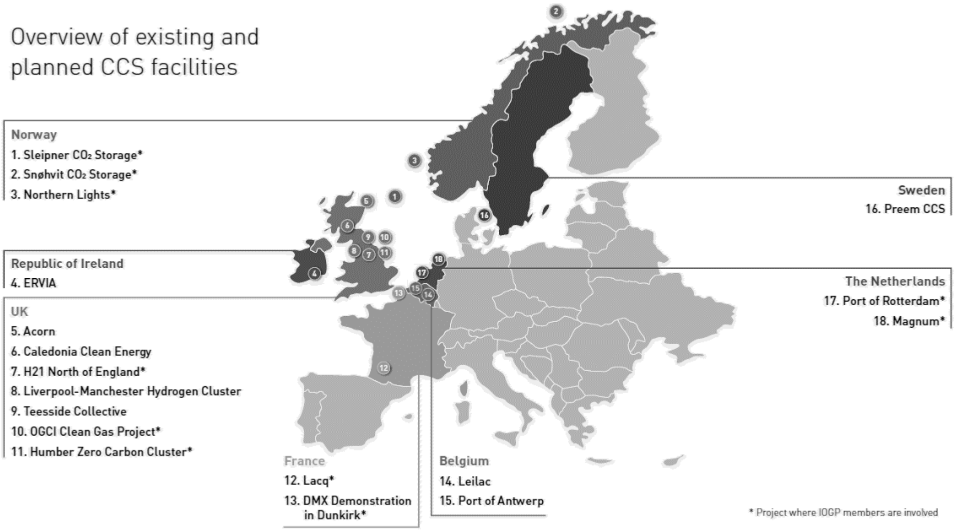


Figure 2-34: EU CCS-Projects [Source: IOGP, International association of Oil and Gas Producers]

2.3.5 Methanol generation process

The generation of methanol from synthesis gas is since a long time an established technique and many companies offer large scale units up to 10 million tons per year of production [96]. The catalysts are today also developed to work with higher carbon dioxide contents in the synthesis gas, which can be provided by carbon dioxide capture and reinjection to the syngas to optimise the gas consumption of the methanol process [97]. This is operational e.g. in Qatar, where the carbon dioxide in captured from the firing of the steam methane reformer and the capture carbon dioxide in injected in the syngas direct before the reactor feed.

As already mentioned in the begin of the chapter a commercial operated plant for the generation of methanol from carbon dioxide and hydrogen is operational since 2011 at the company CRI in Iceland [98]. It is today producing 4,000 tons of methanol per year, but was in the beginning only operated at 30% of its capacity. It is using the Davy Process Technologies tube cooled converter for the methanol synthesis in a recycle loop [99].

But there are also other plants in operation, mostly as demonstration or pilots [100]. Here are 10 plant mentioned with a daily production of 1.5 tons or less (pilot plants), which demonstrate the technology readiness. Additional there are 2 plants mentioned operational with significant production of more than 3 tons per day, where the one of CRI is included. Beside this there are also 12 announced plants reported, which shall become operational within the next years and capacities up to more than 100,000 tons per year of production.

2.3.5.1 Process basics

The basis reaction to produce methanol from hydrogen and carbon dioxide can be visualised as follows. This main reaction is not necessarily directly reached, because hydrogen and carbon dioxide can also form carbon monoxide and water. There are three main reactions which are in chemical equilibrium while the methanol forming in the reactor [101].

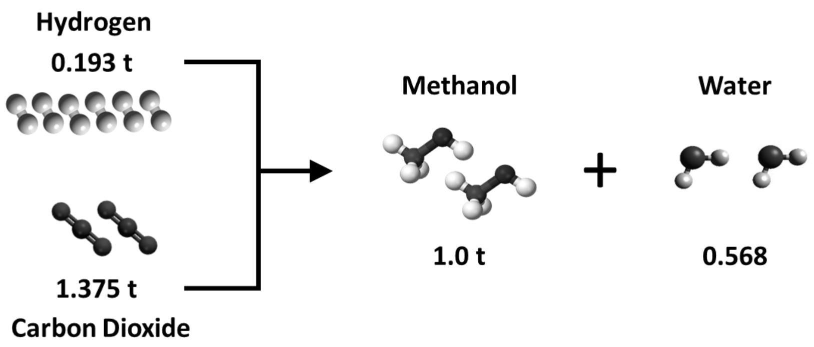


Figure 2-35: Visualisation of the chemical main reaction for the methanol production

These reaction in in general exothermic acc. to thermodynamics and it can be shown that the reaction is in the presence of catalysts promoted by lower temperatures and high pressure [102].

$$\begin{array}{llll}
\text{reaction (1)} & CO_2 + 3\,H_2 \xrightleftharpoons{k_1} CH_3OH + H_2O & \Delta H_R^{0} = -\,49.57\ \text{kJ mol}^{-1} \\
\text{reaction (2)} & CO_2 + H_2 \xrightleftharpoons{k_2} CO + H_2O & \Delta H_R^{0} = +\,41.27\ \text{kJ mol}^{-1} \\
\text{reaction (3)} & CO + 2\,H_2 \xrightleftharpoons{k_3} CH_3OH & \Delta H_R^{0} = -\,90.84\ \text{kJ mol}^{-1}
\end{array}$$

Equation 2-9: Main reactions to form methanol from hydrogen and carbon dioxide

It is also of advantage to have hydrogen stoichiometric in excess surplus for the reaction. From this follows, that the reactor must be operated in a loop process.

In literature are several kinetic models available to design this loop, but this work needs to be executed with the catalyst supplier and the plant designer, because catalyst activity, recirculation rates, purges and plant parameters are working together.

2.3.5.2 Catalysts for methanol production from carbon dioxide and hydrogen

The today use catalysts are coming from an evolution since the 1930th and had several significant changes in the material [103]. The presence of copper is here the constant. From last decades improvements followed that the reaction of carbon dioxide is accelerated and today also feeds with 100% of carbon dioxide instead of CO/CO_2 mixtures are suitable.

For this thesis it was collaborated with the company CLARIANT (Südchemie)[13], which is one of the leading companies for methanol synthesis catalysts. The collaboration was based on the joint design of the reactor loop which is later described. The basis is also given in the literature [104,105]. The advantage was seen here to work with a today available commercial catalyst (MegaMax®[106]) tested capable to be used in a commercial plant including warranties (see also Table 2-12).

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[13] https://www.clariant.com/de/Business-Units/Catalysts/Syngas-Catalysts/Methanol

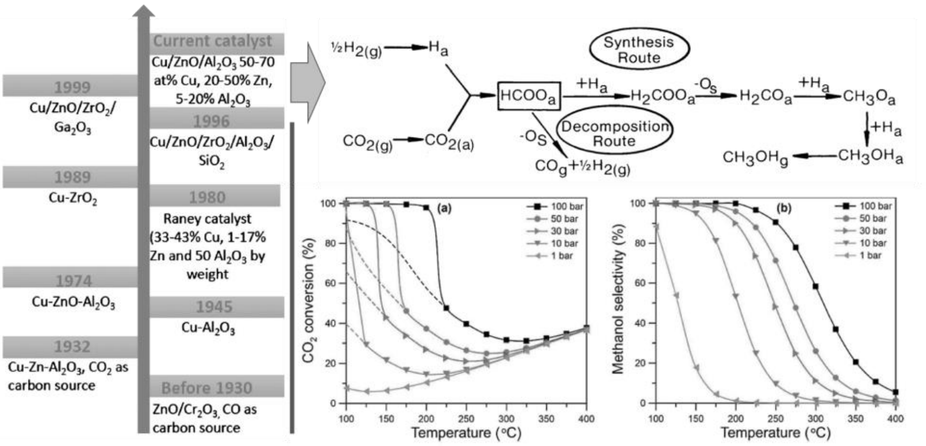
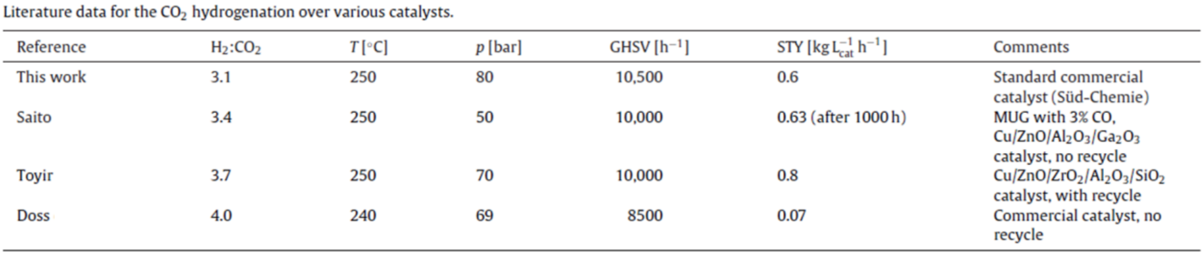


Figure 2-36: Evolution of copper-based catalysts for methanol synthesis [81, 107]

The reactions using pure carbon dioxide and hydrogen from carbon capture and electrolysis have also another advantage. The side reactions are still present, but compared to a standard synthesis gas the feed to the loop is much cleaner. This results in less forming of by products in the reactor, which is a significant advantage. So the necessary purge stream from the recycle can be minimised and also the later purification is eased.

Table 2-12: Chosen catalyst in comparison with some other catalyst [83]

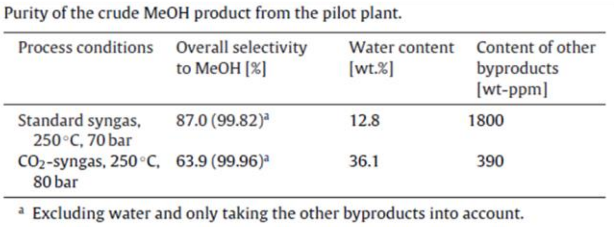


Literature data for the CO_2 hydrogenation over various catalysts.

Reference	H_2:CO_2	T [°C]	p [bar]	GHSV [h^{-1}]	STY [kg L_{cat}^{-1} h^{-1}]	Comments
This work	3.1	250	80	10,500	0.6	Standard commercial catalyst (Süd-Chemie)
Saito	3.4	250	50	10,000	0.63 (after 1000 h)	MUG with 3% CO, Cu/ZnO/Al$_2$O$_3$/Ga$_2$O$_3$ catalyst, no recycle
Toyir	3.7	250	70	10,000	0.8	Cu/ZnO/ZrO$_2$/Al$_2$O$_3$/SiO$_2$ catalyst, with recycle
Doss	4.0	240	69	8500	0.07	Commercial catalyst, no recycle

The better selectivity and the minor forming of by-products related to the used catalyst is expressed in the next Figure. The data is coming from long term operation of a test facility for catalyst testing and is operating data.

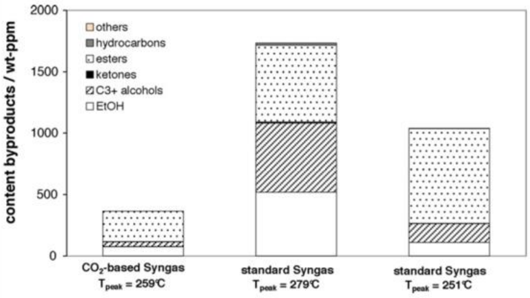
Table 2-13: Illustrated Table for selectivity of the used catalyst [83]



Purity of the crude MeOH product from the pilot plant.

Process conditions	Overall selectivity to MeOH [%]	Water content [wt.%]	Content of other byproducts [wt-ppm]
Standard syngas, 250 °C, 70 bar	87.0 (99.82)[a]	12.8	1800
CO_2-syngas, 250 °C, 80 bar	63.9 (99.96)[a]	36.1	390

[a] Excluding water and only taking the other byproducts into account.



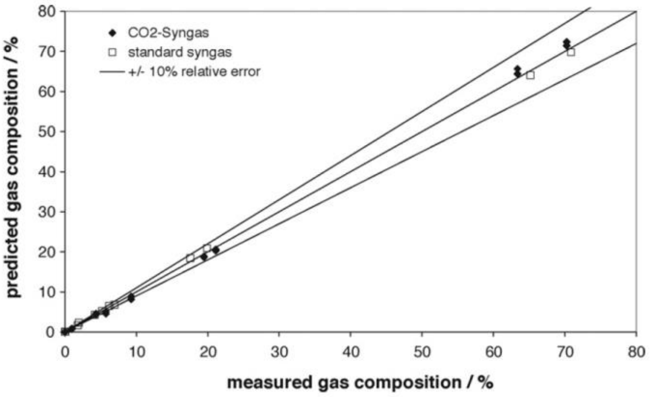


Figure 2-37: Parity plot of calculated vs. experimental gas composition for CO2-based feed gas and standard syngas [83]

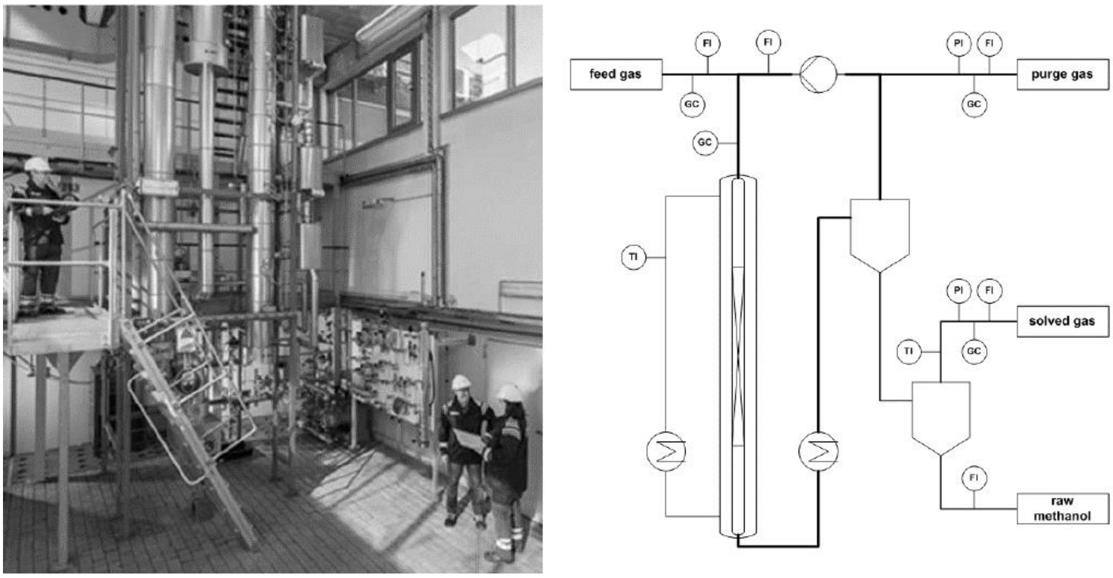


Figure 2-38: Process development unit for synthesis gas to methanol at Air Liquide Forschung & Entwicklung, Frankfurt a. M., Germany collaborating with Clariant [83]

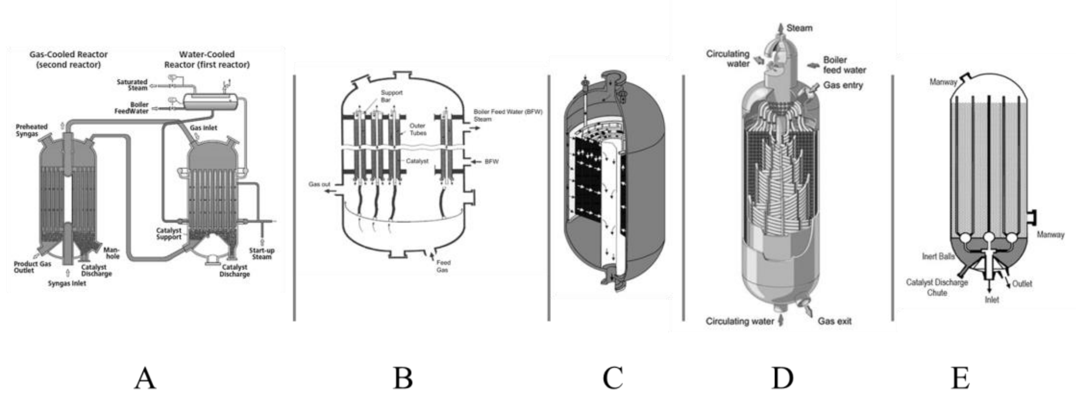
The measure data have here been checked with the calculation model for the process design and the correlation of the calculation model was as expected good. The next Figure is expressing the relation between calculated data and the measurements.

The expected lifetime of the catalyst is approx. 5 years, but can exceed this duration significantly. Now as the catalyst as basis for the further design is chosen, we need to discuss the reactor.

2.3.5.3 Reactor types for methanol production from carbon dioxide and hydrogen

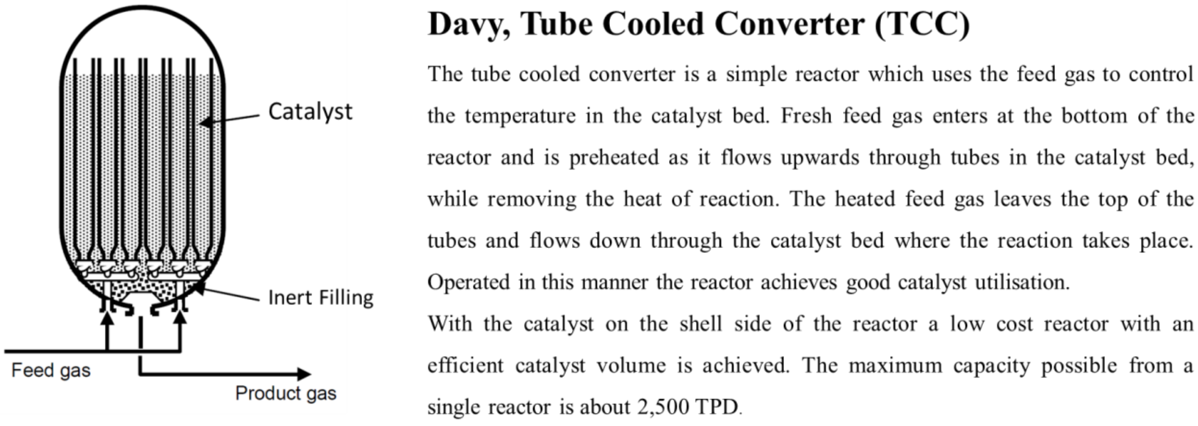
There are various reactor types available for the methanol synthesis. In general, the reactors can be divided in adiabatic reactors (without cooling), gas cooled reactors and liquid cooled reactors, which also are including the steam generating reactors.

Also combined version are in operation with two reactors, where the gas cooling and liquid cooling are combined [108].



A: Lurgi Combined Reactor B: Mitsubishi Super-Converter C: IMC Axial/Radial Reactor D: Linde Reactor E: Davy Tube Cooled Converter

Figure 2-39: Various reactor concepts for methanol productions [86]



Davy, Tube Cooled Converter (TCC)

The tube cooled converter is a simple reactor which uses the feed gas to control the temperature in the catalyst bed. Fresh feed gas enters at the bottom of the reactor and is preheated as it flows upwards through tubes in the catalyst bed, while removing the heat of reaction. The heated feed gas leaves the top of the tubes and flows down through the catalyst bed where the reaction takes place. Operated in this manner the reactor achieves good catalyst utilisation.

With the catalyst on the shell side of the reactor a low cost reactor with an efficient catalyst volume is achieved. The maximum capacity possible from a single reactor is about 2,500 TPD.

Figure 2-40: Picture and description of the TCC reactor type by Davy[109]

As described the reaction is best operated at low temperature levels and so a cooling is preferable for large reactors. As well the complexity is going up with more sophisticated cooling concepts. For today´s Mega-Methanol plants today are liquid cooled concepts common. The before mentioned largest commercial operated plant for methanol from carbon dioxide and hydrogen is operating a Davy tube cooled converter (TCC).

Due to the reason that the reaction temperature for the reaction compared with synthesis gas is lower, because the heat generated by carbon dioxide is below 50% compared to the reaction with carbon monoxide, a simpler reactor can be chosen. It still will be able to keep the temperature far below 250°C. This and the reported experience with the reactor type are the reasons why the author has chosen this reactor type for the further work.

2.3.5.4 Process for methanol production from carbon dioxide and hydrogen

Basing on the data before the design of the reactor loop can be done. The calculation of the reactor loop was, as mentioned already, executed with the support of Clariant and the result is as follows. The pressure of the process was chosen at 80 bar(g) and the pressure drop is designed to 7 bar(a).

The maximum loop temperature at the end of the reactor was calculated below 210°C. The recirculation rate is calculated to 5.6 with the recycle to feed ratio. Figure 2-43 is showing the full process flow incl. the hydrogen recovery from the pure gas. The recovery here is > 90% of the purged hydrogen.

All compressions are by turbo compressors and this was checked together with a compressor manufacturer for its feasibility. This was especial necessary for the recirculation circuit, because its high hydrogen content and the connected low-pressure ratios possible for low density gases.

The crude methanol from the process is purified in a distillation unit which is energy optimised. It is a system with three distillation columns. The distillation purity is set to the IMPCA standard [110]. This purity is sufficient for any use, either as direct chemical use or as fuel mixing species. The distillation unit, as a standard technology is not in detail examined here. Deeper information can be gained from the given literature [86].

As shown the off-gasses of the system as well as the gaseous part of the distillation goes to the power plant and is burned in the boiler to avoid emissions of the system. The waste water of the distillation needs to be treated. This is discussed shortly in a following chapter.

When looking at figure 2-41 and the connected table 2-14 one can see the high recirculation amount with low pressure ratio below 1.1 (S45 to S46), which makes the use of the turbo compression technology viable.

The mentioned low reactor operation temperature is reached by this high recirculation and as discussed before the low temperature is minimising as well the side products in the reaction.

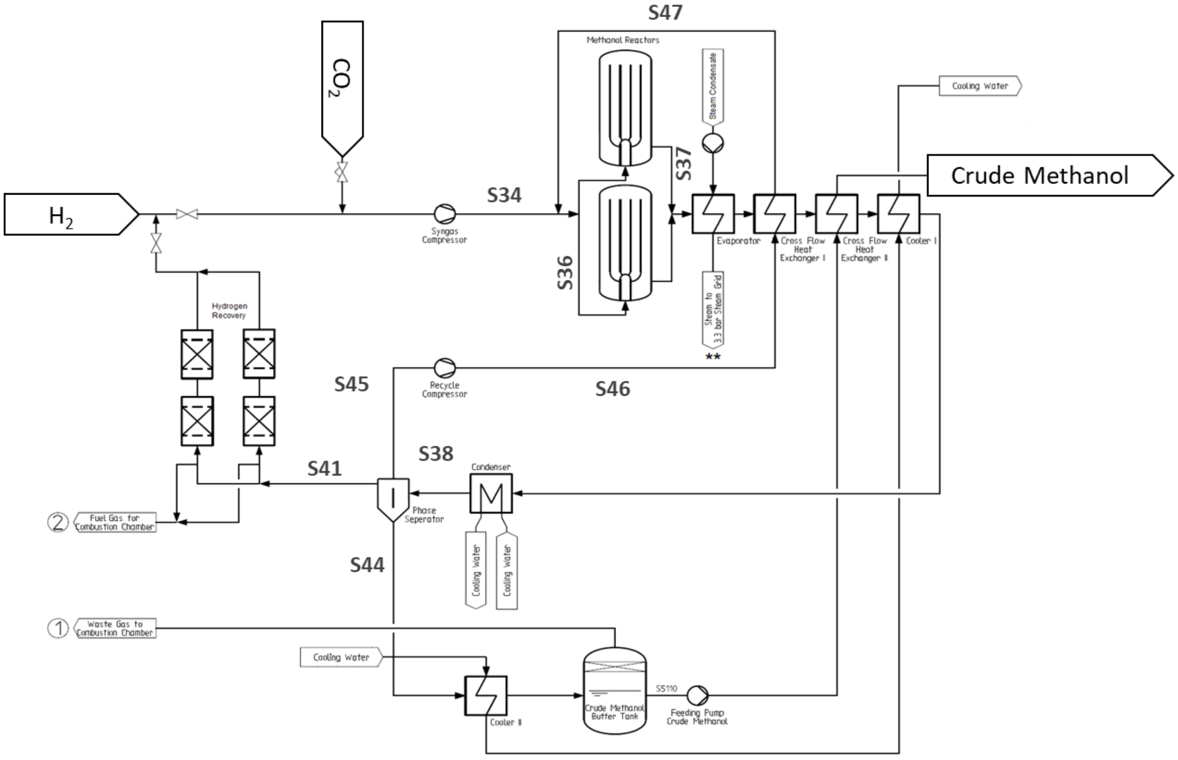


Figure 2-41: Process flow diagram for the process loop incl. process stream numbers without start-up heater developed in collaboration with Clariant and Mitsubishi Power in an Aspen Model

Table 2-14: Operation data for the reactor loop of the methanol reactor with TCC reactors

		H_2 CO_2								CH_3OH CH_2O			
Stream Name		**S34**	**S35**	**S36**	**S37**	**S38**	**S39**	**S40**	**S41**	**S44**	**S45**	**S46**	**S47**
Component Flow		Nm³/h	Nm³/h	Nm³/h	Nm³/h	Nm³/h	Nm³/h	Nm³/h	Nm³/h	kg/h	Nm³/h	Nm³/h	Nm³/h
CO		1,97	477	477	476	476	476	476	0,57	0,0	475	475	475
CO_2		6.556	8.379	8.379	1.838	1.838	1.825	1.825	2,19	24,5	1.823	1.823	1.823
H_2		19.853	191.229	191.229	171.592	171.592	171.584	171.584	205,94	0,7	171.376	171.376	171.376
O_2		4,60	4,60	4,60	0	0	0	0	0	0	0	0	0
N_2		2,63	1.781	1.781	1.781	1.781	1.781	1.781	2,14	0,5	1.779	1.779	1.779
CH_3OH		0,00	628	628	7.171	7.171	628	628	0,75	9.352	628	628	628
H_2O		36,98	164	164	6.715	6.715	127	127	0,15	5.295	127,3	127,3	127,3
Temperature	°C	146,6	144,1	144,1	207,1	45,0	45,0	44,9	44,9	45,0	44,9	59,6	144,0
Pressure	BARA	81,0	81,0	80,4	78,0	74,5	74,5	74,0	74,0	74,5	74,0	81,8	81,0
Vapour Fraction	[-]	100%	100%	100%	100%	93,06%	100%	100%	100%	0%	100%	100%	100%
Liquid Fraction	[-]	0%	0%	0%	0%	6,94%	0%	0%	0%	100%	0%	0%	0%
Recycle to Total Feed (Vol) =		5,6	Nominal Yearly Capacity (kton/a) =				81,0	splitted in two Reactors for easier Turndown Operation					

Having clarified this, we can step forward to the overall mass balance including the distillation, which is not discussed here in detail, due to the reason it is considered as a standard technology. Nevertheless it shall be mentioned that it is possible here also to optimise the process together with the manufacturers, especially for the steam consumption. The chosen technology is with its three-column system considered as usual state of the art. Further optimisation shall be possible.

2.3.5.5 Water treatment for effluents from methanol generation

During purification of the crude methanol water has to be separated, but also the contaminants from the pure methanol. The contaminants are mainly higher alcohols as ethanol and butanol, etc. but also some other hydrocarbons, while also dissolved gases as carbon dioxide and hydrogen and dimethylether are present. The gaseous parts are already separated in the distillation itself, but the others stay in the waste water. This leads to the situation that the water cannot be directly reused in the process are fresh water for the hydrogen electrolysis.

To reuse the water, it is necessary to eliminate these contaminants and clean the water again with fine cleaning methods. The central device is here an anaerobic membrane bio-reactor (AnMBR) [111,112]. With this device the total chemical oxygen demand can be reduced by 97 to 99%. This means that almost all oxidisable content as hydrocarbons is removed and the water can be used in the following water treatment processes needed to clean the fresh water to demineralised water used in the electrolysis. From the hydrocarbons a biogas is forms and burned in the CHP power plant.

The water is mixed also with the other wastewater coming from the water treatment, where the water of the after scrubber, the carbon dioxide compression and the flue gas desulphurisation is treated, and afterwards cleaned by an ultrafiltration followed by a reverse osmosis and a continuous electro deionisation. These processes are here not described in detail, because these are industrial standard processes operated on power plants worldwide. Please find the process flow diagram for the entire water treatment as a part of the overall process flow diagram in the attachments.

It is especial necessary to have a very low carbon dioxide in the water returned to the water electrolysis. This if for the reason of the following reactions as side reaction in the electrolyser.

$$2\ KOH + CO2 \rightarrow K2CO3 + H2O \rightarrow KHCO3 + KOH \quad \text{(Reversible with Heat)}$$

Equation 2-10: Chemical forming of potassium hydrogen carbonate in the KOH-lye

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (E^o=-0.53V)$

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (E^o=-0.24V)$

Equation 2-11: Electrochemical forming of carbon monoxide and methane in KOH-lye on hydrogen side

These equations show that the degassing of the water is very important to avoid on one hand gaseous contaminations by CO_2, CO and CH_4 of the formed hydrogen and oxygen, but on the other hand solid clocking from accumulated solids. Even if $KHCO_3$ is very good soluble in water its behaviour might be more difficult in the continuous operated KOH lye and shall be avoided.

3 Mass balances and cost for equipment

In this chapter the mass balance is more in detail described in its sub-chapters. Figure 3-1 is giving the overview which chapter is containing the mass balance used in the overall process. The full mass balance can also be reviewed in the attachment, which was developed in this thesis as an full Excel-model from given literature executed with Excel incl. XSteam Excel v2.6 steam tables.

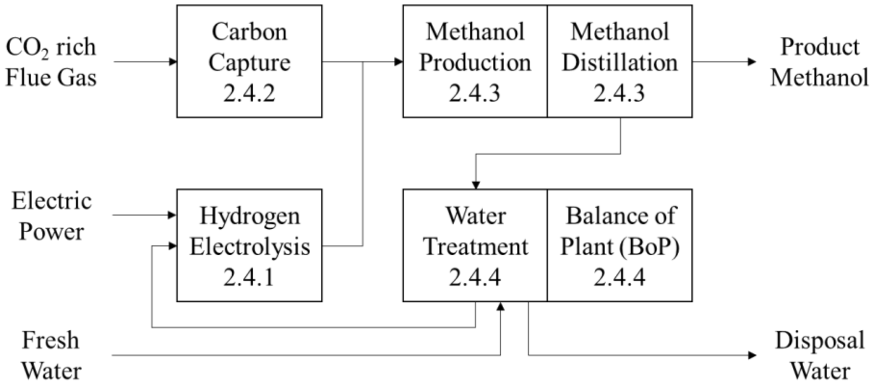


Figure 3-1: Block flow diagram with sub-chapter numbers for the mass balances

In the attachment also the full process flow diagram can be reviewed. The sub-chapters only give the sub-process flows related to the described process.

The mass balances are always followed by the cost estimation for the sub-system as it is later used in the techno-economic part of the thesis. The tables for the cost estimation also contain the information on the electric consumption.

The used cost estimation method used in the following is according to various literature and a mixture of the methodologies. The use was decided by the author´s experience from plant equipment calculation at any time as its best possible estimated. For main equipment a cost estimate was determined by basic budget offer of suppliers (e.g. electrolyser, large pumps, compressors, columns). For tanks, piping or similar statistic data was used [113,114,115], while price escalations were executed acc. to common standards [116,117].

3.1 Process parameters and cost of alkaline electrolyser process

We now describe the alkaline electrolyser system chosen for the entire planned electrolysis to be implemented in the power plant. It will be a conservative set-up with the 2nd generation electrodes.

Table 3-1: Mass Balance of Electrolyser Unit incl. Cooling Water (CW)

Alkaline Electrolyser UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	KOH
Demin Water to AEL	01	5	25	liquid	kg/h							15.871,9	
KOH Lye to AEL	02	5	25	liquid	m³/h							0,0	0,0
KOH Lye on H2-Side	03	32	79,9	liquid	m³/h							122,0	52,0
KOH Lye on O2-Side	04	32	79,9	liquid	m³/h							122,0	52,0
Hydrogen from AEL	05	30	40	gaseous	Nm³/h			19.747,3	39,5	1,8		2,1	traces
Hydrogen after DeOxo	06	30	46	gaseous	Nm³/h		traces	19.852,5	4,6	1,8	0,001	71,9	
Hydrogen from Recovery	07	30	44,9	gaseous	Nm³/h	0,01	0,01	175,1		0,002	0,001	0,0	
Wastewater from AEL (disposal)	08	30	40	liquid	m³/h							0,8	0,0
Oxygen from AEL	09	30	40	gaseous	Nm³/h			34,6	9.873,6	0,9		1,1	
CW in	10	7	30	liquid	m³/h							1.328,4	
CW out	11	6	40	liquid	m³/h							1.328,4	

The electrolyser system than will consist of 24 stacks, where always two stacks are combined to one electrolyser module, with an individual power electronics set and a gas separator unit, where for the deoxidation is always one reactor delegated to a module. Please see Figure 3-2 and Table 3-1.

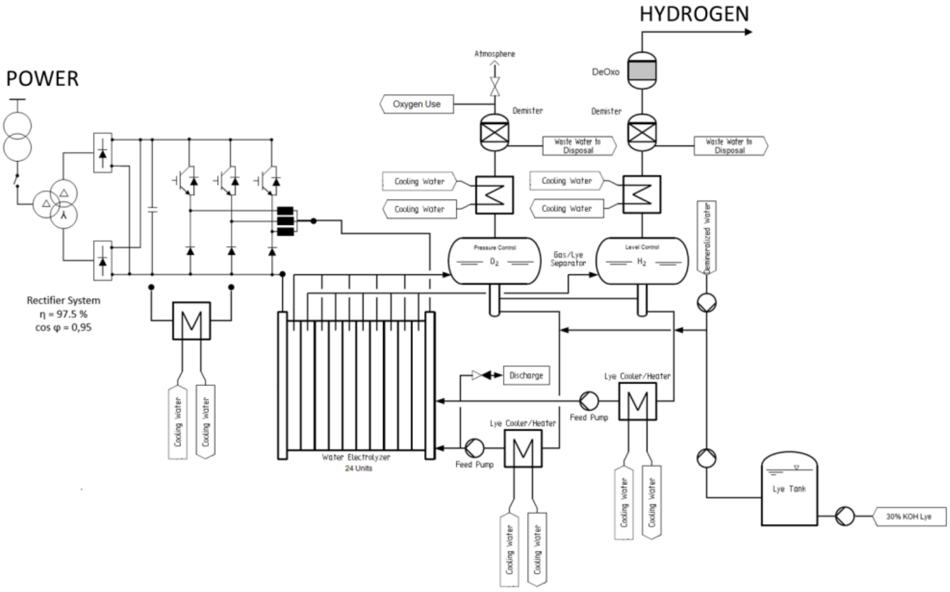


Figure 3-2: Process Flow Diagram of Electrolyser Unit

The feed of the KOH lye in the process is here expressed with zero, but of course there is a consumption of lye. The lye is exchanged completely every 5 years latest but as well once in a while it is necessary to give some dosing of additional lye.

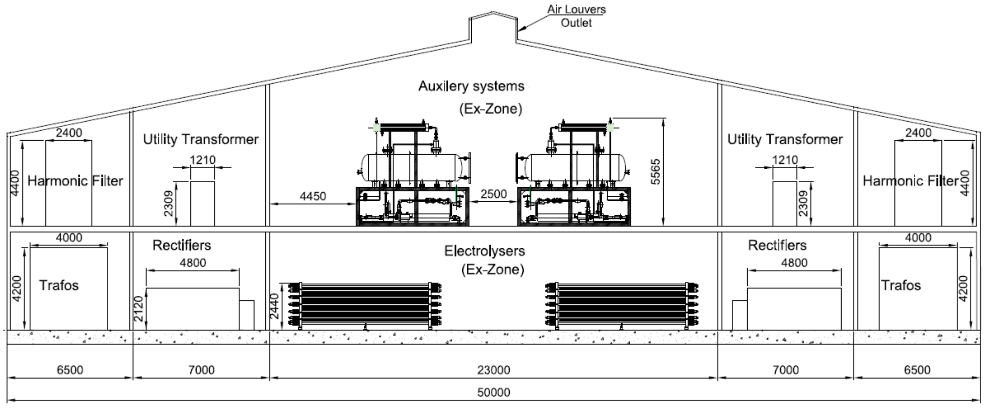
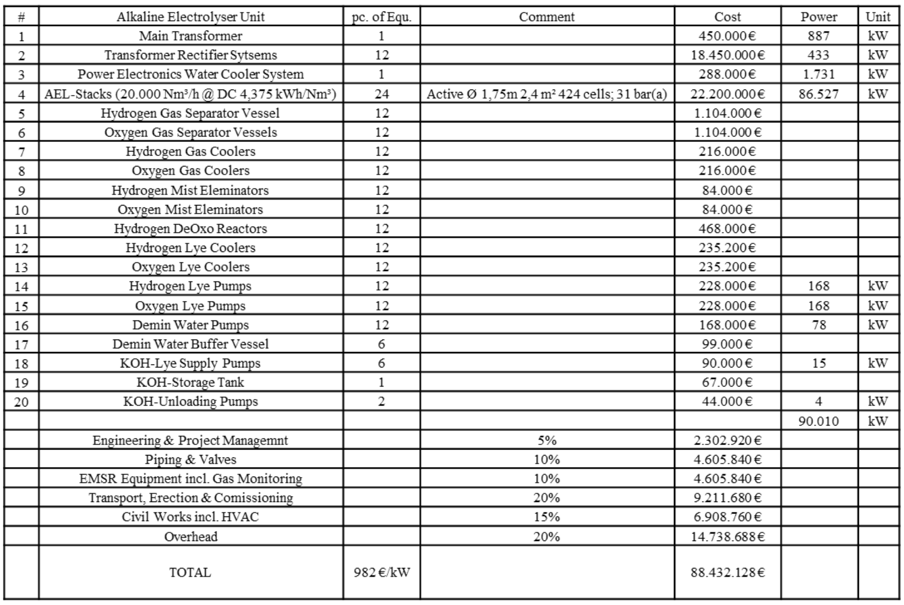


Figure 3-3: Principal Section Cut through electrolyser Unit, Installation Area is 50 x 50 m for 24 Stacks

The area requirements of the plant are 50 by 50 meters. A principal section cut of the plant is given in Figure 2-30, while Table 2-14 is giving the calculated cost and the electrical consumptions.

This is the plant configuration, which is used in the further work, but of course one cis interested, which optimisation is possible in the future using the automated manufacture rectangular stacks discussed before. It is possible to reach significant savings in space of approximated 30% including service roads. But the gained advantages are anyhow more in the economy of scale for the gas separating units, less electrical works and measurement and control devices. Even the building is of lower specific costs.

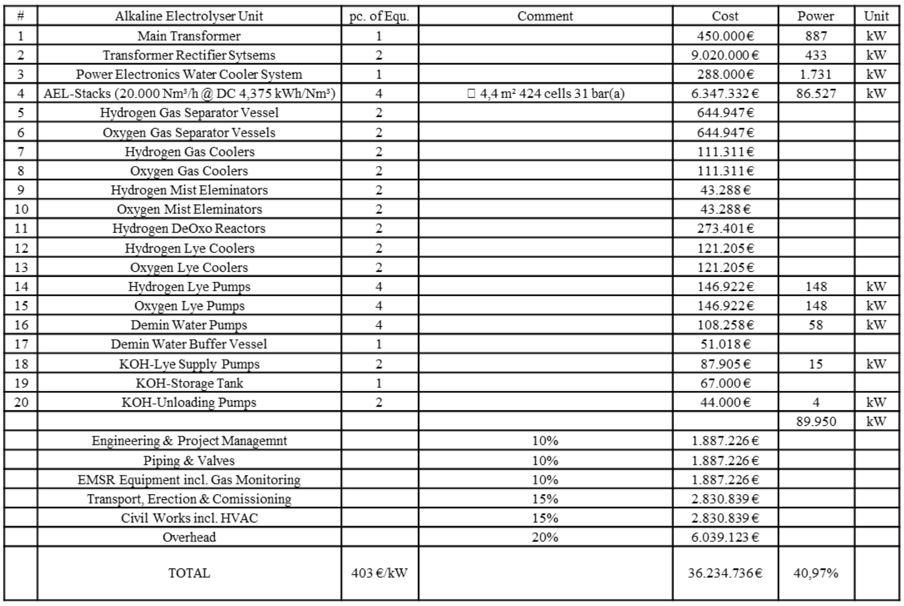
Table 3-2: Cost Calculation for Electrolyser Unit and electrical Consumptions (90 MW total)



#	Alkaline Electrolyser Unit	pc. of Equ.	Comment	Cost	Power	Unit
1	Main Transformer	1		450.000€	887	kW
2	Transformer Rectifier Sytsems	12		18.450.000€	433	kW
3	Power Electronics Water Cooler System	1		288.000€	1.731	kW
4	AEL-Stacks (20.000 Nm^3/h @ DC 4,375 kWh/Nm^3)	24	Active Ø 1,75m 2,4 m^2 424 cells; 31 bar(a)	22.200.000€	86.527	kW
5	Hydrogen Gas Separator Vessel	12		1.104.000€		
6	Oxygen Gas Separator Vessels	12		1.104.000€		
7	Hydrogen Gas Coolers	12		216.000€		
8	Oxygen Gas Coolers	12		216.000€		
9	Hydrogen Mist Eleminators	12		84.000€		
10	Oxygen Mist Eleminators	12		84.000€		
11	Hydrogen DeOxo Reactors	12		468.000€		
12	Hydrogen Lye Coolers	12		235.200€		
13	Oxygen Lye Coolers	12		235.200€		
14	Hydrogen Lye Pumps	12		228.000€	168	kW
15	Oxygen Lye Pumps	12		228.000€	168	kW
16	Demin Water Pumps	12		168.000€	78	kW
17	Demin Water Buffer Vessel	6		99.000€		
18	KOH-Lye Supply Pumps	6		90.000€	15	kW
19	KOH-Storage Tank	1		67.000€		
20	KOH-Unloading Pumps	2		44.000€	4	kW
					90.010	kW
	Engineering & Project Managemnt		5%	2.302.920€		
	Piping & Valves		10%	4.605.840€		
	EMSR Equipment incl. Gas Monitoring		10%	4.605.840€		
	Transport, Erection & Comissioning		20%	9.211.680€		
	Civil Works incl. HVAC		15%	6.908.760€		
	Overhead		20%	14.738.688€		
	TOTAL	982 €/kW		88.432.128€		

The change in the overall calculation is showing that the total cost can be reduced significantly, but a cost reduction of 71% as for the stack only is not reached. It is “only” a cost reduction by 59%, when the same calculation assumptions as before are taken. Please find this in detail in Table 3-4.

Table 3-3: Cost Calculation for “NEW” Electrolyser Unit and electrical Consumptions (90 MW total)



#	Alkaline Electrolyser Unit	pc. of Equ.	Comment	Cost	Power	Unit
1	Main Transformer	1		450.000€	887	kW
2	Transformer Rectifier Sytsems	2		9.020.000€	433	kW
3	Power Electronics Water Cooler System	1		288.000€	1.731	kW
4	AEL-Stacks (20.000 Nm^3/h @ DC 4,375 kWh/Nm^3)	4	□ 4,4 m^2 424 cells 31 bar(a)	6.347.332€	86.527	kW
5	Hydrogen Gas Separator Vessel	2		644.947€		
6	Oxygen Gas Separator Vessels	2		644.947€		
7	Hydrogen Gas Coolers	2		111.311€		
8	Oxygen Gas Coolers	2		111.311€		
9	Hydrogen Mist Eleminators	2		43.288€		
10	Oxygen Mist Eleminators	2		43.288€		
11	Hydrogen DeOxo Reactors	2		273.401€		
12	Hydrogen Lye Coolers	2		121.205€		
13	Oxygen Lye Coolers	2		121.205€		
14	Hydrogen Lye Pumps	4		146.922€	148	kW
15	Oxygen Lye Pumps	4		146.922€	148	kW
16	Demin Water Pumps	4		108.258€	58	kW
17	Demin Water Buffer Vessel	1		51.018€		
18	KOH-Lye Supply Pumps	2		87.905€	15	kW
19	KOH-Storage Tank	1		67.000€		
20	KOH-Unloading Pumps	2		44.000€	4	kW
					89.950	kW
	Engineering & Project Managemnt		10%	1.887.226€		
	Piping & Valves		10%	1.887.226€		
	EMSR Equipment incl. Gas Monitoring		10%	1.887.226€		
	Transport, Erection & Comissioning		15%	2.830.839€		
	Civil Works incl. HVAC		15%	2.830.839€		
	Overhead		20%	6.039.123€		
	TOTAL	403 €/kW		36.234.736€	40,97%	

At this point we stop the considerations about the alkaline hydrogen electrolyser unit and possible cost reduction options. Now we step to the second main source for the methanol production the carbon dioxide, which shall be captured from the flue gas of the power plant.

3.2 Process parameters and cost of amine scrubbing process

Figure 2-44 is showing the process flow of amine carbon capture unit. It included already a reclaimer unit for the separation of heat stable soluble salts and other contaminants from the mono ethanol amine solvent. This reclaimer unit is usually only operated in batch operation. The reclaiming in detail can be reviewed in literature [118].

Before we show the mass balance of the system need to discuss the parameters of the flue gas feed to the system and the allowed environmental emissions for such system.

The flue gas from the before shown power plant is feed to the absorber of the unit without any treatment. This is for the reason that the intercooled double scrubber system, which is implemented to the power plant unit, is taking over the duty of the usual integrated flue gas cooling and cleaning system. The emission from the retrofitted or new power plant is expected to be clean to the state-of-the-art limits. The power plant is operated with a flue gas cleaning of SCR for NOx minimisation, a FGD for SOx minimisation and in addition a flue gas condenser and cooler. The flue gas temperature is calculated at 38°C before FID-fan, Low SOx < 5 mg/Nm³-FG, low NOx < 50 MG/Nm³-FG and dust < 1mg/Nm³-FG. This is already acc. to the possibilities which can also be proofed by the given literature for power plants and flue gas cooling. The considered fuel can be various. As the planned standard fuel biomass and natural gas in any mix are considered, but with the techniques implemented in the power plant also coal, sulphur consisting gases and other fuels can be operated keeping the emission limits.

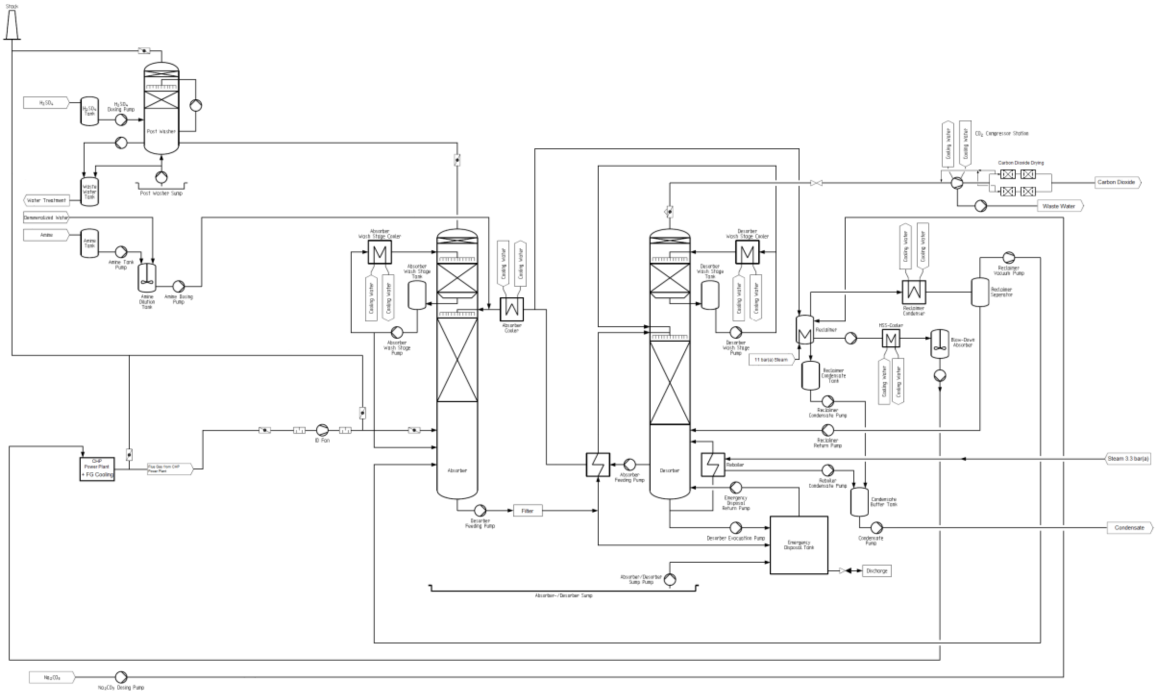


Figure 3-4: Process Flow of Carbon Capture plant incl. Reclaimer and Pollution Control Scrubber

The emissions caused by the absorber scrubbing process is so of higher attention, while implementing the carbon capture. These emissions are topic of research, because some of them are considered as serious environmental impact. This was in detail studied at the test facility in Mongstad [119]. There have been losses of solvent at the capture of carbon dioxide and this is cited below as the conclusions of the given literature:

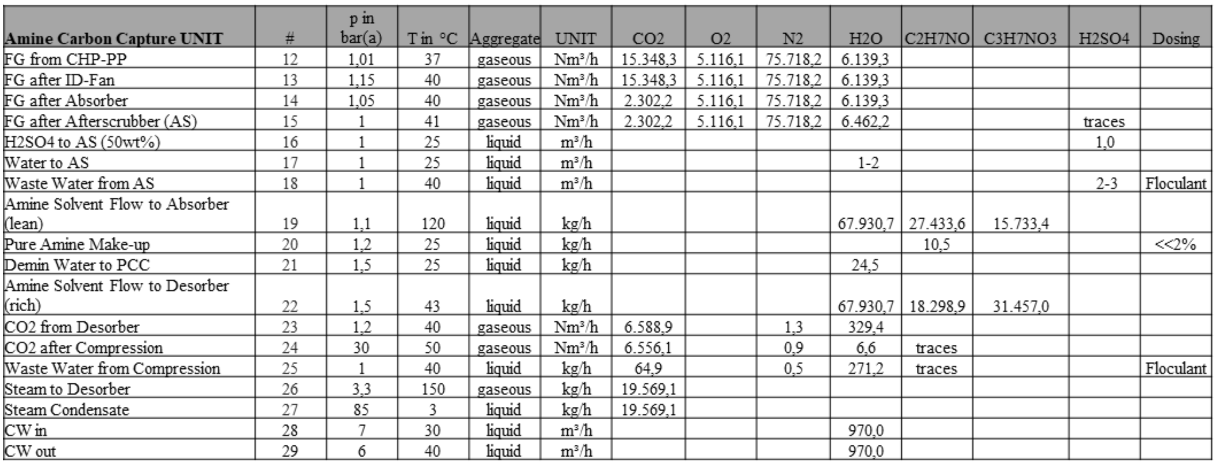
Excerpt: "During the MEA 2015 campaign at TCM the degradation products being formed in the solvent and released to the atmosphere were closely monitored. Based on an overall nitrogen mass balance it was concluded that less than 8% of total nitrogen introduced into the plant was not identified. The solvent loss calculated as pure MEA was 1.6 ± 0.1 kg/ton CO2 captured. The major contributors to the loss were ammonia emission (67% of loss) and identified degradation products in the solvent (16% of loss). Emissions to air from the absorber stack were monitored by five different independent on-line measurement instruments and by regular manual sampling. The four on-line methods provided very similar results. The manual sampling results confirmed results from earlier MEA campaign at TCM. The MEA and alkyl amines emissions are in the parts per billion ranges and nitrosamines and nitramines were below detectable levels."

While this measurement campaign the first 1,800 operation ours the reclaimer was not in operation and the emissions of the absorber in regards of ammonia where low, while these raised during operation to the max factor ca. 10 before starting reclaiming operation. With reclaiming in operation, the emissions dropped again fast and significant. This shows the importance of the reclaiming operation in regular terms as e.g. every week.

This leads also to the explanation, why there an acid scrubber with sulphuric acid as additional cleaning device is implemented in the plant. Even if the ammonia and other emissions are not outside today´s legal requirements it shall be reduced as to avoid opponents while permitting phase.

Now we give the basic mass balance of the carbon capture process (Table 2-17) and the reclaimer operation (Table 2-18), which is once a week for 24 operating hours. This mass balances together with the flow diagram are the basis for the equipment list and the cost calculation given in Table 2-16.

Table 3-4: Basic Mass Balance of the Carbon Capture Unit



Amine Carbon Capture UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	CO2	O2	N2	H2O	C2H7NO	C3H7NO3	H2SO4	Dosing
FG from CHP-PP	12	1,01	37	gaseous	Nm^3/h	15.348,3	5.116,1	75.718,2	6.139,3				
FG after ID-Fan	13	1,15	40	gaseous	Nm^3/h	15.348,3	5.116,1	75.718,2	6.139,3				
FG after Absorber	14	1,05	40	gaseous	Nm^3/h	2.302,2	5.116,1	75.718,2	6.139,3				
FG after Afterscrubber (AS)	15	1	41	gaseous	Nm^3/h	2.302,2	5.116,1	75.718,2	6.462,2			traces	
H2SO4 to AS (50wt%)	16	1	25	liquid	m^3/h							1,0	
Water to AS	17	1	25	liquid	m^3/h				1-2				
Waste Water from AS	18	1	40	liquid	m^3/h							2-3	Floculant
Amine Solvent Flow to Absorber (lean)	19	1,1	120	liquid	kg/h				67.930,7	27.433,6	15.733,4		
Pure Amine Make-up	20	1,2	25	liquid	kg/h					10,5			<<2%
Demin Water to PCC	21	1,5	25	liquid	kg/h				24,5				
Amine Solvent Flow to Desorber (rich)	22	1,5	43	liquid	kg/h				67.930,7	18.298,9	31.457,0		
CO2 from Desorber	23	1,2	40	gaseous	Nm^3/h	6.588,9		1,3	329,4				
CO2 after Compression	24	30	50	gaseous	Nm^3/h	6.556,1		0,9	6,6	traces			
Waste Water from Compression	25	1	40	liquid	kg/h	64,9		0,5	271,2	traces			Floculant
Steam to Desorber	26	3,3	150	gaseous	kg/h	19.569,1							
Steam Condensate	27	85	3	liquid	kg/h	19.569,1							
CW in	28	7	30	liquid	m^3/h				970,0				
CW out	29	6	40	liquid	m^3/h				970,0				

With this data we now have clarified the supply of the main components needed for the methanol synthesis from carbon dioxide and hydrogen.

Amine Reclaimer UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	H2O	C2H7NO	C3H7NO3	Dosing	Contaminats
Amine Solvent to Reclaimer	30	2	40	liquid	kg/h	1.415,2	571,5	327,8	NaCO3	HSS
Amine Solvent from Reclaimer	31	3	40	liquid	kg/h	1.233,2	498,0	285,6		
Reclaimer Waste	32	3	40	liquid	kg/h	182,0	73,5	42,2		HSS
Steam to Reclaimer	33	11	200	liquid	kg/h	2.661,7				
Condensate from Reclaimer	34	3	85	liquid	kg/h	2.661,7				
CW in	35	7	30	liquid	m³/h	115,0				
CW out	36	6	40	liquid	m³/h	115,0				

Table 3-5: Basic Mass Balance of the Reclaimer Process 24 Hours per 168 Operating Hours

Table 3-6: Equipment List of entire Carbon Capture Unit incl. Cost and electrical Consumptions

#	Carbon Capture MEA-Solvent Unit	pc. of Equ.	Comment	Cost	Power	Unit
1	Crude Flue Gas Dampers	4	Double Flap Dampers	104.000 €	5	kW
2	FID-Fan with Silencers	1		380.000 €	260	kW
3	Absorber Column with Internals	1		1.770.000 €		
4	Absober Head Cooling Pumps	2		28.000 €	70	kW
5	Absorber Head Cooler	1		23.000 €		
6	Absorber Head Buffer Tank	1		9.200 €		
7	Absorber Bottom Solvent Pumps	2		42.000 €	140	kW
8	Solvent Solid Filters	2		14.000 €		
9	Emergency Emtying Tank	1		49.000 €		
10	Solvent Return Pump	1		20.000 €	0	kW
11	Main Cross Flow Solvent Heat Exchanger	1	Hot Side Inconel	48.000 €		
12	Desorber Column with Internals	1	2 bar(a) Vessel	2.301.000 €		
13	Desorber Head Cooling Pumps	2		17.200 €	70	kW
14	Desorber Heat Cooler	1		39.000 €		
15	Desober Head Buffer Tank	1		8.600 €		
16	Desober Emptying Pumps	2		36.000 €	0	kW
17	Carbon Capture Sump Pumps	2		34.000 €		
18	Main Solvent Recirculation Pumps	2		53.000 €	160	kW
19	Main Lean Solvent Cooler	1		62.000 €		
20	Main Steam Control Valves	3		42.000 €		
21	Reboiler Systems	3	Natural Criculation Type	262.500 €		
22	Condensate Pumps	2		42.000 €	30	kW
23	Condensate Collection Tank	1		7.500 €		
24	Main Condensate Pumps	2		39.000 €	55	kW
25	Clean Flue Gas Dampers	2		67.600 €		
26	After Scrubber incl. Internals	1		81.000 €		
27	After Scrubber Recirculation Pumps	2		33.000 €	30	kW
28	H2SO4 Sosing Pump	2		15.800 €	2	kW
29	Waste Water Buffer Tanks AS	1		6.400 €		
30	Waste Water Pump	1		11.500 €		
31	AS Sump Pump	1		11.500 €	0	kW
32	H2SO4 Storage Tank	1		12.500 €		
33	Amine Storage Tank	1		19.300 €		
34	Amine Solvent Dosing Pump	2		28.000 €	10	kW
35	Solvent Mixing Tank incl. Agitator & Dosing	1	incl. Anti-Foam & Anti-Corrosion	16.300 €	8	kW
36	Solvent Supply Pumps	2		37.000 €		
37	Reclaimer Batch Vessel	1	Cattle Type	136.000 €		
38	Steam Valve	1		17.500 €		
39	Condensate Buffer Tank	1		8.600 €		
40	Reclaimer Condensate Pump	1		13.500 €	0	kW
41	Reclaimer Waste Pump 1	1		13.500 €	0	kW
42	Reclaimer Waste Cooler	1		6.800 €		
43	Recoverd Solvent Cooler	1		7.800 €		
44	Recoverd Solvent Tank	1		6.300 €		
45	Reclaimer Vacuum Pump	1		18.600 €		
46	Reclaimer Waste Tank incl. Agitator	1		12.700 €	5	kW
47	Reclaimer Waster Pump 2	1		11.400 €	0	kW
48	Na2CO2 Dosing Pump	1		11.400 €	0	kW
49	4 Stage CO2-Compressor System 2 x 50%	2		2.196.835 €	1.100	kW
50	Compressor Cooling Heat Exchangers	3	Inlet Guide Vale Control 30 bar(a)	279.000 €		
51	CO2-Drying System	1		236.000 €	40	kW
52	CO2-compressor Waste Water Pump	2		24.600 €	5	kW
					1.990	kW
	Engineering & Project Management		20%	1.754.287 €		
	Piping & Valves		35%	3.070.002 €		
	EMSR Equipment		25%	2.192.859 €		
	Transport, Erection & Comissioning		25%	2.192.859 €		
	Structural Steel & Civil Works incl. HVAC		25%	2.192.859 €		
	Overhead		20%	4.034.860 €		
	TOTAL			24.209.162 €		

These two basic chemicals are now supplied to the methanol generation unit. This is described in the following chapter including the necessary distillation of the produced crude methanol and necessary water treatment of effluent water.

3.3 Process parameters and cost of methanol production process

We now discussed the necessary process for the methanol generation and the following tables are showing the mass balance for the entire methanol production process. Table 3-8 is showing extended the mass balance for the methanol generation.

Table 3-7: Mass balance methanol reactor unit

Methanol Production UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O
Feed to MeOH Process	37	81,0	146,6	gaseous	Nm³/h	2,0	6.556,1	19.852,5	4,6	2,6		37,0
Reactor Feed	38	81,0	144,1	gaseous	Nm³/h	477,1	8.379,3	191.228,5	4,6	1.781,5	627,7	164,3
Reactor Feed after E-Heater	39	80,4	144,1	gaseous	Nm³/h	477,1	8.379,3	191.228,5	4,6	1.781,5	627,7	164,3
Procuct after Reactor	40	78,0	207,1	gaseous	Nm³/h	475,8	1.837,7	171.591,8		1.781,5	7.170,7	6.715,0
Cooled Product	41	74,5	45,0	gaseous	Nm³/h	475,8	1.837,7	171.591,8		1.781,5	7.170,7	6.715,0
Purge stream	42	74,0	44,9	gaseous	Nm³/h	0,6	2,2	205,9		2,1	0,8	0,2
Hydrogen from PSA	43	72,0	44,9	gaseous	Nm³/h	0,0	0,0	175,1		0,0	0,0	0,0
Waste Gas to CHP	44	24,0	30,0	gaseous	Nm³/h	0,6	2,2	30,9		2,1	0,8	0,2
Liquid Product 1	45	74,5	45,0	liquid	kg/h		24,5	0,7		0,5	9.351,9	5.294,8
Recycle to Compression	46	74,0	44,9	gaseous	Nm³/h	475,2	1.823,2	171.376,1		1.778,9	627,7	127,3
Recycle from Compression	47	81,8	59,6	gaseous	Nm³/h	475,2	1.823,2	171.376,1		1.778,9	627,7	127,3
Recycle after Heating	48	81,0	144,0	gaseous	Nm³/h	475,2	1.823	171.376		1.779	628	127,3
Liquid Product 1 after Throttle	49	10,0	44,9	liquid	kg/h		25	1		0,453	9.352	5.294,8
Waste gas from Flash 2	50	10,0	44,9	liquid	Nm³/h		21,23	0,64		0,39	1,17	0,6
Liquid Product 2	51	10,0	44,9	liquid	kg/h		3,3	0,1		0,061	9.350,1	5.294,0
Steam Condensate in	52	4,0	85,0	liquid	kg/h							5.266,6
Steam out	53	3,3	150,0	gaseous	kg/h							5.266,6
CW in	54	7,0	30,0	liquid	m³/h							563,0
CW out	55	6,0	40,0	liquid	m³/h							563,0

Table 3-9 is showing the methanol distillation for a methanol quality acc. IMPCA standard, which is considered as high-quality methanol usable for all purposes, either in chemistry or as a mixing component for fuel applications.

Table 3-8: Mass balance methanol distillation

Methanol Destillation UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	Dosing
IMPCA Standard MeOH	56	1,0	35,0	liquid	kg/h						9.245,4	0,1 /(wt)	
Waste gas to CHP	57	1,0	35,0	gaseous	Nm³/h		3,3	0,1		0,1	1,7	0,9	
Fussel Oil to CHP expr. as MeOH	58	8,0	35,0	liquid	kg/h						14,4	7,2	
Waste Water to Treatment	59	1,5	45,0	liquid	kg/h						87,7	5.286,9	Phosphor
Steam Condensate out	60	6,0	140,0	liquid	kg/h							5.266,6	
Steam in [5,4 bar(a) compressed]	61	11,0	263,0	gaseous	kg/h							5.266,6	
CW in	62	7,0	30,0	liquid	m³/h							275,0	
CW out	63	6,0	40,0	liquid	m³/h							275,0	

Figure 3-5 is showing the extended process flow diagram, which also includes parts of the total water treatment mentioned later.

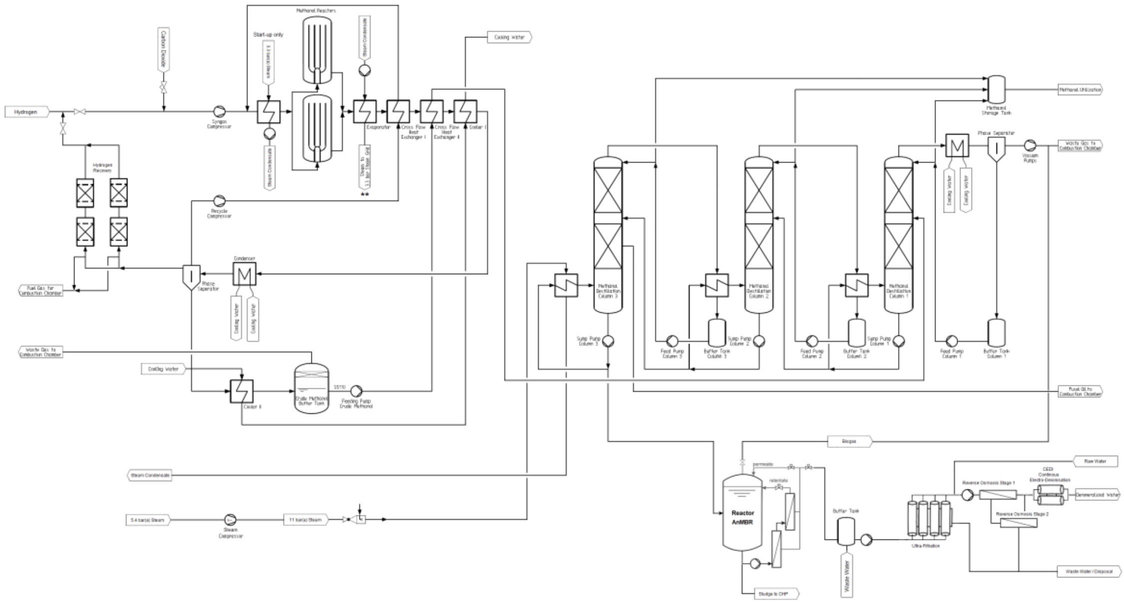
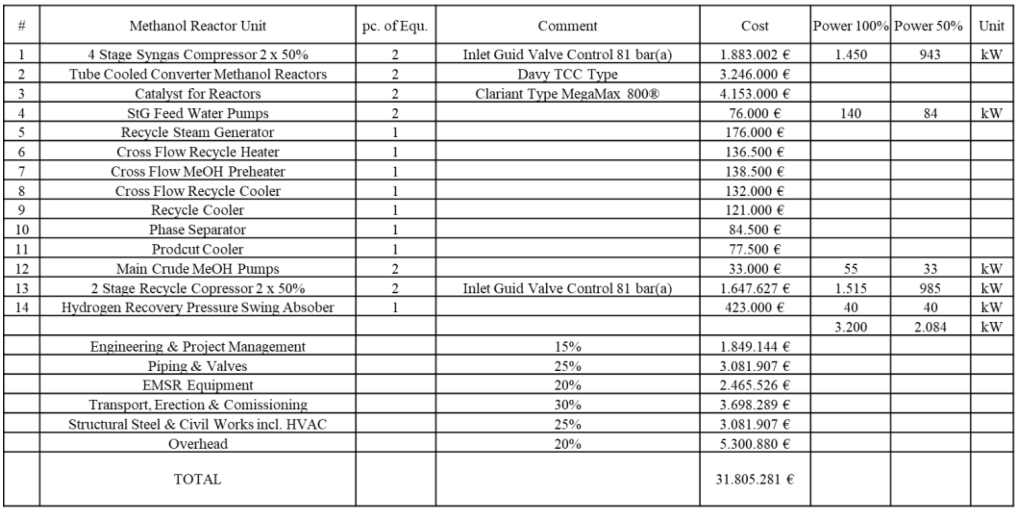


Figure 3-5: Process flow diagram of methanol production unit and parts of wastewater treatment

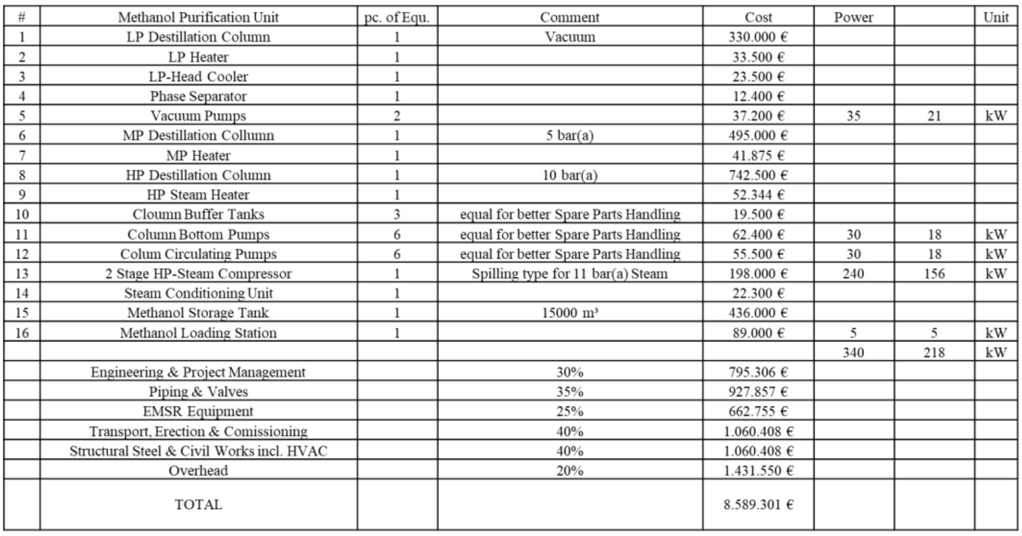
The cost and power consumptions are listed in the following two tables 3-10 and 3-11 for the reactor loop and the distillation, where it is not necessary to source both plants from one supplier, but in most cases, this will be the most cost-effective option.

Table 3-9: Equipment list incl. cost and power consumption for reactor-loop



#	Methanol Reactor Unit	pc. of Equ.	Comment	Cost	Power 100%	Power 50%	Unit
1	4 Stage Syngas Compressor 2 x 50%	2	Inlet Guid Valve Control 81 bar(a)	1.883.002 €	1.450	943	kW
2	Tube Cooled Converter Methanol Reactors	2	Davy TCC Type	3.246.000 €			
3	Catalyst for Reactors	2	Clariant Type MegaMax 800®	4.153.000 €			
4	StG Feed Water Pumps	2		76.000 €	140	84	kW
5	Recycle Steam Generator	1		176.000 €			
6	Cross Flow Recycle Heater	1		136.500 €			
7	Cross Flow MeOH Preheater	1		138.500 €			
8	Cross Flow Recycle Cooler	1		132.000 €			
9	Recycle Cooler	1		121.000 €			
10	Phase Separator	1		84.500 €			
11	Prodcut Cooler	1		77.500 €			
12	Main Crude MeOH Pumps	2		33.000 €	55	33	kW
13	2 Stage Recycle Copressor 2 x 50%	2	Inlet Guid Valve Control 81 bar(a)	1.647.627 €	1.515	985	kW
14	Hydrogen Recovery Pressure Swing Absober	1		423.000 €	40	40	kW
					3.200	2.084	kW
	Engineering & Project Management		15%	1.849.144 €			
	Piping & Valves		25%	3.081.907 €			
	EMSR Equipment		20%	2.465.526 €			
	Transport, Erection & Comissioning		30%	3.698.289 €			
	Structural Steel & Civil Works incl. HVAC		25%	3.081.907 €			
	Overhead		20%	5.300.880 €			
	TOTAL			31.805.281 €			

Table 3-10: Equipment list incl. cost and power consumption for distillation unit



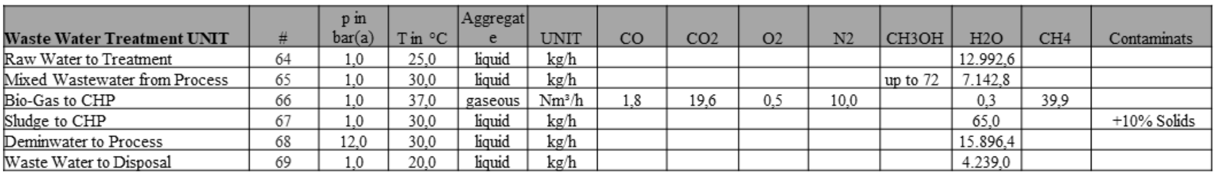
#	Methanol Purification Unit	pc. of Equ.	Comment	Cost	Power		Unit
1	LP Destillation Column	1	Vacuum	330.000 €			
2	LP Heater	1		33.500 €			
3	LP-Head Cooler	1		23.500 €			
4	Phase Separator	1		12.400 €			
5	Vacuum Pumps	2		37.200 €	35	21	kW
6	MP Destillation Collumn	1	5 bar(a)	495.000 €			
7	MP Heater	1		41.875 €			
8	HP Destillation Column	1	10 bar(a)	742.500 €			
9	HP Steam Heater	1		52.344 €			
10	Cloumn Buffer Tanks	3	equal for better Spare Parts Handling	19.500 €			
11	Column Bottom Pumps	6	equal for better Spare Parts Handling	62.400 €	30	18	kW
12	Colum Circulating Pumps	6	equal for better Spare Parts Handling	55.500 €	30	18	kW
13	2 Stage HP-Steam Compressor	1	Spilling type for 11 bar(a) Steam	198.000 €	240	156	kW
14	Steam Conditioning Unit	1		22.300 €			
15	Methanol Storage Tank	1	15000 m³	436.000 €			
16	Methanol Loading Station	1		89.000 €	5	5	kW
					340	218	kW
	Engineering & Project Management		30%	795.306 €			
	Piping & Valves		35%	927.857 €			
	EMSR Equipment		25%	662.755 €			
	Transport, Erection & Comissioning		40%	1.060.408 €			
	Structural Steel & Civil Works incl. HVAC		40%	1.060.408 €			
	Overhead		20%	1.431.550 €			
	TOTAL			8.589.301 €			

With this balance and cost the core process is described and in the next steps the attention is given to the water treatment and the balance of plant.

3.4 Balance for waste water treatment and cost

Table 3-12 is showing the overall mass balance of the treatment. The raw water here can be exchanged with treated waste water from the power plant. This optional water flows are also shown in the overall process flow diagram in the attachment. This operation will save additional fresh water consumption. It will also not change the mass balance of the water treatment significantly and the overall water treatment is capable to operate both ways.

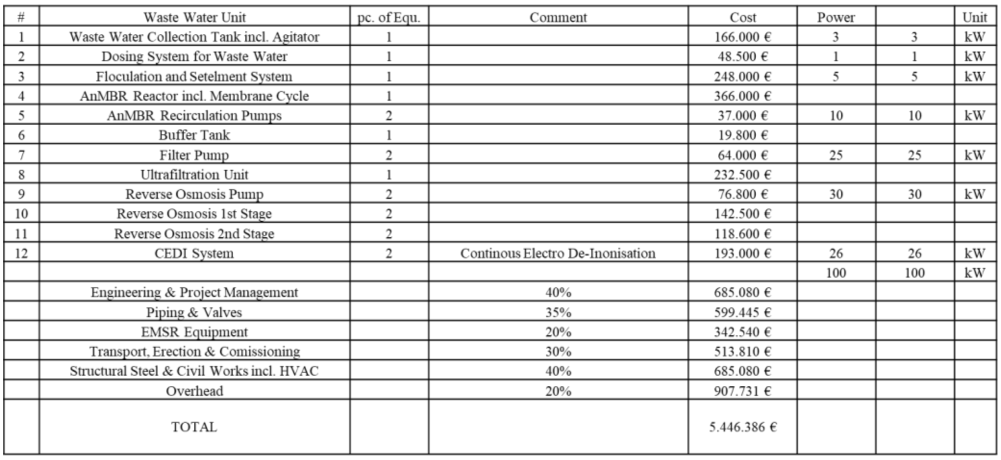
Table 3-11: Mass balance wastewater treatment without additional FGD waste water



Waste Water Treatment UNIT	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	O2	N2	CH3OH	H2O	CH4	Contaminats
Raw Water to Treatment	64	1,0	25,0	liquid	kg/h						12.992,6		
Mixed Wastewater from Process	65	1,0	30,0	liquid	kg/h					up to 72	7.142,8		
Bio-Gas to CHP	66	1,0	37,0	gaseous	Nm³/h	1,8	19,6	0,5	10,0		0,3	39,9	
Sludge to CHP	67	1,0	30,0	liquid	kg/h						65,0		+10% Solids
Deminwater to Process	68	12,0	30,0	liquid	kg/h						15.896,4		
Waste Water to Disposal	69	1,0	20,0	liquid	kg/h						4.239,0		

Table 3-13 is showing the equipment needed for the water treatment, which is necessary in addition to the water treatment of the power plant site as 100% new build. Reusing of power plant equipment can also be considered, but is neglected here.

Table 3-12: Equipment list of the water treatment incl. power consumption and cost

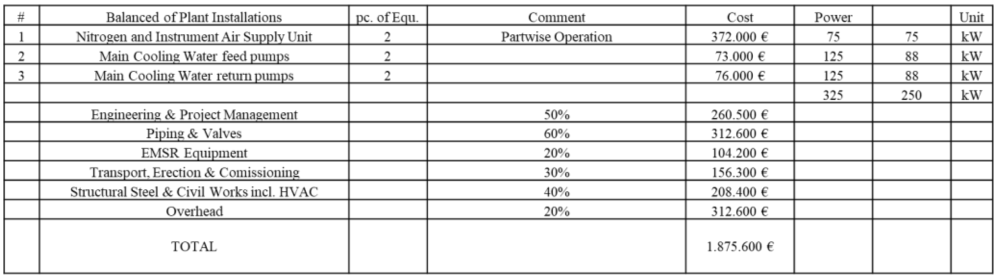


#	Waste Water Unit	pc. of Equ.	Comment	Cost	Power		Unit
1	Waste Water Collection Tank incl. Agitator	1		166.000 €	3	3	kW
2	Dosing System for Waste Water	1		48.500 €	1	1	kW
3	Floculation and Setelment System	1		248.000 €	5	5	kW
4	AnMBR Reactor incl. Membrane Cycle	1		366.000 €			
5	AnMBR Recirculation Pumps	2		37.000 €	10	10	kW
6	Buffer Tank	1		19.800 €			
7	Filter Pump	2		64.000 €	25	25	kW
8	Ultrafiltration Unit	1		232.500 €			
9	Reverse Osmosis Pump	2		76.800 €	30	30	kW
10	Reverse Osmosis 1st Stage	2		142.500 €			
11	Reverse Osmosis 2nd Stage	2		118.600 €			
12	CEDI System	2	Continous Electro De-Inonisation	193.000 €	26	26	kW
					100	100	kW
	Engineering & Project Management		40%	685.080 €			
	Piping & Valves		35%	599.445 €			
	EMSR Equipment		20%	342.540 €			
	Transport, Erection & Comissioning		30%	513.810 €			
	Structural Steel & Civil Works incl. HVAC		40%	685.080 €			
	Overhead		20%	907.731 €			
	TOTAL			5.446.386 €			

3.5 Balance of plant installations and total cost

In addition to the before discussed equipment for the workability of the plant also some additional equipment is necessary and listed in the following table.

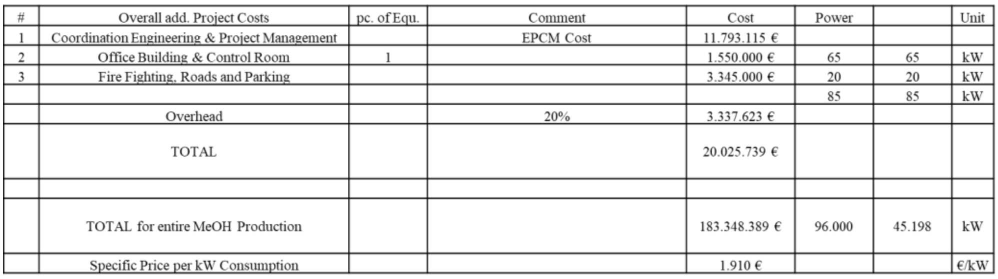
Table 3-13: Balance of plant equipment incl. power consumption and cost



#	Balanced of Plant Installations	pc. of Equ.	Comment	Cost	Power		Unit
1	Nitrogen and Instrument Air Supply Unit	2	Partwise Operation	372.000 €	75	75	kW
2	Main Cooling Water feed pumps	2		73.000 €	125	88	kW
3	Main Cooling Water return pumps	2		76.000 €	125	88	kW
					325	250	kW
	Engineering & Project Management		50%	260.500 €			
	Piping & Valves		60%	312.600 €			
	EMSR Equipment		20%	104.200 €			
	Transport, Erection & Comissioning		30%	156.300 €			
	Structural Steel & Civil Works incl. HVAC		40%	208.400 €			
	Overhead		20%	312.600 €			
	TOTAL			1.875.600 €			

It is in the overall planning also necessary to calculate additional costs for planning, office buildings, roads and firefighting. Summing up all costs mentioned before the total costs are complete and listed in table 3-15. (Please see also appendix for full list)

Table 3-14: Overall Cost and power consumption for the methanol production exciding the heat pumps



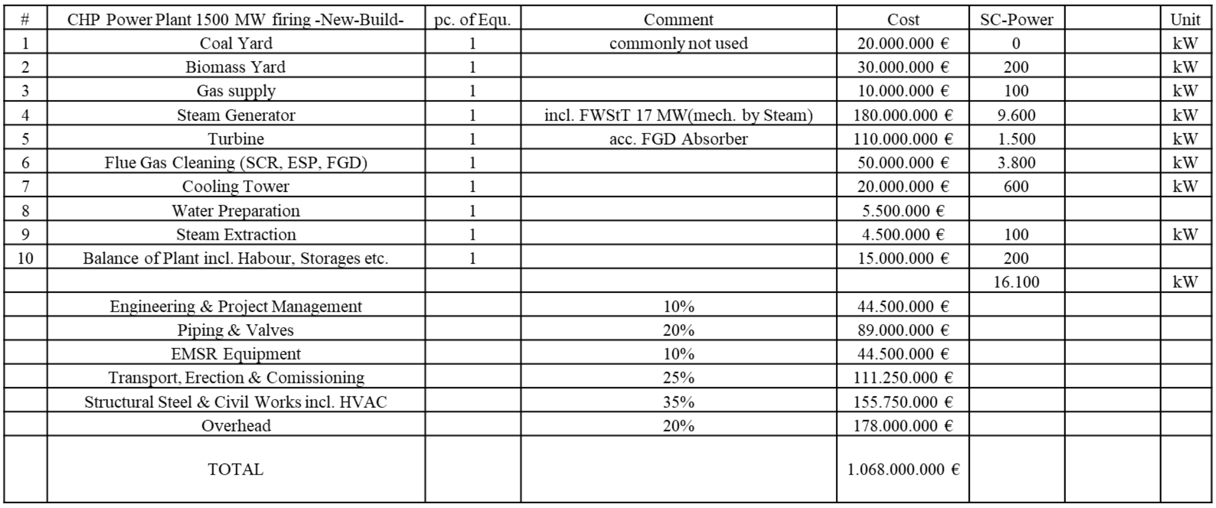
#	Overall add. Project Costs	pc. of Equ.	Comment	Cost	Power		Unit
1	Coordination Engineering & Project Management		EPCM Cost	11.793.115 €			
2	Office Building & Control Room	1		1.550.000 €	65	65	kW
3	Fire Fighting, Roads and Parking			3.345.000 €	20	20	kW
					85	85	kW
	Overhead		20%	3.337.623 €			
	TOTAL			20.025.739 €			
	TOTAL for entire MeOH Production			183.348.389 €	96.000	45.198	kW
	Specific Price per kW Consumption			1.910 €			€/kW

3.6 CHP Power plant installations and total cost

Finally also the cost for the in chapter 2.1 described power plant have to be estimated. Table 2-3 is giving the assumed today´s new build cost of such a power plant and figure 2-3 is giving the plant layout which was considered as the basis to start from.

A retrofit on an existing site is usual a higher challenge and if the changes a major, which can be concluded for the chapters before it is also considered that a new permit would be necessary. For this it must be seen that the CCS directive must be fulfilled, and the plant also has to be “capture ready”, which means that in addition a full CCS implementation must be possible in a later stage and so the space for such an installation must be part of the planning [120].

Table 3-15: “New Build” investment for the virtual CHP power plant site



#	CHP Power Plant 1500 MW firing -New-Build-	pc. of Equ.	Comment	Cost	SC-Power		Unit
1	Coal Yard	1	commonly not used	20.000.000 €	0		kW
2	Biomass Yard	1		30.000.000 €	200		kW
3	Gas supply	1		10.000.000 €	100		kW
4	Steam Generator	1	incl. FWStT 17 MW(mech. by Steam)	180.000.000 €	9.600		kW
5	Turbine	1	acc. FGD Absorber	110.000.000 €	1.500		kW
6	Flue Gas Cleaning (SCR, ESP, FGD)	1		50.000.000 €	3.800		kW
7	Cooling Tower	1		20.000.000 €	600		kW
8	Water Preparation	1		5.500.000 €			
9	Steam Extraction	1		4.500.000 €	100		kW
10	Balance of Plant incl. Habour, Storages etc.	1		15.000.000 €	200		
					16.100		kW
	Engineering & Project Management		10%	44.500.000 €			
	Piping & Valves		20%	89.000.000 €			
	EMSR Equipment		10%	44.500.000 €			
	Transport, Erection & Comissioning		25%	111.250.000 €			
	Structural Steel & Civil Works incl. HVAC		35%	155.750.000 €			
	Overhead		20%	178.000.000 €			
	TOTAL			1.068.000.000 €			

The retrofit cost will be lower compared to the new build cost. The assumption taken on this are described later in chapter 3 as well as the arrangement planning including all installations.

Having defined all building blocks for the entire system we can now step to the process integration of the methanol production to the CHP power plant.

3.7 Process integration of methanol production in a steam power plant

The co-generation of methanol in a power plant was already investigated in 2018 [121]. There the implementation of a power to methanol unit was considered for a power plant not operated in CHP. In 2014 it was investigated as well with a similar view [122]. Summarising both sources it was found that at higher carbon price certificates in the German market it is economic feasible to operate such a configuration, but the carbon footprint of the methanol will not be suitable to be market under the renewable energy directive of the EU. This is the reason that in this implementation we added the heat pumps as described above and undertake a fuel switch from coal to a combined firing of biomass and natural gas. The reason for both investigations was the need for flexible power needed for power plants in the future. Here the author is following the same target. Continuing our exercise form the beginning the overall process flow for such a power to methanol implementation looks as shown in figure 3-6 with the full load operating data given in table 3-1.17

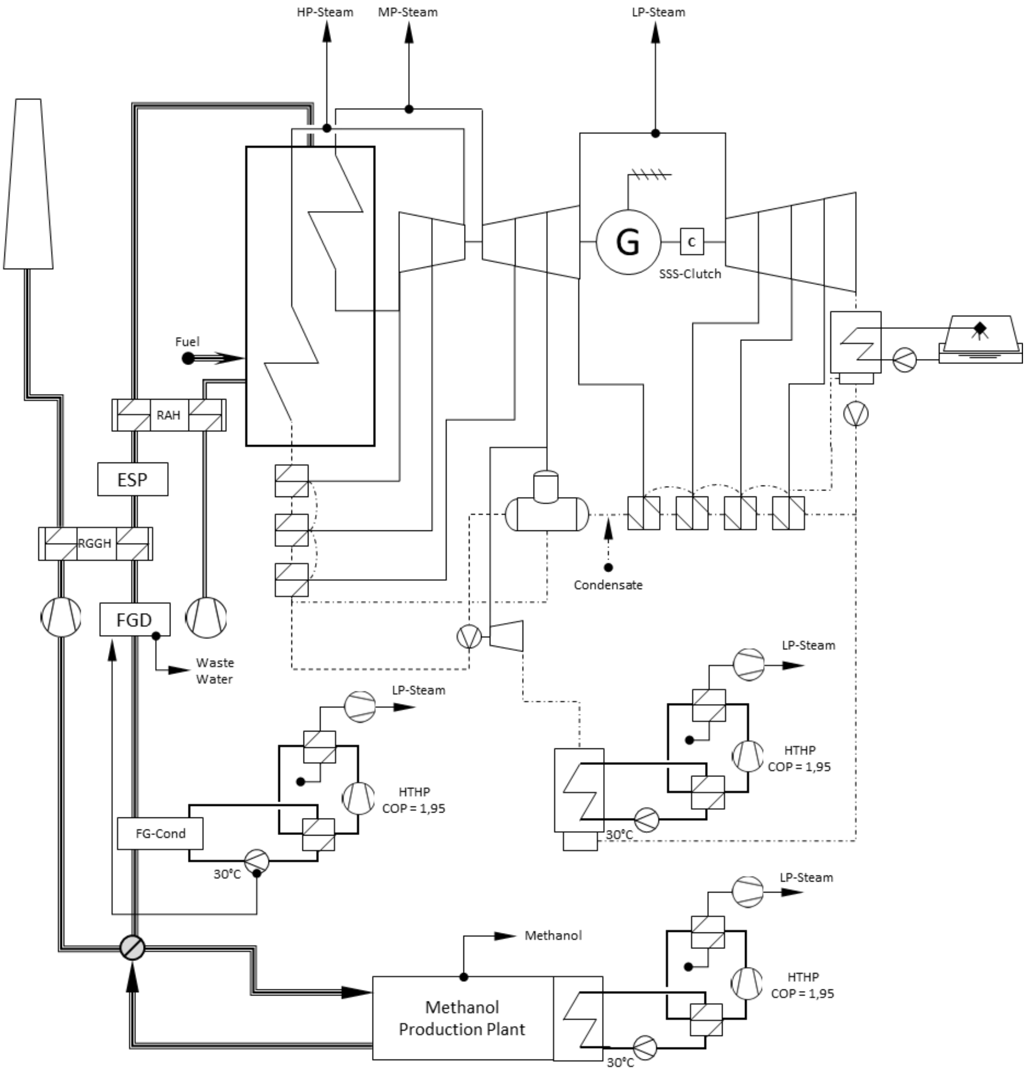


Figure 3-6: CHP steam power plant with integrated heat pumps and power to methanol unit

This operating data can of course be varied, and it is a full flexibilization of the power plant. It makes it possible to run with variations in heat extraction, power and methanol production independently from each other production. This three-vector production will be more deeply discussed later in this thesis in terms of load case and related fuel efficiency.

Table 3-16: Full load operating data of plant as shown in figure 3-6

No.	Flow Data @ 100% Load	m, kg/s	T, °C	p, bar(a)
3	HP Steam from Steam Generator (Variable)	522	571	254
4	HP Steam Extraction [40 MW] (Constant)	12.5	571	254
7	MP Steam Extraction [160 MW] (Constant)	47	569	41
9	LP Steam Extraction [max. 748 MW] (Variable)	282	267	5.4
	Extended Heat Recover @ 100% Load	**Heat, MW**		
F	LP Steam @ HTHP A/B/MeOH (Variable)	506	267	5.4
	Power Generation Data @ 100% Load			**P, MW**
X	Net. Power Generation @ Generator (Variable)			39.3
	Fuel Generation Data @ 100% Load	**m, kg/s**		**P, MW**
Y	Methanol Generation **(AEL 4.5 @ kWh/Nm³)** (Variable)	2.57		51.1
	Firing Data @ 100% Load			**P, MW**
12	Fuel Consumption (LHV) (Variable)			1,512
	Efficiency Data @ 100% Load			**Eff.-, %**
13	Power Generation Efficiency (LHV) (Variable)			2.6 %
14	Fuel Efficiency (LHV) (Variable)			104.5 %

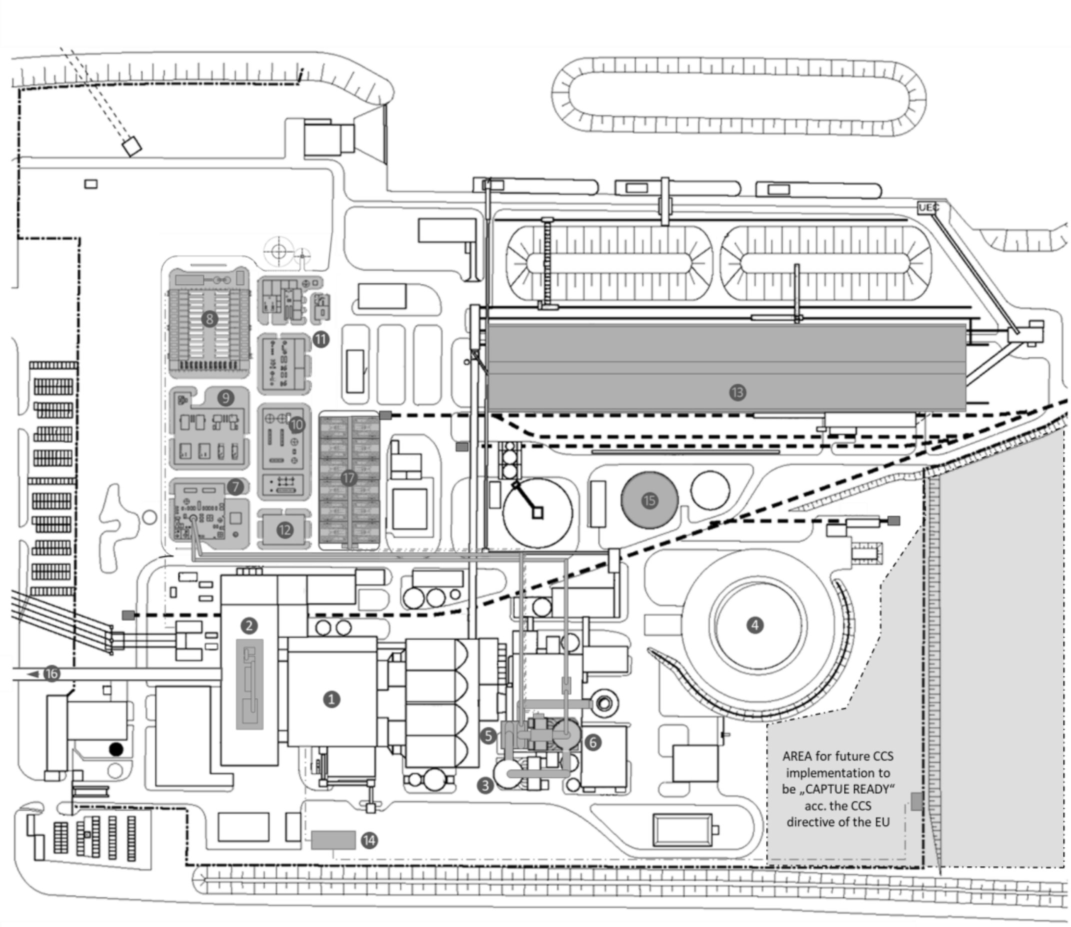


Figure 3-7: Layout of the retrofitted site of the CHP power plant

The arrangement acc. Figure 3-7 is consisting of:

1. Steam Generator 2. Turbine 3. Flue Gas Desulphurisation Scrubber 4. Cooling Tower 5. Implemented regenerative Gas/Gas Heater 6. Secondary Flue Gas Scrubber 7. Carbon Capture Unit 8. Alkaline Electrolyser 9. Compressor House 10. Methanol Reactor and Purification Unit 11. Water Treatment Unit 12. Electrical Building 13. Retrofitted Coal Yard for Biomass Storage 14. Connection to Natural Gas Grid 15. Retrofitted Oil Tank as Methanol Storage Tank 16. Pipe Bridge for Steam Connection to Chemical Park and 17. High Temperature Heat Pump Bay with twelve Heat Pumps for LP-Steam Generation.

This arrangement exercise is clearly showing that the implementation of a heat pump bay and methanol production integration to an existing site is possible, but of course the owner must have available a significant free space. To total required space is about the same area as it is needed for the power plant itself. The cost for the additional flue gas scrubber and heat pump bay integration are shown in tables 3-18 and 3-19.

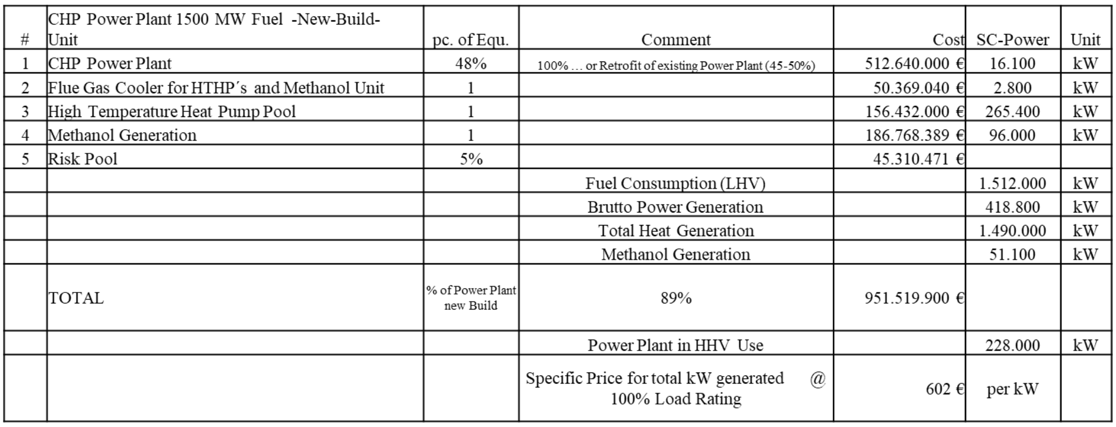
Table 3-17 Cost and power consumption of the flue gas cooling system

#	Flue Gas Cooling Unit	pc. of Equ.	Comment	Cost	Power		Unit
1	Flue Gas Dampers	4		720.000 €	10	10	kW
2	Regenerative Gas/Gas Heater (RGGH)	1		2.730.000 €	30	30	kW
3	Crude Gas Ducts		2.000.000 Nm³/h	3.450.000 €			
4	Cooling Vessel incl. Internals	1	acc. FGD Absorber	12.950.000 €			
5	Recirculation Pumps	3		705.000 €	2.250	2.250	kW
6	Mist Eleminator Wasing Pumps	2		76.000 €	90	90	kW
7	Heat Exchangers	2		636.000 €			
8	Cooling Water Pumps	2		178.000 €	320	320	kW
9	NaOH Tank	1		48.000 €			
10	NaOH Loading	2		36.000 €	10	10	kW
11	NaOH Dosing	2		18.000 €	5	5	kW
12	Waste Water Pumps	2		72.000 €	85	85	kW
13	Clean Gas Dampers	4		140.000 €			
14	Clean Gas Ducts		110.000 Nm³/h	1.560.000 €			
					2.800	2.800	kW
	Engineering & Project Management		8%	1.865.520 €			
	Piping & Valves		12%	2.798.280 €			
	EMSR Equipment		10%	2.331.900 €			
	Transport, Erection & Comissioning		30%	6.995.700 €			
	Structural Steel & Civil Works incl. HVAC		20%	4.663.800 €			
	Overhead		20%	8.394.840 €			
	TOTAL			50.369.040 €			

Table 3-18: Cost and power consumption of the heat pump bay with 12 heat pump units

#	High Temperature Heat Pump Pool Unit	pc. of Equ.	Comment	Cost	Power		Unit
1	Compressors incl. Motor & Control	12	Each System 21,6 MW(el)	63.075.000 €	260.092	239.022	kW
2	Heat Exchangers sets (5 pc.)	12		13.104.000 €			
3	E-Heater	12	Start-up heater only	576.000 €			
4	Pumps	24		432.000 €	5.308	4.878	kW
5	Throttle & plus Water Injection System	12		2.940.000 €			
6	Flare System	1	Emergency System	198.000 €			kW
7	Drain Tank incl. Vacuum Pump	1	Emptying only	286.000 €			
8	Insulation			864.000 €			
					265.400	243.900	kW
	Engineering & Project Management		10%	8.147.500 €			
	Piping & Valves		10%	8.147.500 €			
	EMSR Equipment		5%	4.073.750 €			
	Transport, Erection & Comissioning		15%	12.221.250 €			
	Structural Steel & Civil Works incl. HVAC		20%	16.295.000 €			
	Overhead		20%	26.072.000 €			
	TOTAL			156.432.000 €			

Table 3-19: Full retrofit cost and main technical data



#	CHP Power Plant 1500 MW Fuel -New-Build-Unit	pc. of Equ.	Comment	Cost	SC-Power	Unit
1	CHP Power Plant	48%	100% … or Retrofit of existing Power Plant (45-50%)	512.640.000 €	16.100	kW
2	Flue Gas Cooler for HTHP´s and Methanol Unit	1		50.369.040 €	2.800	kW
3	High Temperature Heat Pump Pool	1		156.432.000 €	265.400	kW
4	Methanol Generation	1		186.768.389 €	96.000	kW
5	Risk Pool	5%		45.310.471 €		
			Fuel Consumption (LHV)		1.512.000	kW
			Brutto Power Generation		418.800	kW
			Total Heat Generation		1.490.000	kW
			Methanol Generation		51.100	kW
	TOTAL	% of Power Plant new Build	89%	951.519.900 €		
			Power Plant in HHV Use		228.000	kW
			Specific Price for total kW generated @ 100% Load Rating	602 €	per kW	

Adding up all costs necessary for the full retrofit, as shown in table 3-20, about 90% of a conventional new build of a plant without heat pumps and methanol production is necessary. This new plant will have more operational options as any new build plant and so this is a real option for the reuse of existing coal fired power plants, as long as it is possible to have a CHP operation. The operation features are discussed in the next chapter.

4 Analysis of various operation modes with implemented methanol generation

In addition to the already mentioned literature also similar scenarios for the cogeneration of methanol with power plans have been executed [123,124]. All of the investigations do not integrate heat as a production vector for the plant. But here is the advantage, because this production vector is rising the overall efficiency significantly.

4.1 Heat pump integration for HHV recovery in the example power plant

To tackle the challenge of the cooperation of the power plant with fluctuation renewable electricity sources as a first measure it is supposed to implement a heat pump system for on the one hand the flexibilization of the operation, but on the other hand the better utilisation of the fuel [125]. The technology is based on state-of-the-art components, which are installed in industry in large scale since several decades [126]. Figures 4-1 and 4-2 are showing the necessary extension of the power plant.

Here is the principle to use the heat of the flue gas condensation, which leads to the use of the higher heating value of the fuel and the energy of the closed cooling water cycle of the plant. The flue gas condensation is implemented by a direct contact cooling with a scrubbing system [127]. This is also known from carbon capture systems and implemented in large scale in steam power plants [128] and keeps also the option for the power plant to install a full-scale carbon capture system.

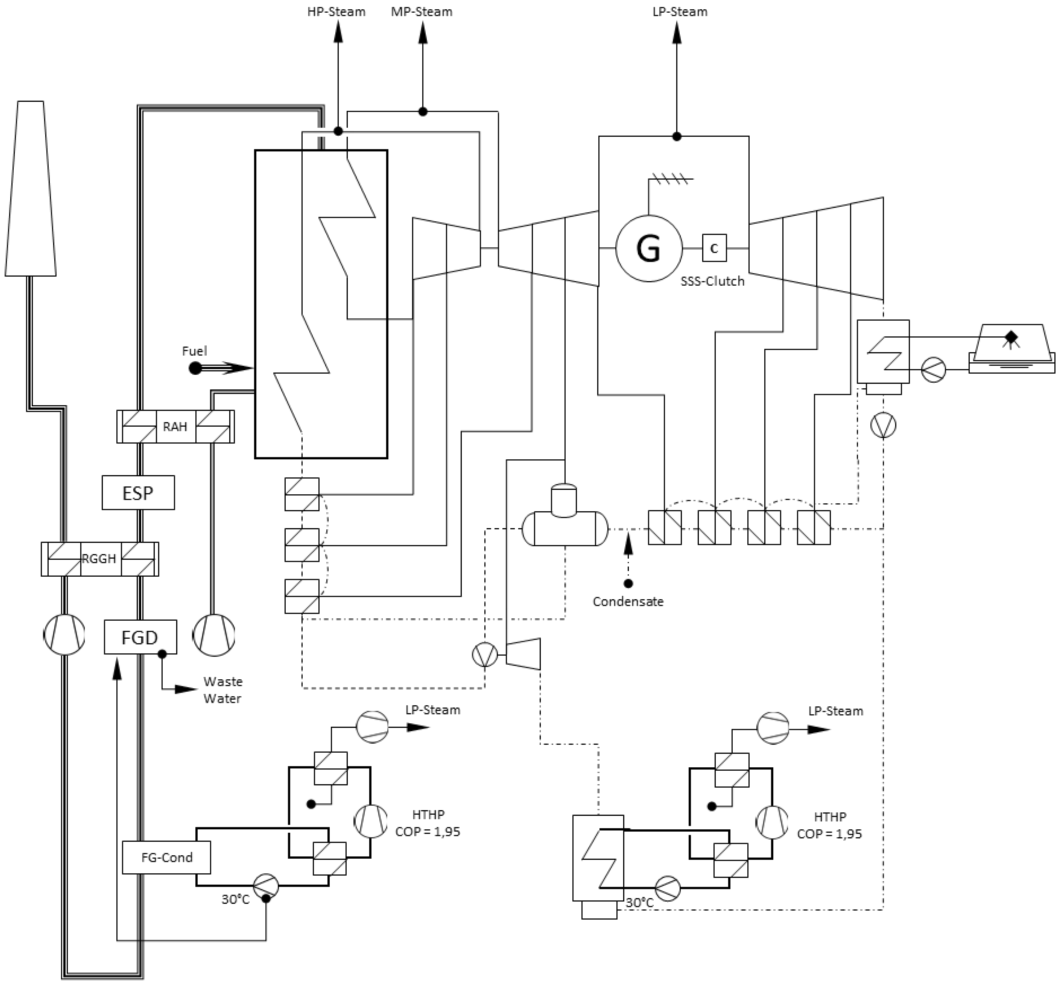


Figure 4-1: Implementation Principal of Heat Pumps in the Power Plant Process

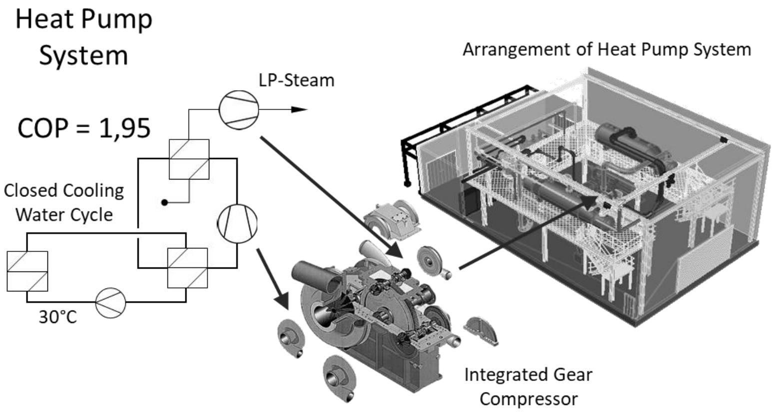


Figure 4-2: Visual Explanation of the implemented Heat Pump Systems

Detail to the heat pump system (HTHP) and its dimensioning can be followed in the given own literature of the author and in chapter 3.2. The system is using R600a as a natural refrigerant with low global warming potential (GWP) and of course zero ozone depletion potential (ODP) and it is already since a long time in industrial use. The basic assumption is that all cooling waters collected haven a return flow temperature of 30°C. the pumping energy in included in the overall COP of the system. The calculated drive power is integrated in performance data given in Table 4-1 in the self-consumption of the power plant at 100% load.

Table 4-1: Process Data from Heat Balance for CHP PP with LP Steam Extraction incl. Heat Pumps

No.	Flow Data @ 100% Load	m, kg/s	T, °C	p, bar(a)
1	Condensate (Variable)	396	50	13
2	Feed water (Variable)	522	284	294
3	HP Steam from Steam Generator (Variable)	522	571	254
4	HP Steam Extraction [40 MW] (Constant)	12.5	571	254
5	HP Steam to HP Turbine (Variable)	509	571	254
6	MP Steam to MP Turbine (Variable)	379	569	41
7	MP Steam Extraction [160 MW] (Constant)	47	569	41
8	Feed Pump Drive Steam (Variable)	29	363	10.8
9	LP Steam Extraction [max. 784 MW] (Variable)	282	267	5.4
	Extended Heat Recover @ 100% Load	**Heat, MW**	**T, °C**	**p, bar(a)**
A	Heat Recovery in Flue gas Cooler (Variable)	160	30	
B	Heat Recovery Condensation FW-Pump (Variable)	69	30	
C	Heat Generation LP Steam @ HTHP A/B (Variable)	448	267	5.4
	Power Generation Data @ 100% Load			**P, MW**
10	Power Generation @ Generator (Variable)			171
11	Self Consumption + HTHP (Variable)			- 248
	Firing Data @ 100% Load			**P, MW**
12	Fuel Consumption (LHV) (Variable)			1,512
D	Fuel Consumption (HHV) (Variable)			1,741
	Efficiency Data @ 100% Load			**Eff.-, %**
13	Power Generation Efficiency (LHV) (Variable)			11.3 %
14	Fuel Efficiency (LHV) (Variable)			106.0 %
E	Fuel Efficiency (HHV) (Variable)			92.1 %

The necessity to install the full capacity of the heat pump system is discussed later in connection with the expected operation range of the entire system.

This analysis is showing that with the heat pump implementation the fuel efficiency can be raised dramatically and exceeds 100% based on a calculation of the lower heating value (LHV). This is due to the reason that this system is using the higher heating value (HHV) of the fuel.

This new operation options will also dramatically raise the power generation flexibly of the installation and as well it will also lead to the fact that the CHP steam power plant can also cover its winter heat duty.

In the heat pump related literature of the author (as per chapter 2.2) this system is also combined with additional electric steam generators to maximise the power flexibility of the installation to become independent. These mentioned electrical steam generators operate with an efficiency of their power to heat generation of 99% and so do not influence the fuel efficiency. This was leading to from now on discussion how power to methanol installation can give an equal service.

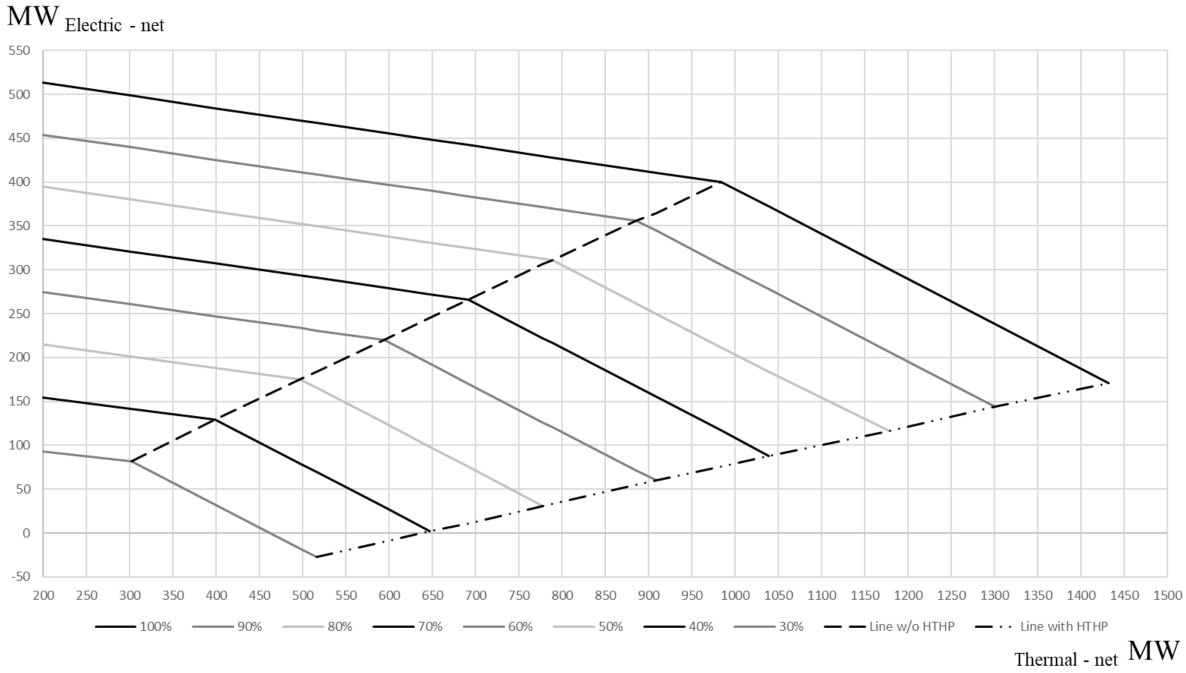


Figure 4-3: Heat Pump System Extended Operation Diagram of the Steam Power Plant

4.2 Heat as energy vector within an electric methanol production and discussion of efficiency

Table 4-2 is showing the energy balance as used in the mass balance for the planned system. It is showing an energy utilisation of 82,6% from power to the lower heating value of methanol, exported steam and fuel gas. Comparing this to an electric boiler with an efficiency of ca. 98% it is of course worse, but the value of the generated exergy is higher, due to the higher value of a chemical compared to simple heat, even if the output of it is only 39% of the electricity input [129]. Its exergy factor is 46% compared to an electric boiler with 16% assuming a heat output on the same pressure and temperature level.

Table 4-2: Energy balance of the isolated methanol production with maximum heat export

Energy Consumption in MW	Power	UNIT	Heat	UNIT	Cooling	UNIT	Methanol	UNIT	Waste Fuel	UNIT
Alkaline Electrolyser UNIT	89,9	MW			-15,3	MW				
Amine Carbon Capture UNIT	2,09	MW	13,1	MW	-11,1	MW				
Methanol Production UNIT	3,20	MW	-3,4	MW	-6,5	MW			-0,01	MW
Methanol Destillation UNIT	0,34	MW	3,5	MW	-3,2	MW	-51,1	MW	-0,09	MW
Waste Water Treatment UNIT	0,10	MW							-0,40	MW
Heat Pump UNIT for max Heat Export	36,3	MW	-70,6	MW	36,2	MW				
TOTAL with max. Heat export by HTHP	131,9	MW	-57,4	MW	0,0	MW	-51,1	MW	-0,50	MW

The next table shows the energy balance of the system, if by a heat pump only the heat is produced to serve the system itself without heat export. It shows that a significant drop in the electricity use takes place down to 50,3%. The exergy factor for this case is equal to the electric use, as fuel and electricity have the exergy factor of 100%.

Table 4-3: Energy balance of the isolated methanol production with heat production for self-supply

Energy Consumption in MW	Power	UNIT	Heat	UNIT	Cooling	UNIT	Methanol	UNIT	Waste Fuel	UNIT
Alkaline Electrolyser UNIT	89,9	MW			-15,3	MW				
Amine Carbon Capture UNIT	2,09	MW	13,1	MW	-11,1	MW				
Methanol Production UNIT	3,20	MW	-3,4	MW	-6,5	MW			-0,01	MW
Methanol Destillation UNIT	0,34	MW	3,5	MW	-3,2	MW	-51,1	MW	-0,09	MW
Waste Water Treatment UNIT	0,10	MW							-0,40	MW
Heat Pump UNIT for PCC Supply	6,77	MW	-13,2	MW	6,7	MW				
TOTAL with Heat by HTHP for PCC only	102,4	MW	0,0	MW	-29,4	MW	-51,1	MW	-0,50	MW

If we compare this to a system with steam import from the combine heat and power plant, where the power loss factor is calculated to 0,149 it shows an electric utilisation of 52,8%. Its pure exergy factor is 51,8%, because exergetically the heat has higher value as by the power loss factor.

This show that actual only two systems are in choice. Either the methanol generation with heat export from the combined heat and power production, or the methanol production with maximised heat export. Due to the reason that heat here is a usable product it is obvious to choose the second variant with maximising the electric utilisation by ca. 30%-points and this is also the variant with highest exergy use.

Table 4-4: Energy balance of the isolated methanol production with heat import for PCC

Energy Consumption in MW	Power	UNIT	Heat	UNIT	CW Cooling	UNIT	Methanol	UNIT	Waste Fuel	UNIT
Alkaline Electrolyser UNIT	89,9	MW			-15,3	MW				
Amine Carbon Capture UNIT	2,09	MW	13,1	MW	-11,1	MW				
Methanol Production UNIT	3,20	MW	-3,4	MW	-6,5	MW			-0,01	MW
Methanol Destillation UNIT	0,34	MW	3,5	MW	-3,2	MW	-51,1	MW	-0,09	MW
Waste Water Treatment UNIT	0,10	MW							-0,40	MW
Power Loss Factor for Heat = 0,149	1,97	MW	-13,2	MW	0,0	MW				
TOTAL with Heat by HTHP for PCC only	97,6	MW	0,0	MW	-36,2	MW	-51,1	MW	-0,50	MW

The next figure shows also another interesting effect. The full heat export is always utilising the full energy send to the electrolyser stacks. This leads to the effect, that its value stay´s almost constant independent from the efficiency of the electrolyser. This is an important information. In case of the degradation of the stacks the energy is not lost, but only transferred to another energy vector. In case later revamps make a higher efficiency possible, as e.g. expected by a retrofit with electrodes of higher efficiency it’s the other way around.

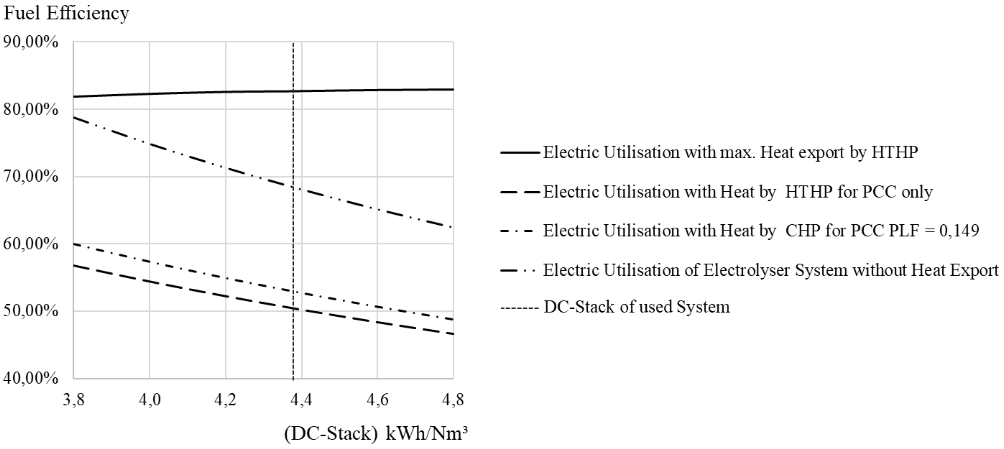


Figure 4-4: Variation of the variant efficiencies over the stack efficiency

This diagram shows that even today the best energy efficiency can be reached and also future more efficient systems are already comparable. This makes this new technology draft also robust versus future technology developments.

4.3 Possible operation modes including mixed fuel operation of the processes

Taking the main conclusions from the sub-chapter before it can be stated that it is proven to operate a methanol production long term and stable integrated in a steam power plant.

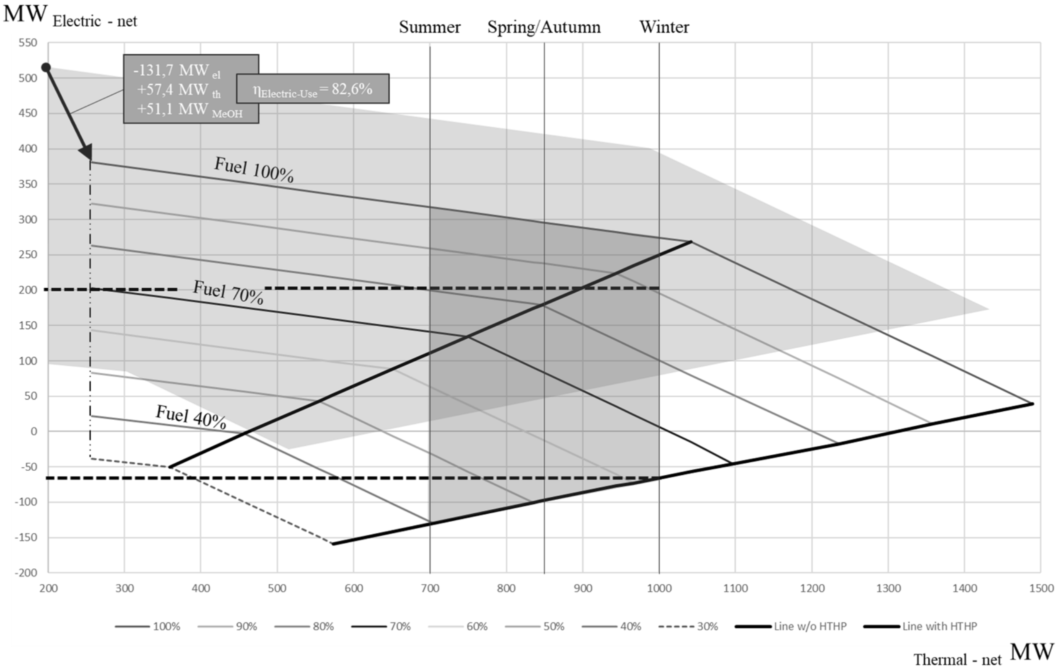


Figure 4-5: Operational diagram of the CHP power plant extended by a methanol production

The operation of the methanol production is not planned to be load following, which makes its operation easier. Coming from the combined heat and power plant example from the beginning we simply shift the operational diagram of the plant down by its total electrical consumption of 131,7 MW and its 57,4 MW steam production. This shift of the operational diagram is shown in figure 4-5. Staying in the operational example that the total heat demand is 700 MW thermal export in summer, 850 MW in spring/autumn and 1000 MW in winter, the given lines give the possible operational point of the plant. From figure 4-6 the fuel efficiency related to any operational point can be seen. (Please also review the Attachment F for usage of diagrams 4-5 and 4-6)

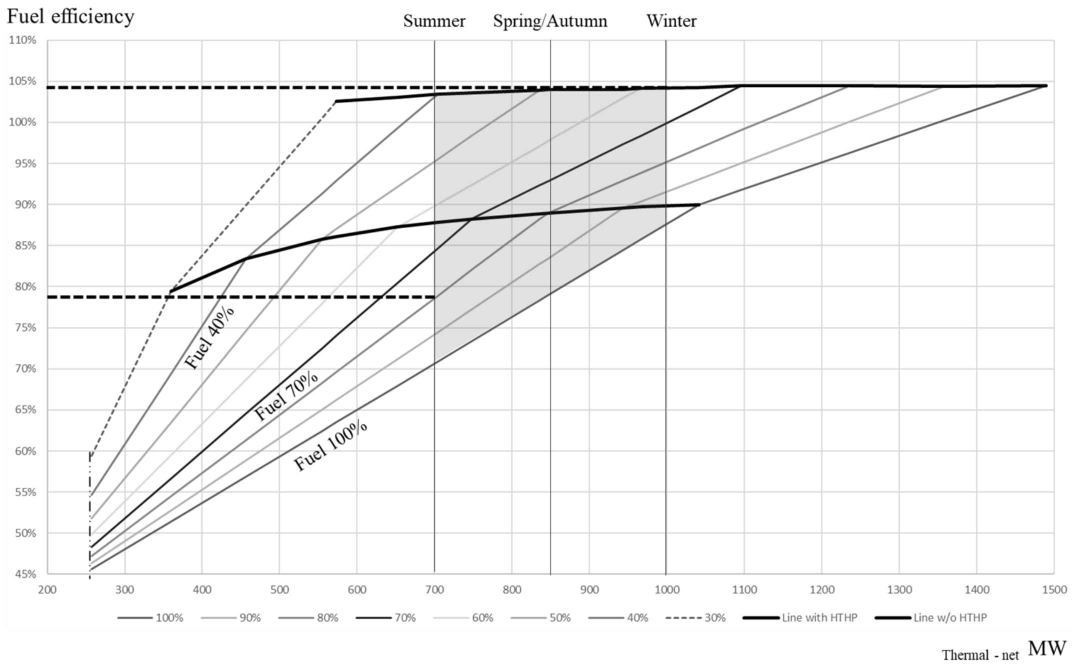


Figure 4-6: Fuel efficiency diagram of the methanol production extended CHP power plant

As the most interesting operational mode it was now seen that the gained flexibility of the plant is used to run the power plant complementary to a renewable production. For this it is necessary to use real data from fluctuation renewable production. Here we use data from Tennet for solar and off-shore wind power [14,15].

These have been from the given data to the output of a 240 MW off-shore wind park combined with a 60 MW solar farm. Figure 4-7 is showing the annual generation line of these combined assets as quarter hour values in leap year 2020.

In the following it was set that the plant is producing constantly 51,1 MW of methanol and its heat duty necessary in the seasons. At all operating points it keeps the electric production of the combination of the wind park, the solar farm and the power plant are 200 MW electrical base load.

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[14] https://www.tennet.eu/electricity-market/transparency-pages/transparency-germany/network-figures/actual-and-forecast-solar-energy-feed-in/nrw/

[15] https://www.tennet.eu/electricity-market/transparency-pages/transparency-germany/network-figures/actual-and-forecast-wind-energy-feed-in/

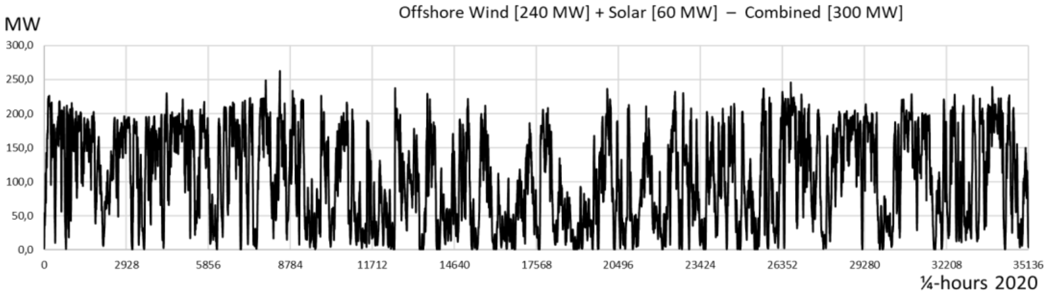


Figure 4-7: Annual power output from a 240 MW off-shore wind park and a NRW solar farm

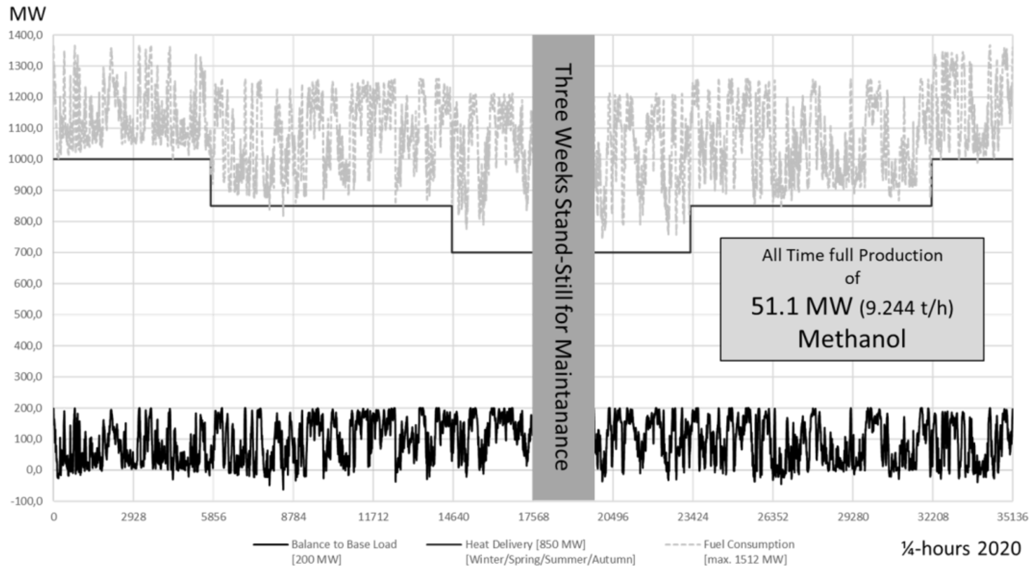


Figure 4-8: CHP plant power output, heat and const. 9,244 t/h methanol vs. firing load

Figure 4-8 is now showing the corresponding power and heat production and as well the needed firing load. It is also assumed that every year a stand-still of three weeks is needed.

From these data the operated fuel utilisation can be calculated an is shown in figure 4-9. This is now also showing, why the stand still time was chosen in summer.

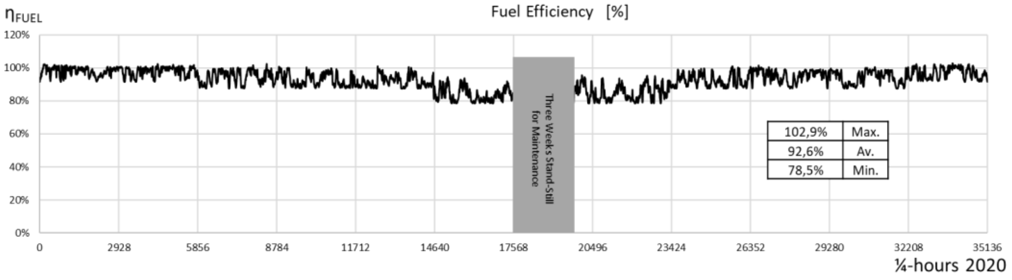


Figure 4-9: Fuel Efficiency (LHV-Utilisation) at the operation over the year

The fist reason is that in this time the fewest amount of heat must be supplied by the back-up systems and second the reachable fuel efficiencies in summer are the lowest in the annual average.

The total reached fuel efficiency over the entire year based on the lower heating value is 92,6% with a maximum of 102,9% and a minimum of 78,5%. This is expressing the high value of the higher heating value use by the fuel gas condensation with heat pump integration.

If the efficiency is reviewed under Carnot efficiency usage assumptions acc. the view of the EU under the RED 2018 Under this assumption the fuels used and produced and the power produced are set with an energy factor of 100%, while the produce heat is calculated by its Carnot factor acc. literature [133]. The on average reached exergy transfer from fuel to its products is than dropping dramatical to 44,3% with an maximum of 46,8% and a minimum of 39,5%.

If the efficiency is now in addition reviewed under exergy usage assumptions the picture is again another one. Under this assumption the fuels used and produced and the power produced are set with an exergy factor of 100%, while the produce heat is calculated by its exergetic factor acc. literature [130]. The on average reached exergy transfer from fuel to its products is than dropping dramatical to 28,9% with an maximum of 33,5% and a minimum of 20,9%.

In the operation the plant is reaching a full load hour operating grade of 67%. It is also possible to build other scenarios, but for this thesis this was set as the further example to discuss the carbon footprint of the products and the overall techno-economics.

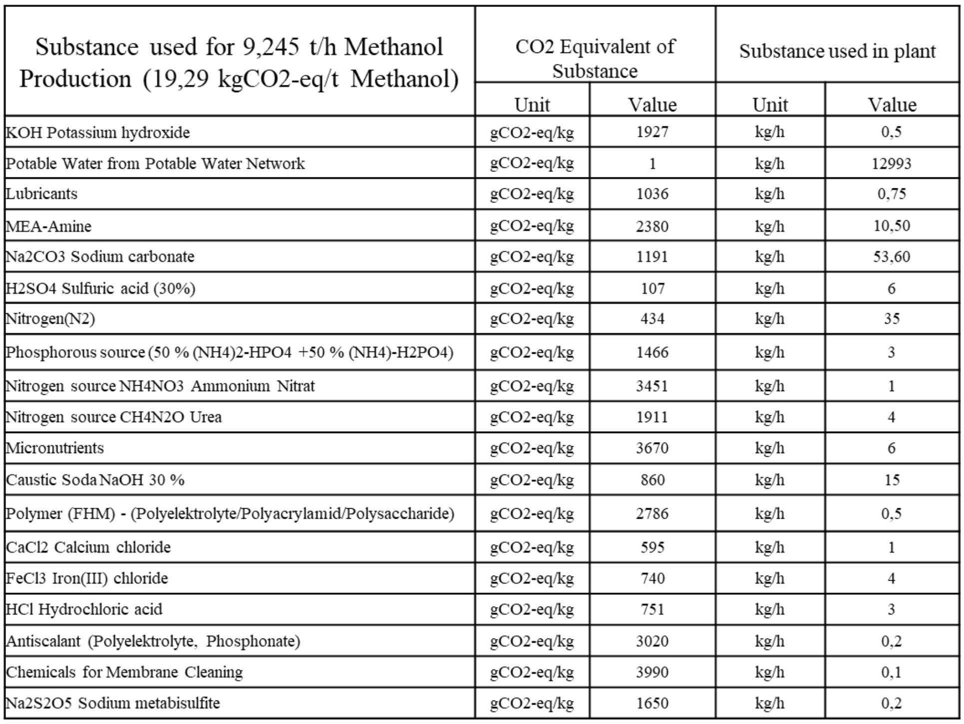
5 Carbon footprint of the process and related methanol production

To define the carbon footprint of the production of the methanol it is necessary to define the consumptions of the process. Best is to separate here the carbon footprint of the consumables and the used fuel for the CHP operation. The consumables are only allocated to the product methanol and the data are mainly taken from the Emission Factor Data Base (EFDB) of the Intergovernmental Panel on Climate Change (IPCC)[16]. Some of the values, if not available in the EFDB were also taken from other literature [131]. Data on the carbon footprint of fuels were taken for biomass from the Renewable Energy Directive of the EU (RED II) and from data of the German government for natural gas [132,133].

5.1 Carbon footprint for power plant implemented methanol production

First it is needed to sum up the carbon impact of the consumables used in the process. Table 5-1 is showing the result. This is summing up to 19,29 kg of CO_2-equivalent per ton of methanol.

Table 5-1: Table of Consumables without electricity and related carbon footprint



Substance used for 9,245 t/h Methanol Production (19,29 kgCO2-eq/t Methanol)	CO2 Equivalent of Substance		Substance used in plant	
	Unit	Value	Unit	Value
KOH Potassium hydroxide	gCO2-eq/kg	1927	kg/h	0,5
Potable Water from Potable Water Network	gCO2-eq/kg	1	kg/h	12993
Lubricants	gCO2-eq/kg	1036	kg/h	0,75
MEA-Amine	gCO2-eq/kg	2380	kg/h	10,50
Na2CO3 Sodium carbonate	gCO2-eq/kg	1191	kg/h	53,60
H2SO4 Sulfuric acid (30%)	gCO2-eq/kg	107	kg/h	6
Nitrogen(N2)	gCO2-eq/kg	434	kg/h	35
Phosphorous source (50 % (NH4)2-HPO4 +50 % (NH4)-H2PO4)	gCO2-eq/kg	1466	kg/h	3
Nitrogen source NH4NO3 Ammonium Nitrat	gCO2-eq/kg	3451	kg/h	1
Nitrogen source CH4N2O Urea	gCO2-eq/kg	1911	kg/h	4
Micronutrients	gCO2-eq/kg	3670	kg/h	6
Caustic Soda NaOH 30 %	gCO2-eq/kg	860	kg/h	15
Polymer (FHM) - (Polyelektrolyte/Polyacrylamid/Polysaccharide)	gCO2-eq/kg	2786	kg/h	0,5
CaCl2 Calcium chloride	gCO2-eq/kg	595	kg/h	1
FeCl3 Iron(III) chloride	gCO2-eq/kg	740	kg/h	4
HCl Hydrochloric acid	gCO2-eq/kg	751	kg/h	3
Antiscalant (Polyelektrolyte, Phosphonate)	gCO2-eq/kg	3020	kg/h	0,2
Chemicals for Membrane Cleaning	gCO2-eq/kg	3990	kg/h	0,1
Na2S2O5 Sodium metabisulfite	gCO2-eq/kg	1650	kg/h	0,2

To this amount of CO_2, the carbon emission from the fuel combustion must be added. These emissions can be calculated with the mentioned sources above and are represented in the later formulas as constant k. The RED II is also taking care about the sustainability of the fired biomass. So related carbon Footprint of the solid biomass fuels take into account all relevant issues as change of land use, fertiliser emission, transport and else. The emission default value (EDV) of fuels according the RED II is 94,1 grams of carbon dioxide per megajoule lower heating value of fuel or 338,76 kilogram of carbon dioxide per megawatt-hour lower heating value of fuel. This value can be expressed for methanol as 1872,6 kilogram of carbon dioxide per ton of methanol. According the best practice of the IPCC fossil methanol

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[16] https://www.ipcc-nggip.iges.or.jp/EFDB/main.php

can reach already 1695,2 kilogram of carbon dioxide per ton of methanol. This methanol is produced from natural gas with carbon injection to the syngas and the EDV is already 9,5% reduced.

RED II is now defining a minimum reduction to be reached for either biofuels or renewable fuels from non-biological origin. These fuels shall be reduced in carbon emission by 70% or, to put this in a EDV for methanol, shall have an EDV of 561,8 kilogram of carbon dioxide per ton of methanol or below. This also can be expressed as 101,6 kilogram of carbon dioxide per megawatt-hour of produced methanol.

It is needed to define an emission value of the fired fuel and below five tables are shown how this can vary. It is now assumed that it is possible to operate the entire plant always with a fuel mix below 50 gram of carbon dioxide equivalent emission per kilowatt-hour. This is a good assumption and makes already a high utilisation of biomass from various sources necessary, but also makes the firing of some fossil fuel possible. Please be aware that the carbon emission factors of fossil fuels can vary depending on the used life cycle analysis used. E.g. for natural gas this can vary from 202 to 240 gram of carbon dioxide per kilowatt-hour as discussed already in chapter 2.3.1.

Table 5-2: 5 Tables with possible fuel mixes used in the designed plant

Carbon Footprint	Carbon Footprint of Pellets for solid firing			Total Average
	gCO2-eq/MJ	gCO2-eq/kWh	Factor	gCO2-eq/kWh
Low	5	18,0	36,0%	25,00
Average	7	25,2	54,5%	
High	14	50,4	9,5%	

Carbon Footprint	Carbon Footprint of Pellets for solid firing			Total Average
	gCO2-eq/MJ	gCO2-eq/kWh	Factor	gCO2-eq/kWh
Low	7	25,2	20,9%	50,0
Average	14	50,4	64,1%	
High	23	82,8	15,0%	

Carbon Footprint	Carbon Footprint of Pellets for solid firing			Total Average
	gCO2-eq/MJ	gCO2-eq/kWh	Factor	gCO2-eq/kWh
BM-Low	7	25,2	61,5%	50,0
BM-High	14	50,4	28,5%	
Natural Gas	56	202	10,0%	

Carbon Footprint	Carbon Footprint of Pellets for solid firing			Total Average
	gCO2-eq/MJ	gCO2-eq/kWh	Factor	gCO2-eq/kWh
BM-Low	7	25	85,6%	50,0
BM-High	14	50	0,4%	
Natural Gas	56	202	14,0%	

Carbon Footprint	Carbon Footprint of Pellets for solid firing			Total Average
	gCO2-eq/MJ	gCO2-eq/kWh	Factor	gCO2-eq/kWh
BM-Low	7	25	21,0%	100,0
BM-High	14	50	44,0%	
Natural Gas	56	202	36,0%	

From a given value of the fuel carbon footprint (CF) it can be calculated down to the carbon footprint of each produced megawatt-hour in the plant by dividing with the reached fuel efficiency, the Carnot efficiency or the exergy efficiency of the methanol unit to use for the first views. Please see also the end of chapter 4 (page 70) for the different efficiency factors

$$CF_{Methanol}\,[kg_{CO2}/MWh_{Methanol}] = CF_{Fuel}\,[kg_{CO2}\,/\,MWh_{Fuel}\,] \div \eta_{Fuel}\,[\%] + k$$

$$CF_{Methanol,Car}\,[kg_{CO2}/MWh_{Methanol}] = CF_{Fuel}\,[kg_{CO2}\,/\,MWh_{Fuel}\,] \div \eta_{Car}[\%] + k$$

$$CF_{Methanol,Ex}\,[kg_{CO2}/MWh_{Methanol}] = CF_{Fuel}\,[kg_{CO2}\,/\,MWh_{Fuel}\,] \div \eta_{Exergy}[\%] + k$$

Equation 5-1: Calculation formulas for a straight forward direct calculation of carbon footprint

It is obvious that these methods might be too easy to use, but it can be shown that as a rule of thumb it is usable quite good. In the figure 5-1 is shown how the equations varies to the usual used Finnish Method [134]. This Finnish Method is the standard practice in Germany and the EU for combined heat and power (CHP) [135]. Any weighting factors for power, heat and chemical production are assumed to be set to one in this set of equations for equal treatment of the products.

The set of formulas for this extended Finnish Method is:

$$\eta_{Fuel,el} = (1 - PEE) \times \frac{\eta_{el}}{\eta_{el,REF}}$$

$$\eta_{Fuel,th} = (1 - PEE) \times \frac{\eta_{th}}{\eta_{th,REF}}$$

$$\eta_{Fuel,MeOH} = (1 - PEE) \times \frac{\eta_{MeOH}}{\eta_{MeOH,REF}}$$

$$PEE = 1 - \frac{1}{\frac{\eta_{th}}{\eta_{th,REF}} + \frac{\eta_{el}}{\eta_{el,REF}} + \frac{\eta_{MeOH}}{\eta_{MeOH,REF}}}$$

$$E_{CO2,el} = spec.Fuel\ CO_2Emission\ [kg/MWh] \times \eta_{Fuel,el} \times Fuel\ Input\ [MWh]$$

$$E_{CO2,th} = spec.Fuel\ CO_2Emission\ [kg/MWh] \times \eta_{Fuel,th} \times Fuel\ Input\ [MWh]$$

$$E_{CO2,MeOH} = spec.Fuel\ CO_2Emission\ [kg/MWh] \times \eta_{Fuel,MeOH} \times Fuel\ Input\ [MWh]$$

$$spec.E_{CO2,el} = E_{CO2,el} \div electric\ Output\ [MWh]$$

$$spec.E_{CO2,th} = E_{CO2,th} \div thermal\ Output\ [MWh]$$

$$CF_{Methanol,Fin}\,[kg_{CO2}/MWh_{Methanol}] = E_{CO2,MeOH} \div Methanol\ Output\ [MWh] + k$$

Equation 5-2: Equation set for extended Finnish method for carbon footprint

For the use of the method the reference efficiencies are chosen as follows. Efficiency for burning solid fuels 46%, because we compare to best practice of large power only steam power plants. For the heat the efficiency was set to the today´s best practice of natural gas boilers (91%) and the best efficiency of the methanol plant was taken from literature for solid fuels with 60% [136]. The primary energy saving of the combined heat, power and chemical production according to the Finnish Method is 13,6% with the given data on an annual average calculated over time series.

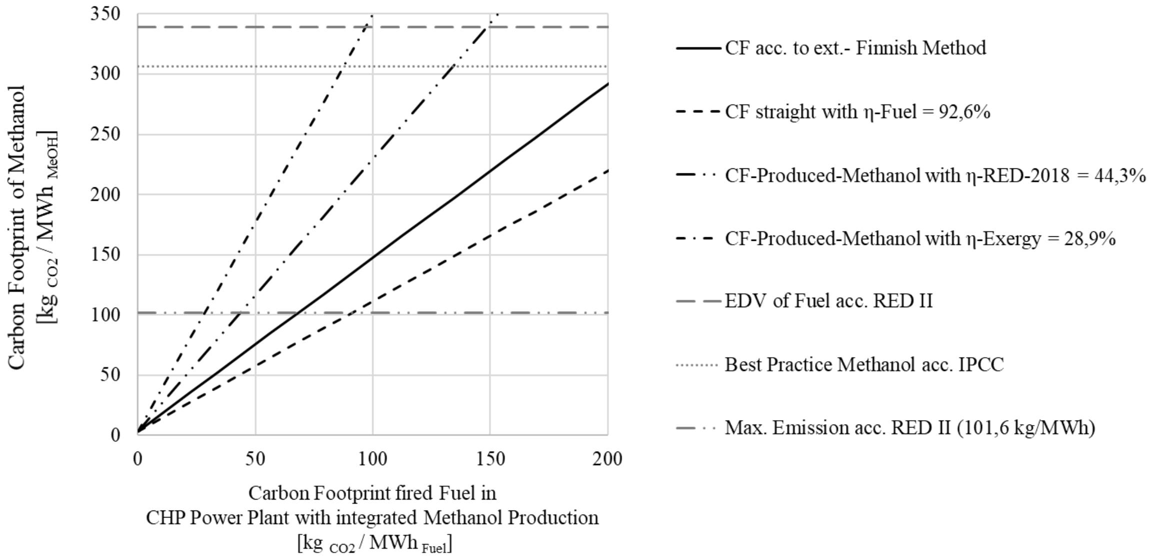

Figure 5-1: Diagram for CF relation between fuel and methanol incl. comparison of allocation method

The Finish Method leads to reasonable values in the carbon footprint of the methanol, but it is today not set standard method to use. The author suggests to use this method for the further calculations.

The use of the exergy factor leads to much higher values compared to the other three method and has the criticism that the exergy factor calculates to 28,9% which is similar to a system without any heat utilisation, which underestimates in the use case the value of produced heat. It is not reasonable to prefer a system with less fuel utilisation.

Neglecting the method with the use of the exergy factor, it is interesting to see in figure 5-1 that even in the operation with 100% natural gas firing the produced methanol will be less carbon intensive as the best practice produced fossil methanol from natural gas.

5.2 Alternative supply options for hydrogen and carbon dioxide for the methanol generation and comparison of the carbon footprint

In this chapter other hydrogen and carbon sources are briefly described and compared with the findings in this thesis.

5.2.1 Alternative hydrogen supply

For the alternative hydrogen supply three other options are taken into consideration. Chlor-alkali electrolysis (CAK), methane pyrolysis (Pyrolysis) and steam methane reforming wit carbon capture

(SMR & CCS). These are compared to the used alkaline electrolysis as used in the described plant, considering the same hydrogen pressure of 30 bar(a).

Chlor-alkali electrolysis

This type of electrolysis is widely used in industry today and data for comparison are taken from the available literature [137,138,139]. Here the best available technique for membrane technology is used. Here the power consumption per ton of chlorine is 2.200 kWh/t and the evaporation heat for the sodium hydroxide lye is 200 kWh/t. Here the hydrogen is produced at atmospheric pressure.

It is operated in industrial complexes to produce chlorine gas and sodium hydroxide lye. Both main products are essential for many chemicals used today. The today´s side product hydrogen is in general not used for chemical processes and only burned for industrial steam production, which is today not the adequate use. The main technical data as well as the process flow are as sown in figure 5-2 and figure 5-3. The mass of the used water is not shown in the balance.

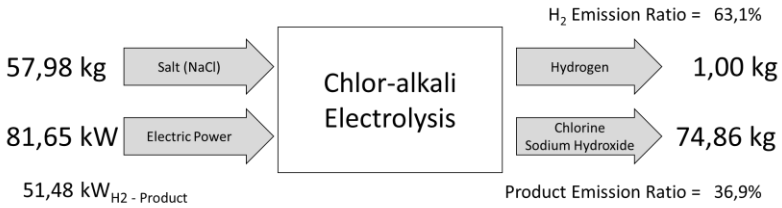

Figure 5-2: Specific balance of CAK electrolysis

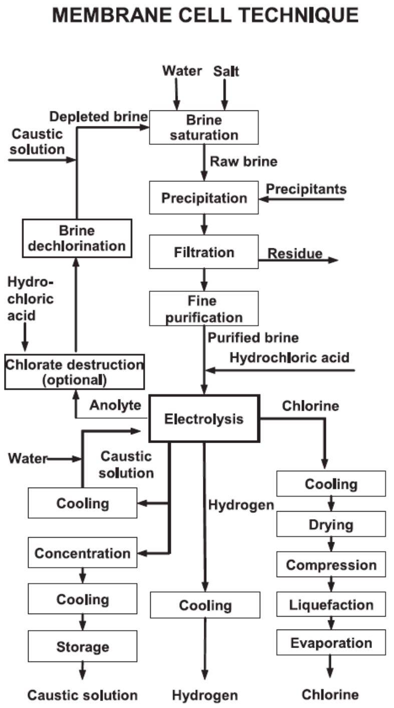

Figure 5-3: Process flow of a membrane CAK process from given literature

As hydrogen is not the only product of this hydrogen source, not all consumption can be surcharged to the product hydrogen. It is split using the individual reaction enthalpies from the main chemical reaction.

Reaction: NaCl + H2O → NaOH + 1/2 H2 + 1/2 Cl2; ΔH=223 kJ/mol

Here 17 kJ/mol are for the chlorine reaction, 63 kJ/mol are for the sodium hydroxide reaction and 143 kJ/mol are for the hydrogen production. Energy used for the water evaporation of the sodium hydroxide product are surcharged only to this product and the hydrogen compression to 30 bar(a) is surcharged to the hydrogen product only. The value is conservative derived from the following figure 5-4.

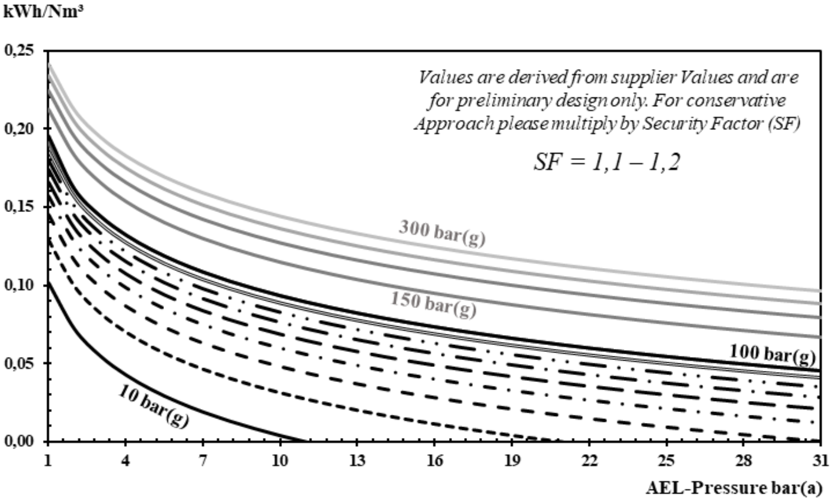

Figure 5-4: Hydrogen compression power consumption vs. electrolysis pressure

Methane Pyrolysis

The methane pyrolysis is a new emerging technology, which was mainly developed for the production of carbon black as its main product. This product is here considered as an option for carbon storage. The produce carbon black can be pelletised and stored in the deep underground as e.g. old coal mines or similar. The technical data are taken for the literature [140,141,142] and are shown in figure 5-5.

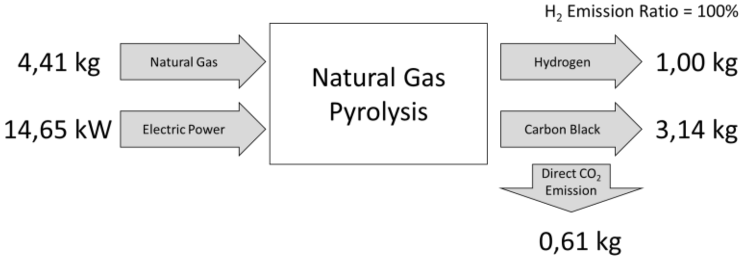

Figure 5-5: Specific balance of methane pyrolysis

The Norwegian company Kvaerner patented in the 90th of the last century a plasma torch for the production of carbon black through pyrolysis of natural gas. In this process, natural gas is fed to a plasma torch which is operated with recirculated hydrogen and electric power. In 2012, the US company Monolith Materials started the development of a plasma process based on the Kvaerner technology.

The technology is not free of direct carbon emissions, but is a very limited emission. As a further illustration here is shown a picture (figure 5-6) of a commissioned plant of the company Monolith in the USA.

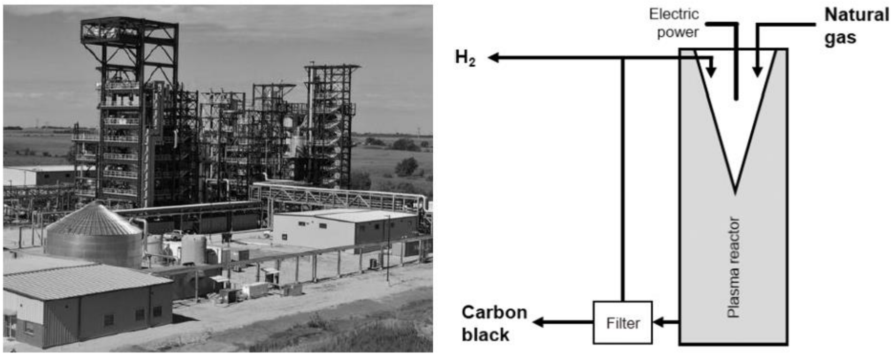

Figure 5-6: Monolith methane pyrolysis plant Olive Creek I (OCI), Nebraska, Commissioned: 2020, H2 Reactor Scale: 600kg/hr, Capacity: 14kT/year Carbon Black

Steam methane reforming with carbon capture

The hydrogen produced with SMR & CCS technology is also widely known as “blue” hydrogen. It is using state of the art steam methane reformers and state of the art carbon capture systems. Data for the steam reformer was taken from the literature [143,144,145,146,147,148].

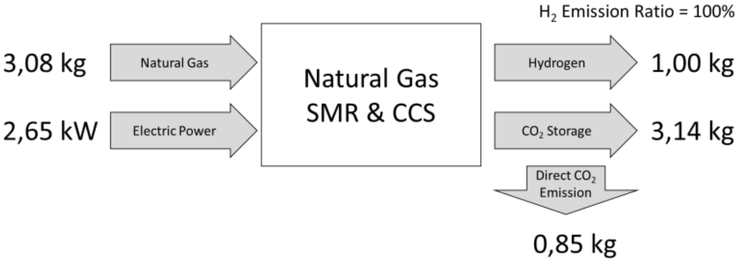

Figure 5-7: Balance for SMR & CCS incl. carbon dioxide transport energy

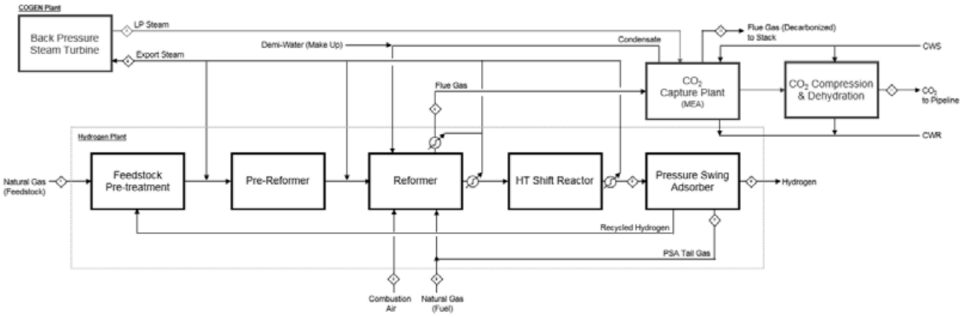

Figure 5-8: IEAGHG – Case 3; SMR Plant with capture of CO2 from SMR flue gas using MEA

The balance is derived from a mix of the described technology, but considering as well a significant transport distance of the carbon dioxide and the related energy consumption. The carbon capture rate is set to 90%.

Reference alkaline electrolyser technology and comparison

As reference the same technology for alkaline electrolysis is used as described before.

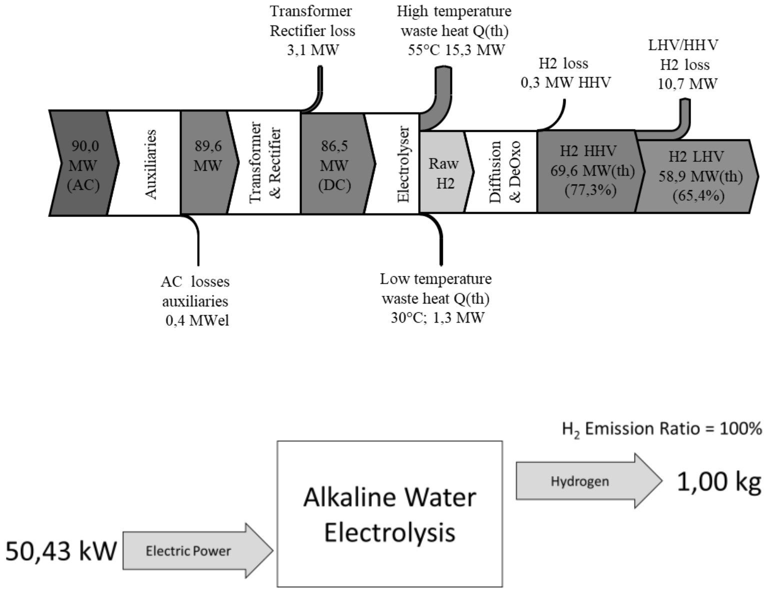

Figure 5-9: Balance for alkaline electrolysis (AEL)

Comparison of the technologies

The technologies can now be compared with this reference regarding their carbon footprint.

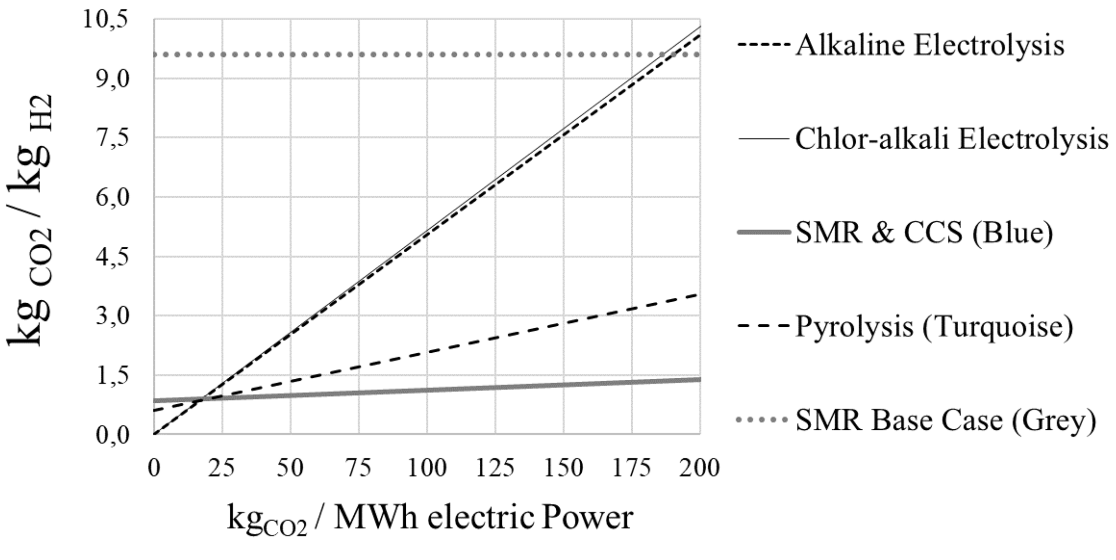

Figure 5-10: Hydrogen carbon footprint of the technologies vs. the carbon footprint of the used electric power as a mix of renewable and fossil

It is obvious that the two electrolyser technologies more or less follow the same path, while pyrolysis derived hydrogen of hydrogen from SMR & CCS are expected less affected by the carbon footprint of the consumed power. This comparison was made not taking into account that also this technologies can be operated in “combined heat & power”, which means that the off-heat of such plants can be used. Either directly or via described heat pump systems.

5.2.2 Alternative carbon sources

As other carbon sources but the used fuels in the described example it must be first discussed, which carbon source shall be considered. These shall be either renewable (derived from solid, liquid or gaseous biomass) or immanent, which shall mean that these are also in future unavoidable even after 2050.

Of course there will be various options for such carbon source, which it are not possible to be discussed here fully in detail. The author decided to choose three examples here. These are first carbon dioxide from waste to energy plants, second carbon dioxide from clinker preparation for cement production and carbon dioxide from steel production using hydrogen derived direct reduced iron. This choice was made as these three carbon sources are representing all the in a far future available sources for carbon dioxide.

1. Due to recycling and other measures, municipal waste in future will be almost carbon neutral [149] and will become important as a renewable carbon source.

2. Even if in future the new derived clinker in cement will be reduced, the cement use will be minimised and the fuels for clinker production will be on renewable basis the energy consuming reaction of limestone ($CaCO_3$) to calcium oxide (CaO) and carbon dioxide (CO_2) will release significant amounts of fossil carbon dioxide. This is an example for immanent carbon emissions.

3. Even if in future the steel production is 100% transformed to hydrogen using technology still some coke (renewable as char coal or not) is used in the electric arc furnace, which is needed in addition to the direct reduction. Here it is needed to add pure carbon to set the steel grade parameters in the carbon content, because steel is an alloy from carbon with iron. While blast furnace hot metal is carrying too much carbon the direct reduce iron using hydrogen is carrying not enough carbon, which needs to be added. In this process also unavoidable carbon emissions take place.

Waste to energy plant (WtE)

Waste to energy plants are in the first place simply steam power plants using grade firing and only moderate steam parameters to avoid excessive corrosion while the operation [150]. The carbon dioxide in the flue gas is usually about 10% of its volume fraction and so very suitable for the already described carbon capturing process. It is also thinkable to operate such WtE in parallel to a described large steam power plant as it is done in the already mentioned power plant Avedoere with a straw fired steam generator. Due to its strong similarity with the carbon capture from steam power plants the description is made brief here and not further described.

Clinker production

Beside other carbon capture options as oxyfuel, carbonate looping or membranes, the carbon capture from cement production can processed by amine scrubbing [151,152]. This process can be added at the stack tail of a today´s state of the art cement clinker production. The carbon dioxide content in the flue gas is high with about 20% of its volume fraction and so it is very suitable for an amine base scrubbing technology. About two third of the carbon dioxide is derived from the limestone reaction. Figure 5-11 is showing the principle process.

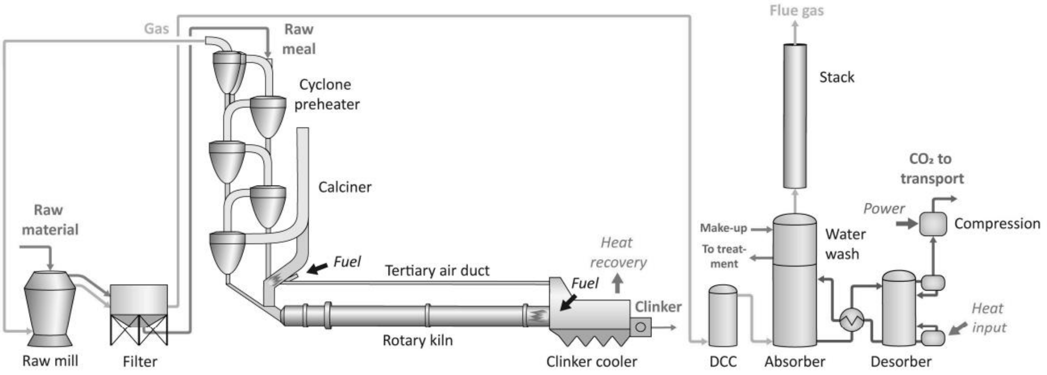

Figure 5-11: Rotary cement kiln with amine carbon capture implementation

The capture rate here can be 90% and easily higher if needed. Even if the fired fuel is assumed to be hydrogen, the carbon content in the flue gas is still high enough for the use of this technology.

Electric arc furnace using H_2-DRI

Electric arc ovens are used today for steel production from scrap, but will be in future used also for the raw steel production from direct reduced iron by hydrogen [153]. Here is made steel from the iron produced also by adding carbon to the carbon/iron alloy called steel [154,155].

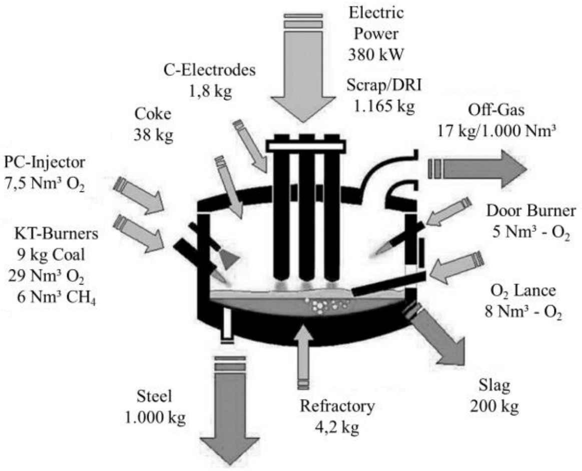

Figure 5-12: Balance of a scrap using electric arc furnace

It can be calculated that for a ton of raw steel about 180-220 kg of carbon oxides (as CO_2) are emitted by the off gas this process, which has a high content of carbon monoxide and carbon dioxide. After its energetic use the flue gas produced by this gas has carbon contents of up to 20% depending on the CO/CO_2 ratio. The off gas itself is generated tap to tap in the process and is not constantly available, but by using a gas holder the energetic use can be on a constant basis in a steam generator. Also this flue gas is very suitable for the amine scrubbing technology.

Conclusion for described carbon sources

All three described technologies are analysed as available in the future, 2050 and beyond, and are suitable for amine scrubbing and are usable with in principal same energetic figures as described in chapter 2.3.3. This will be used in the comparison of the methanol carbon footprints using the discussed alternative hydrogen sources.

5.2.3 Comparison of the resulting methanol carbon footprints

For the comparison of the carbon footprints with the described deep implementation in a steam power plant we need to take the following assumptions.

1. The used electric power is produced by a power plant with solid biomass combustion in the mix with natural gas combustion and variation of the carbon footprint of the fired fuel between zero and 200 $kg_{CO2}/MWh_{LHV\text{-}Fuel}$
2. The power production efficiency for solid biomass is set at 45% based on the lower heating value (LHV)
3. Due to the possibility that all hydrogen production variants feed the same methanol process the same power consumption for the process of 0,2 $MWh_{el}/MWh_{LHV\text{-}MeOH}$ is added as well as the same surcharge for consumables. This is an assumption taken, which is a good approximate and more details need deeper investigation
4. For the alternative hydrogen/carbon source options in chapter 4.2 not heat extraction or any other combine production is considered

Using the four assumptions the following diagram can be estimated from the before calculated data for the hydrogen production.

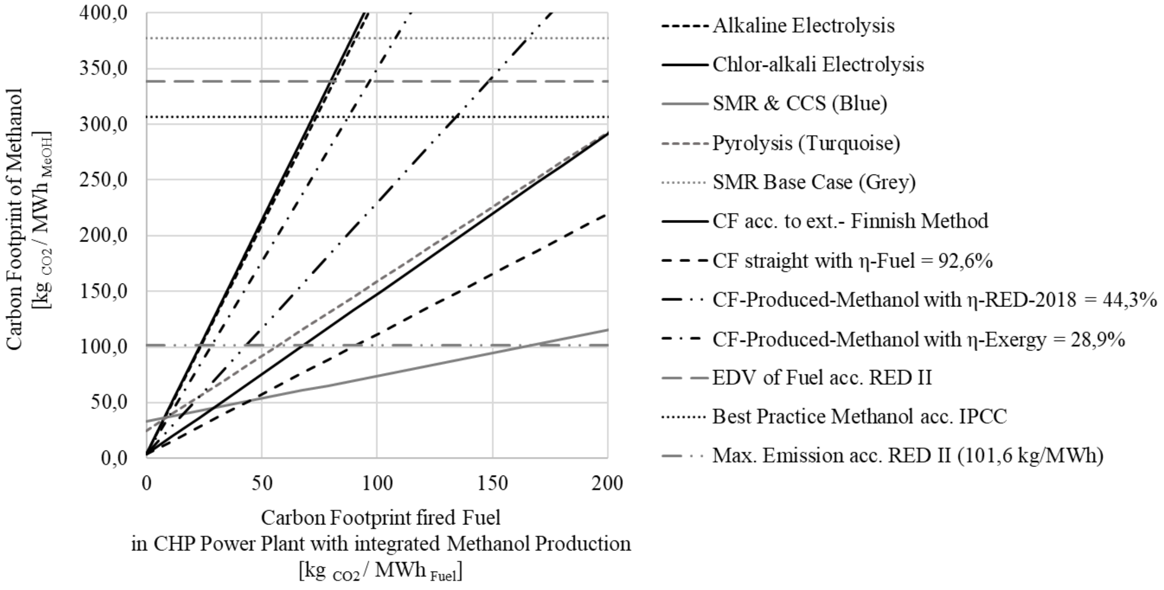

Figure 5-13: Methanol carbon footprint vs. carbon footprint of fired fuel – Comparison Diagram

The diagram in figure 5-13 is showing that the investigated methanol production method in combination with heat and power production is highly effective, if biomass is used as a power source. The method is even as carbon efficient as the use of methane pyrolysis as the main energy source. This is proofing the advantage of the combined production in three vectors.

The diagram is showing as well that within the multi vector production the alkaline water electrolysis can be easily exchanged by a chlor-alkali electrolysis. This would be than even a five vector production of sodium hydroxide lye, chlorine, methanol heat and power.

The diagram proofs that in the case of a lack of low carbon electricity sources “blue” hydrogen is the best choice for low carbon methanol. Blue hydrogen production can be operated with the use of power produced by combined cycle gas power plants with CCS, which leads to very low carbon emissions for the power production below 20 kg_{CO2}/MWh. Of course storage options for the fossil carbon are necessary, while sources of green carbon need to be available. This is raising the question, if a simple sequestration of bio-carbon e.g. from WtE in the combination with fossil methanol production can have the same effect at lower cost.

6 Techno-economic analysis of implementation scenario

In the chapters before the technology, its carbon emissions and the necessary investment cost of the implementation have been discussed. To have a full data set for an economic analysis it is necessary to make several assumptions and to define other side costs. Starting such a project today needs also development time and here is now assumed that the planning starts today and project development, planning an engineering will take approximately 5 years. So a cost calculation needs to be projected in the future from 2026 onwards.

6.1 Cost of carbon emissions and fuel cost

There are to relevant carbon cost, which will have an impact on the plant operation and its fuel cost. The first is the known carbon emission certificated traded in the European emission trading system (ETS) [156]. The price history is reviewable in the internet [17]. The price history of the ETS carbon pricing is shown in figure 6-1. Beside the EU ETS for Germany also the “new” national carbon pricing will get important especial for biomass, because the emissions related to biomass combustion are not included. The n actual legislation is now tackling all emissions not gathered by the EU ETS and so also emissions from biomass combustion from 2023 on [157]. The carbon price of the so called nEHS (**n**ationales **E**missions-**H**andels-**S**ystem) is with a fixed pricing step curve until 2025 and will also be free traded from 2026 onwards.

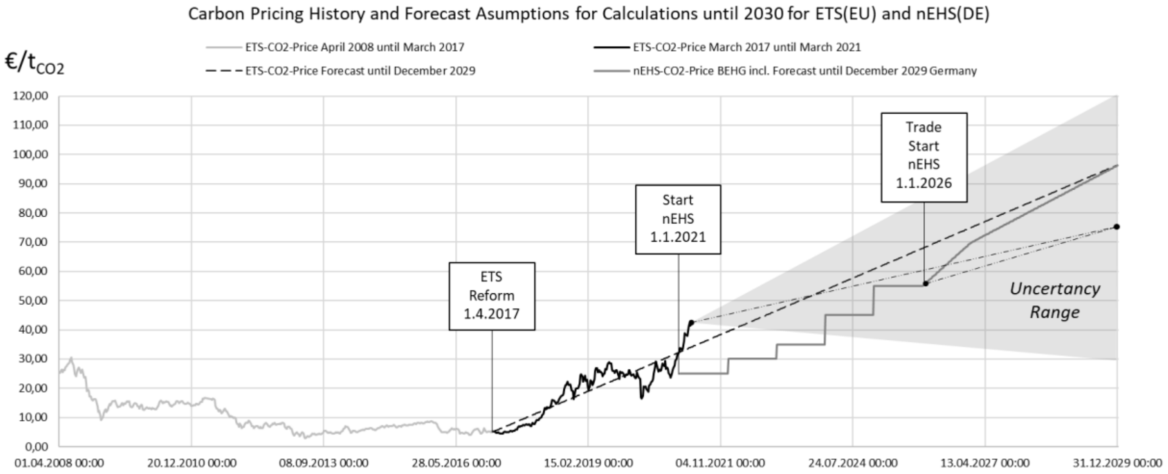

Figure 6-1: Price history and pricing scenarios of EU ETS and nEHS of Germany

This carbon pricing has an impact on the fuel prices as an add-on on their trade and handling pricing. The taken assumption is now that in 2025 the carbon price at the ETS and the nEHS is at 26 at average of 60 €/t and will rise until 2030 to 75 €/t for both markets. It is assumed and not legally clear today that the EDV of the biomass acc. to the RED II will be subject to the nEHS trade system, but this was taken here as one reasonable condition.

Mark Twain stated once that predictions are very difficult and especial if they are about the future and the author sometime has the feeling that computer tools for fuel price prediction are very expensive random number machines. Nevertheless assumptions have to be taken to give some ideas for an

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[17] https://ember-climate.org/data/carbon-price-viewer/

economic behaviour of an investment. For the price prediction some literature has been reviewed and it was concentrated on solid biomass and natural gas in the EU only [158]. The price history for both fuels were taken from the European Energy Exchange platform (EEX) [18]. The found scenario is shown in figure 6-2. Please recognise that for the biomass already future pricing is involved from future prices of the EEX platform.

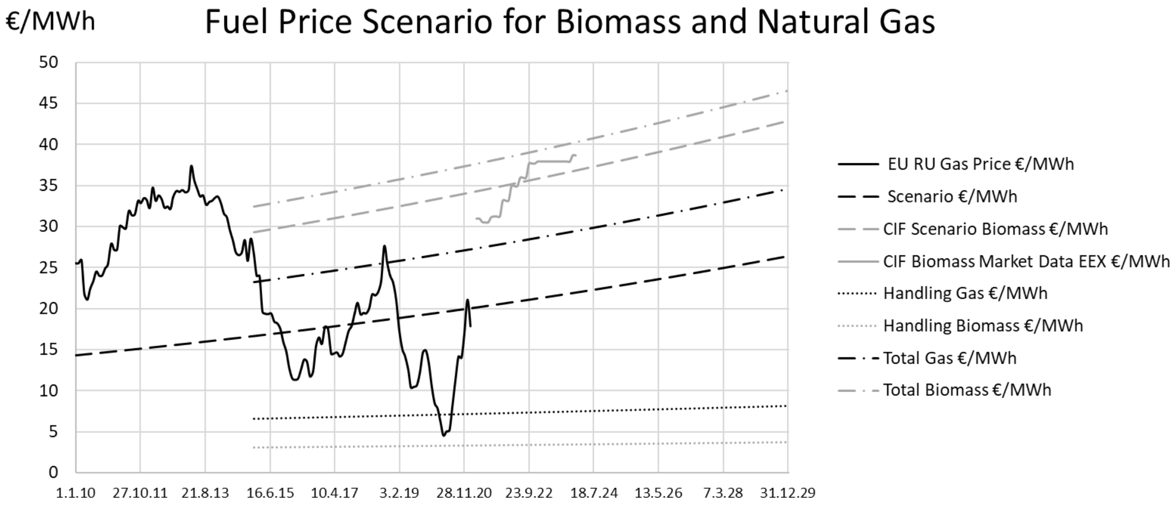

Figure 6-2: Price History and scenarios for natural gas and solid biomass (wood pellets)

These data have been checked for reasonability with some other literature and was found reasonable for the purpose [159, 160, 161, 162].

Once the fuel side has a developed pricing scenario, we need to have a look at the product side. Figure 6-3 is showing the trend of development on the EEX electricity pricing.

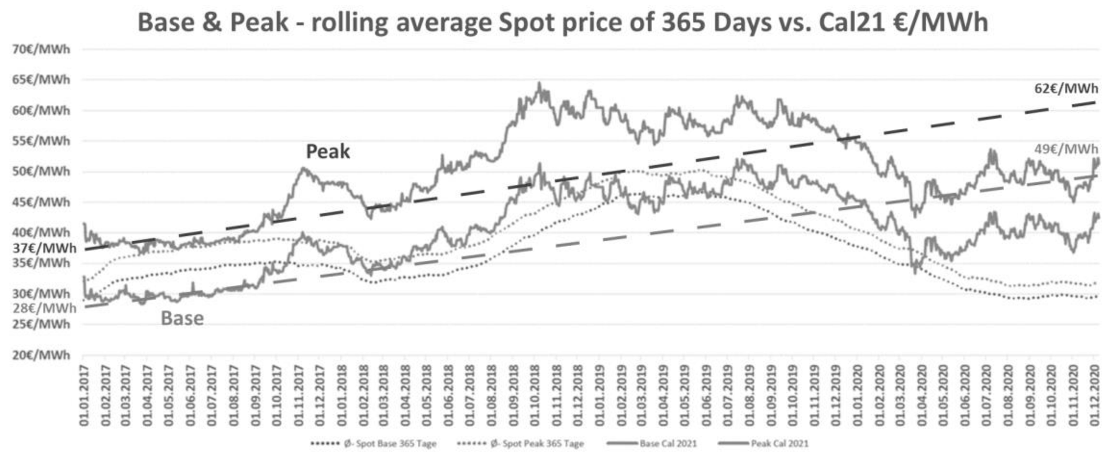

Figure 6-3: Price history of base load and peak power price 2017 until 2020

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[18] https://www.eex.com/de/

It is shown and the opinion of several specialists that the electric prices are rising [163] [19]. Due to the reason that the operation characteristic of such a described plant is closer to the peak power market for the working scenario chosen it is for 2025 assumed that the peak megawatt-hour can be sold in 2026 for 75 €/MWh. This means that the biomass peak power energy is valued on the higher end of assumed off-shore electricity cost at these days [164]. See for this also figure 6-4.

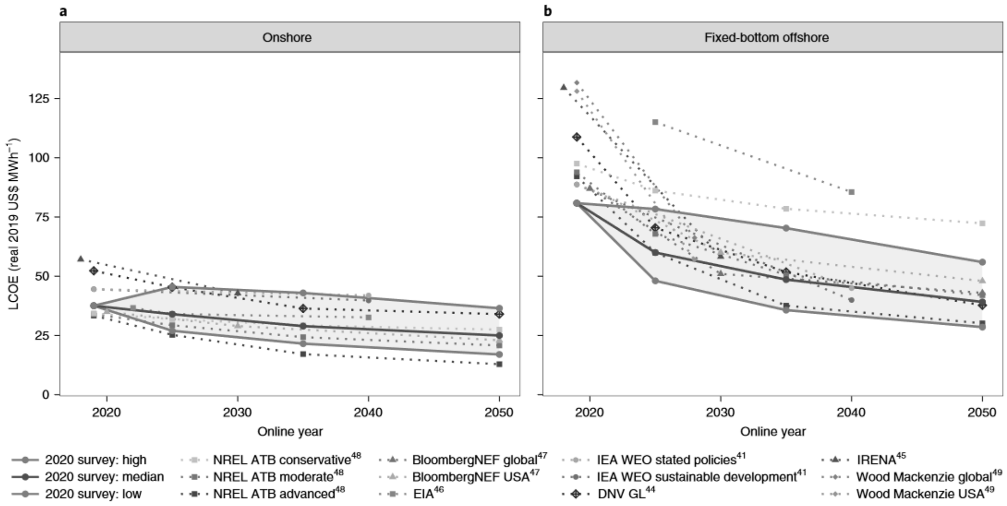

Figure 6-4: Price development expectation on future onshore and offshore wind energy prices

The levelized cost of utility scale solar power is according to the literature about similar values as the higher prices of the onshore wind [165].

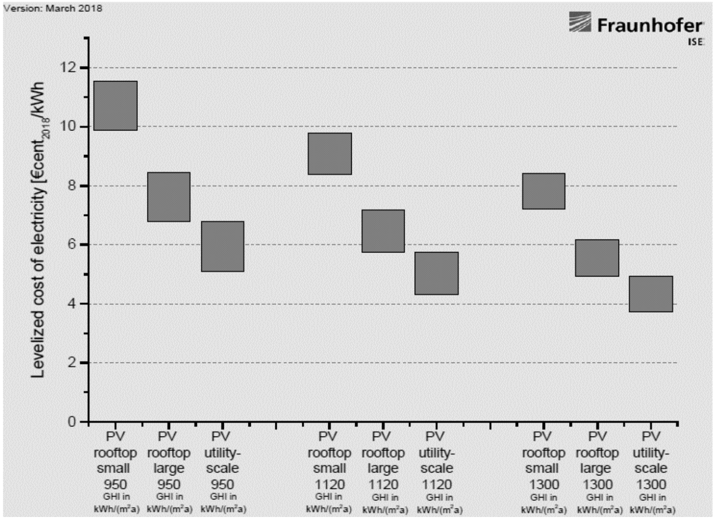

Figure 6-5: PV-LCOE in Germany

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[19] https://www.egt-energievertrieb.de/geschaeftskunden/energie-blog/details/news/energieeinkauf-unternehmen-spotmarkt-mittelfristig-vorteil

It shall be logical that a peak balancing pricing of energy is above the LOCE of the balanced technologies and so this assumption was taken and it correlates in the opinion of the author with the shown pricing development in the electricity market as shown in figure 6-3.

6.2 Fossil and renewable methanol pricing

The methanol price is taken from the published data of the company Methanex, which is publishing regular the long-term pricing for the EU market [20].

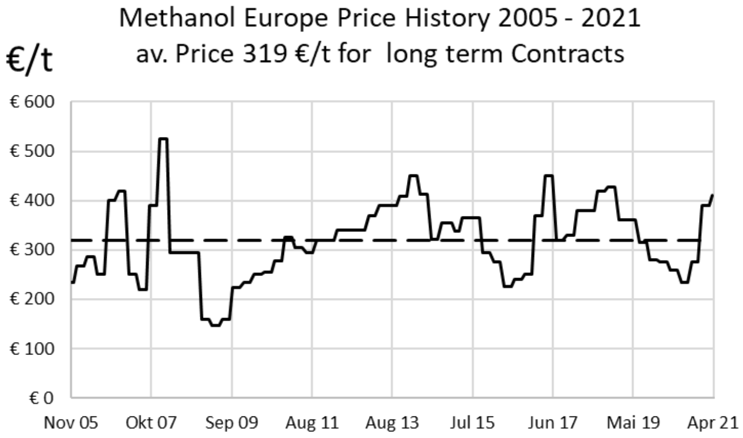

Figure 6-6: Methanex methanol price history

This price is of course for the fossil fuel-based methanol price. Additionally the price premium for renewable based fuels has to be considered. For Germany this premium pricing is basing on the law regulating emission in Germany, where in §37 a fuel penalty of 470 € per ton of carbon dioxide is written [166]. This penalty payment is necessary in the case the fuel distributor is not able to reduce the carbon footprint of the distributed fuel by 6% from the EDV of 94,1 g/MJ acc. to the RED II. From this value it can be calculated that a ton of penalty affected methanol mixed to the fuel has the maximum penalty value of additional 880 €/t of methanol. From this results that every ton of 100% certified carbon free methanol can reach a price of the market price plus a premium below this value multiplied by its carbon reduction value. The premium can be seen in the bioethanol and biodiesel market. For these also a merit order rule applies from which results the market pricing of carbon reduced fuels such as methanol. The pricing for the chemical market results as well from this fuel market, as any product follows the highest price option in the market. We come back to this in the economic discussion.

6.3 Pricing of steam as sales product

The costs of produced steam are general a function of the fuel cost. Here we take the assumption that the steam also can be supplied by natural gas steam boilers. This kind of boilers have usual an efficiency of 90%, have a specific investment of 150 €/kW and a maintenance ratio of 5 €/kW/year at an availability of 90%. From these values, as a rule of thumb, can be calculated down to the steam costs with the following formula.

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[20] https://www.methanex.com/our-business/pricing

$$Steam\ Cost\ NG\ [€/t] = (Nat.Gas\ plus\ CO_2\ Cost\ [€/MWh] \div 0{,}9 + 0{,}65\ €/MWh) \times 0{,}7\ [MWh/t]$$

Equation 6-1: Steam price calculation formula for steam from natural gas

The calculation for the steam from biomass is in principle similar but here usual an efficiency of 80%, have a specific investment of 450 €/kW and a maintenance ratio of 10 €/kW/year at an availability of 90%.

$$Steam\ Cost\ BM\ [€/t] = (Biomass\ plus\ CO_2\ Cost\ [€/MWh] \div 0{,}8 + 1{,}55\ €/MWh) \times 0{,}7\ [MWh/t]$$

Equation 6-2: Steam price calculation formula for steam from biomass

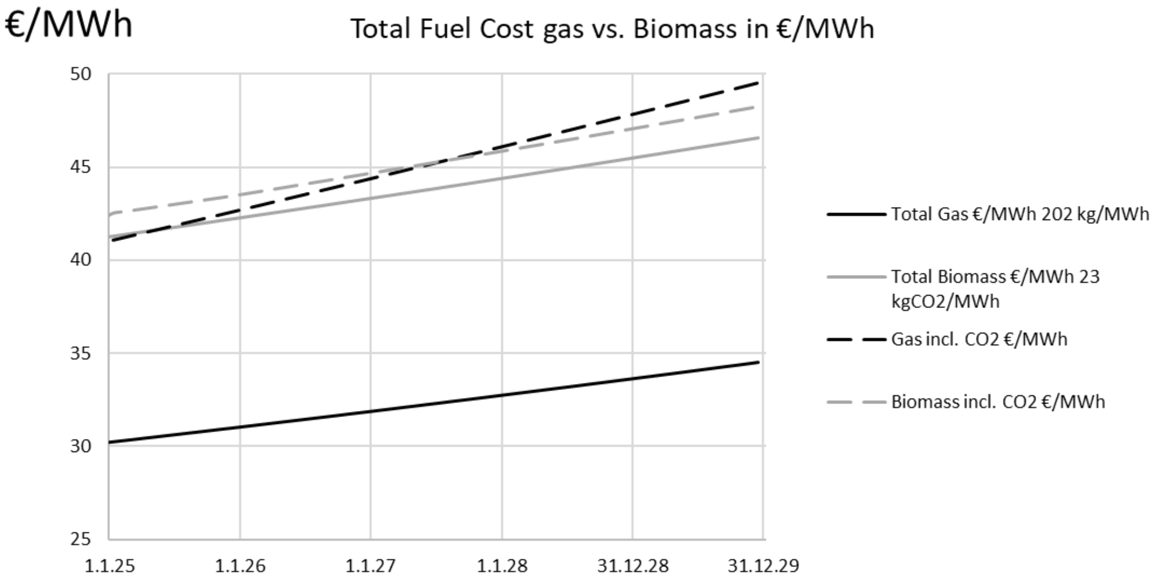

Figure 6-7: Concluding fuel cost for biomass and natural gas acc. assumption 2025 to 2030

From the values in the figure for 2025 concludes that the steam price is between 40 €/t and 48 €/t assuming a common overhead of 25% on the basic cost (Factor of 1,25). These are of course also values which can be discussed, but are the basis of this work.

6.4 Operating cost of example case

Beside the fuel cost in the operation of plant also occur other cost. These costs must be spitted in variable costs and fixed cost. In the following these costs are listed to the best knowledge of the author. The costs of chemicals are mainly taken from known internet platforms [21]. These costs are of course only pictures of the moment and need to be checked frequently.

Table 6-1 is showing the variable cost of the methanol production and it is listing all known consumption of the plant. As the main variable cost can be seen the maintenance, water, wastewater, solvent and sodium carbonate for solvent reclaiming. The consumed electricity is not listed here. The total value is 14,419 €/t of produced methanol.

Table 6-1: Variable cost of operation of the methanol plant expressed per ton methanol produced

Denomination	Item							EUR/h
	Unit	Value		MeOH				133,310
Methanol Production				t/h			EUR/MWh-LHV	EUR/t-MeOH
				9,245			2,61	14,419
Variable Maintanance	EUR/h	43	FL-OPH	8500	Firing	9,2	EUR/t-MeOH	4,67641
KOH Potassium Hydroxide	kg/h	0,5	kg/t-MeOH	0,05408	EUR/t	850,0	EUR/t-MeOH	0,04597
Potable Water from Potable Water Network	kg/h	12993	kg/t-MeOH	1.405	EUR/t	1,3	EUR/t-MeOH	1,82695
Waste Water Discharge	kg/h	4239	kg/t-MeOH	458	EUR/t	3,1	EUR/t-MeOH	1,42134
Lubricants	kg/h	0,75	kg/t-MeOH	0,08143	EUR/t	3.750,0	EUR/t-MeOH	0,30536
MEA - Ethanol Amine	kg/h	10,50	kg/t-MeOH	1,13570	EUR/t	1.500,0	EUR/t-MeOH	1,70355
Na2CO3 Sodium Carbonate	kg/h	53,60	kg/t-MeOH	5,79734	EUR/t	300,0	EUR/t-MeOH	1,73920
H2SO4 Sulfuric Acid (30%)	kg/h	6	kg/t-MeOH	0,64897	EUR/t	400,0	EUR/t-MeOH	0,25959
Nitrogen (N2)	kg/h	35	kg/t-MeOH	3,78188	EUR/t	48,0	EUR/t-MeOH	0,18153
Phosphorous Source (NH4)2-HPO4	kg/h	3	kg/t-MeOH	0,32449	EUR/t	900,0	EUR/t-MeOH	0,29204
Nitrogen Source NH4NO3 Ammonium Nitrat	kg/h	1	kg/t-MeOH	0,10816	EUR/t	500,0	EUR/t-MeOH	0,05408
Nitrogen Source CH4N2O Urea	kg/h	4	kg/t-MeOH	0,43265	EUR/t	250,0	EUR/t-MeOH	0,10816
Micronutrients	kg/h	6	kg/t-MeOH	0,64897	EUR/t	1.200,0	EUR/t-MeOH	0,77877
Caustic Soda NaOH 30 %	kg/h	15	kg/t-MeOH	1,62243	EUR/t	200,0	EUR/t-MeOH	0,32449
Polymer (FHM) - (Polyelektrolyte/Polyacrylamid/Polysaccharide)	kg/h	0,5	kg/t-MeOH	0,05408	EUR/t	1.400,0	EUR/t-MeOH	0,07571
CaCl2 Calcium Chloride	kg/h	1	kg/t-MeOH	0,10816	EUR/t	500,0	EUR/t-MeOH	0,05408
FeCl3 Iron(III) Chloride	kg/h	4	kg/t-MeOH	0,43265	EUR/t	500,0	EUR/t-MeOH	0,21632
HCl Hydrochloric Acid	kg/h	3	kg/t-MeOH	0,32449	EUR/t	450,0	EUR/t-MeOH	0,14602
Antiscalant (Polyelektrolyte, Phosphonate)	kg/h	0,2	kg/t-MeOH	0,02163	EUR/t	1.800,0	EUR/t-MeOH	0,03894
Chemicals for Membrane Cleaning	kg/h	0,1	kg/t-MeOH	0,01082	EUR/t	3.500,0	EUR/t-MeOH	0,03786
Na2S2O5 Sodium Metabisulfite	kg/h	0,2	kg/t-MeOH	0,02163	EUR/t	285,0	EUR/t-MeOH	0,00617
Solid Waste	kg/h	6,5	kg/t-MeOH	0,70305	EUR/t	180,0	EUR/t-MeOH	0,12655

The variable costs of the methanol production have been separated from the variable costs of the power plant because they are better expressed per ton of produced methanol than per megawatt-hour of fired fuel.

The other variable costs for the operation of the power plant and the heat pump bay are listed in following table 6-2. Main costs are here the high wastewater discharge cost and the variable maintenance. Compared to common steam power plants the wastewater discharge costs are much higher, as due to the water production in the flue gas cooler the waste water amount is rising significantly compared to standard operation. The total value is 1,263 €/MWh of fired fuel.

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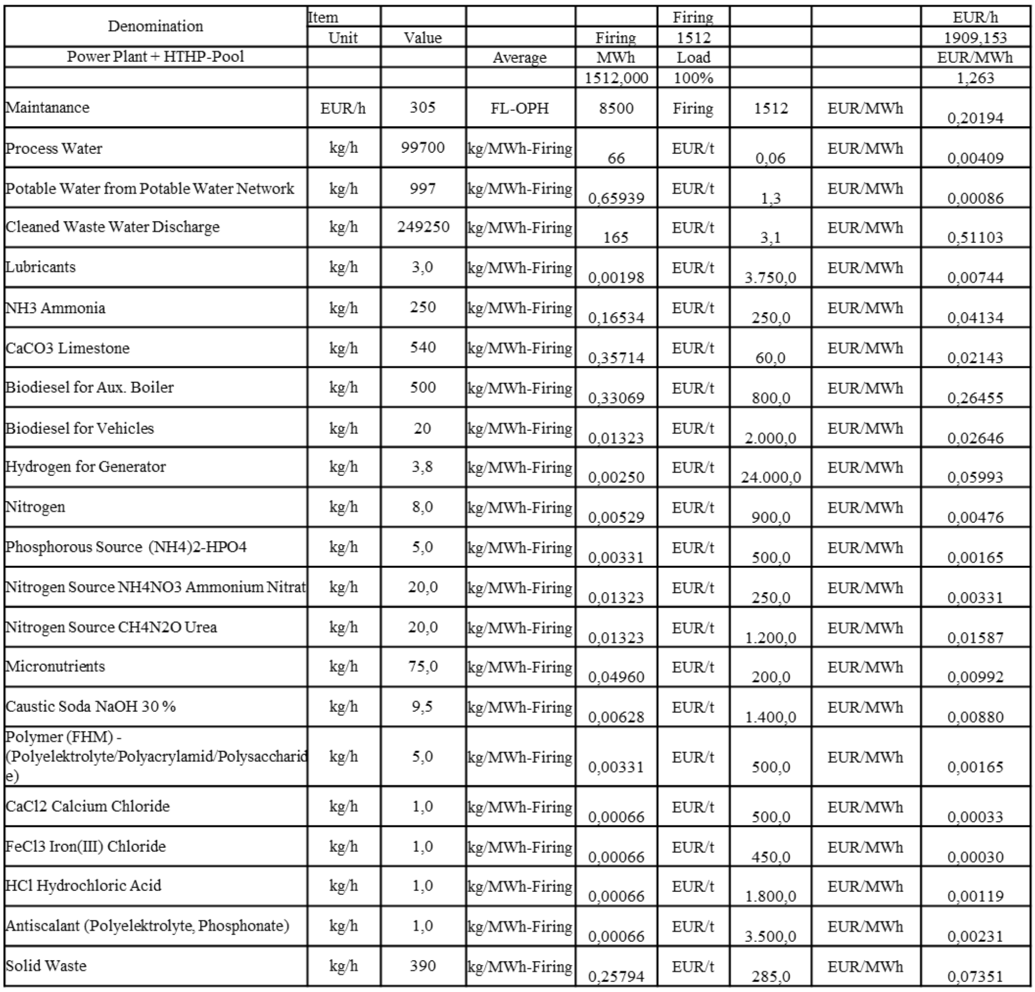
[21] https://www.alibaba.com, https://www.chembid.com

Table 6-2: Variable cost of operation of the methanol plant expressed per megawatt-hour fuel fired



Denomination	Item				Firing			EUR/h
	Unit	Value		Firing	1512			1909,153
Power Plant + HTHP-Pool			Average	MWh	Load			EUR/MWh
				1512,000	100%			1,263
Maintanance	EUR/h	305	FL-OPH	8500	Firing	1512	EUR/MWh	0,20194
Process Water	kg/h	99700	kg/MWh-Firing	66	EUR/t	0,06	EUR/MWh	0,00409
Potable Water from Potable Water Network	kg/h	997	kg/MWh-Firing	0,65939	EUR/t	1,3	EUR/MWh	0,00086
Cleaned Waste Water Discharge	kg/h	249250	kg/MWh-Firing	165	EUR/t	3,1	EUR/MWh	0,51103
Lubricants	kg/h	3,0	kg/MWh-Firing	0,00198	EUR/t	3.750,0	EUR/MWh	0,00744
NH3 Ammonia	kg/h	250	kg/MWh-Firing	0,16534	EUR/t	250,0	EUR/MWh	0,04134
CaCO3 Limestone	kg/h	540	kg/MWh-Firing	0,35714	EUR/t	60,0	EUR/MWh	0,02143
Biodiesel for Aux. Boiler	kg/h	500	kg/MWh-Firing	0,33069	EUR/t	800,0	EUR/MWh	0,26455
Biodiesel for Vehicles	kg/h	20	kg/MWh-Firing	0,01323	EUR/t	2.000,0	EUR/MWh	0,02646
Hydrogen for Generator	kg/h	3,8	kg/MWh-Firing	0,00250	EUR/t	24.000,0	EUR/MWh	0,05993
Nitrogen	kg/h	8,0	kg/MWh-Firing	0,00529	EUR/t	900,0	EUR/MWh	0,00476
Phosphorous Source (NH4)2-HPO4	kg/h	5,0	kg/MWh-Firing	0,00331	EUR/t	500,0	EUR/MWh	0,00165
Nitrogen Source NH4NO3 Ammonium Nitrat	kg/h	20,0	kg/MWh-Firing	0,01323	EUR/t	250,0	EUR/MWh	0,00331
Nitrogen Source CH4N2O Urea	kg/h	20,0	kg/MWh-Firing	0,01323	EUR/t	1.200,0	EUR/MWh	0,01587
Micronutrients	kg/h	75,0	kg/MWh-Firing	0,04960	EUR/t	200,0	EUR/MWh	0,00992
Caustic Soda NaOH 30 %	kg/h	9,5	kg/MWh-Firing	0,00628	EUR/t	1.400,0	EUR/MWh	0,00880
Polymer (FHM) - (Polyelektrolyte/Polyacrylamid/Polysaccharide)	kg/h	5,0	kg/MWh-Firing	0,00331	EUR/t	500,0	EUR/MWh	0,00165
CaCl2 Calcium Chloride	kg/h	1,0	kg/MWh-Firing	0,00066	EUR/t	500,0	EUR/MWh	0,00033
FeCl3 Iron(III) Chloride	kg/h	1,0	kg/MWh-Firing	0,00066	EUR/t	450,0	EUR/MWh	0,00030
HCl Hydrochloric Acid	kg/h	1,0	kg/MWh-Firing	0,00066	EUR/t	1.800,0	EUR/MWh	0,00119
Antiscalant (Polyelektrolyte, Phosphonate)	kg/h	1,0	kg/MWh-Firing	0,00066	EUR/t	3.500,0	EUR/MWh	0,00231
Solid Waste	kg/h	390	kg/MWh-Firing	0,25794	EUR/t	285,0	EUR/MWh	0,07351

Coming from the fixed cost of the plant we now have to define the fixed costs. Here also some literature was used, which had also some influence on the variable cost of the power plant [167]. In this cost one can find also fixed maintenance cost as e.g. coming from long term service agreements or from provisions for catalysts exchange. The other costs are for staff in operation, administration and security, provisions for retrofits leasing and rent fees and costs for the notified bodies as well as the fire brigade. These costs sum up to 24.207.100 € per year. The details are listed in table 6-3.

All costs are also a topic to the inflation and the inflation ratio is set to 1,015 (1,5% per year). This value is used in the net present value calculation. The discount factor for the net present value calculations is set to 4%. This is a moderate value representing the earning of capital in the stock market. The price increase per year for biomass, methanol power and steam are set to 2,4% while acc. to the discussed literature the price increase for natural gas is set to 4,3%. These costs for fuel include already the carbon pricing cost as discussed front-up.

Table 6-3: Fixed cost of the entire plant

Denomination	Item					
	Unit	Value		a = Year		EUR/a
Fixed Cost both Plants						24.207.078
Administration	pc.	25	Wage per Pc.	95.000	EUR/a	2.375.000
Operating Staff	pc.	70	Wage per Pc.	85.000	EUR/a	5.950.000
Fix Maintanance Staff (LTSA´s etc.)	% Invest	0,35%	EUR Invest	951.519.900	EUR/a	3.330.320
Insurance and property tax	% Invest	0,40%	EUR Invest	951.519.900	EUR/a	3.806.080
Loan Loss Provisioning for Retrofits (incl. Cat & AEL-Stacks)	% Invest	0,45%	EUR Invest	951.519.900	EUR/a	4.281.840
Leasing and Rent fees	EUR	150.000	[-]	150.000	EUR/a	150.000
Loan Loss Provisioning for Dismanteling (HTHP & MeOH only!)	% Invest	0,55%	EUR Invest	438.879.900	EUR/a	2.413.839
Security Staff	pc.	20	Wage per Pc.	50.000	EUR/a	1.000.000
Fire Brigade	EUR	150.000	[-]	150.000	EUR/a	150.000
Notified Body Monitoring Costs (TÜV)	EUR	750.000	[-]	750.000	EUR/a	750.000

6.5 Capital expenditure cost (CAPEX)

Having now set the main operating cost we need to define the capital expenditure cost for the entire plant from the already calculated necessary investment costs. The assumption taken here are discussed in the following. The equity share is 25% with an interest rate of 12% and a payback time of 4 years. The debt share is 75% with an interest rate of 2,3% and a payback time of 15 years. The repayment of the equity starts in year 1, while the repayment of the debt starts after four years. The plant depreciation in the balance sheet is within 20 years.

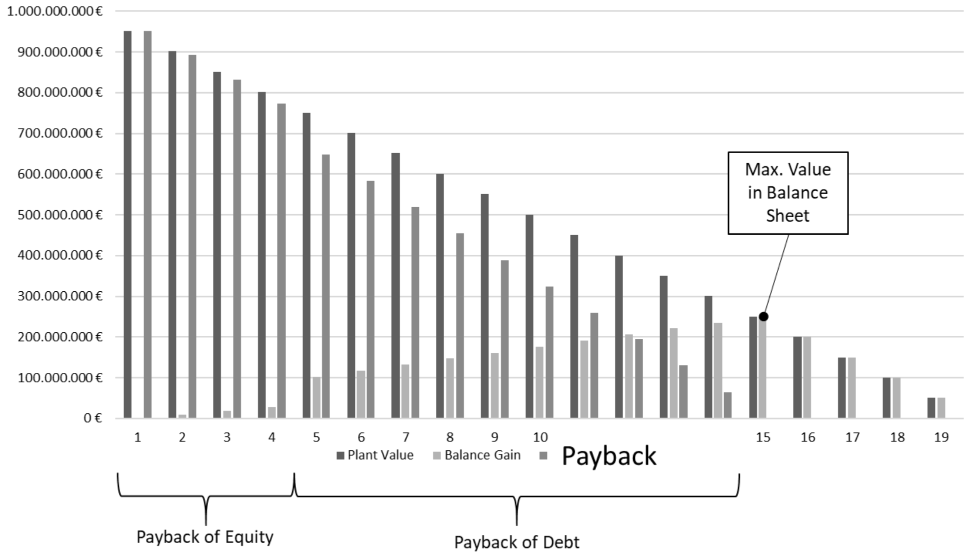


Figure 6-8: balance sheet development model for discussed economic calculations

This leads to a total annual payment of 104.429.309 €/year in the years 1-4 and to a total annual payment of 109.835.672 €/year in the year 5 dropping to a total annual payment of 94.914.110 €/year in the year 15. While this period of 15 Years the balance sheet gain will be 250.399.974 €. Please see also figures 6-8 and 6-9 for the support.

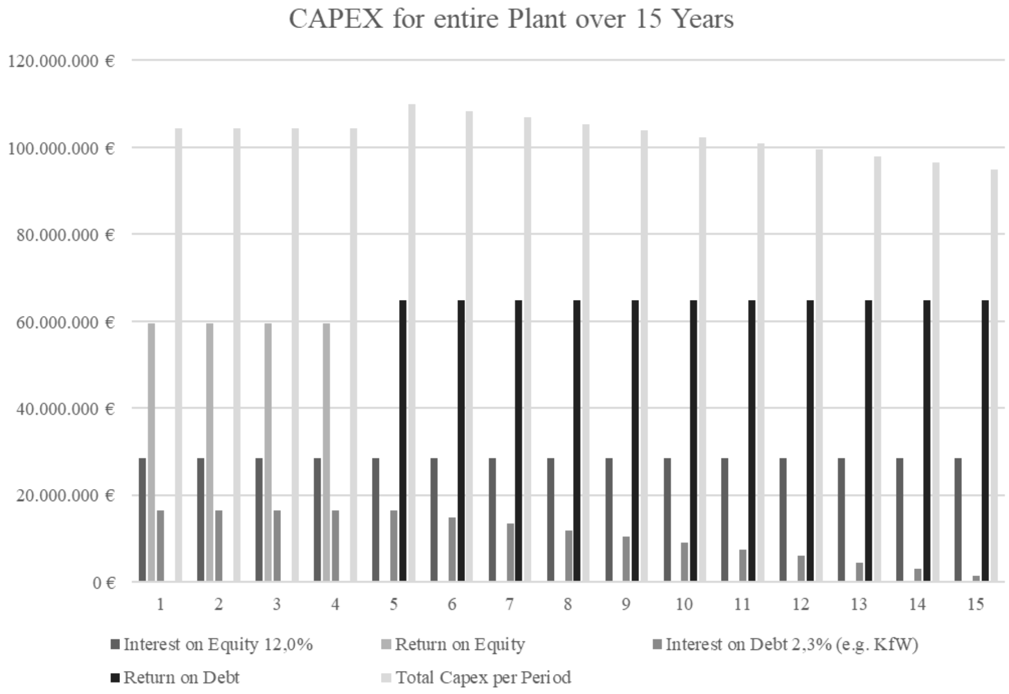


Figure 6-9: Split of the CAPEX cost payments over the full 15-year period

It was chosen to use this payback model to make the investment figures attractive for the direct investors with a high interest rate and a shore payback period. For the investment in a new and technology as Power to X it was assumed that this will be supported by the government. This is not expressed in a direct capital support, but in the low interest rate for the debt. The 2,3% were chosen, because at that value for the used figures for the net present value, the government would have no losses on their money and keep the investment without any loss for the tax payer.

It is obvious that the investors interest payments are constant all the times at 28.545.597 €/year. This is expressing the intention of the investors to operate the plant for a long time with the expectation for constant earnings and is in a mathematical way not correct. This can be used in the later discussion of the sensitivity of the investment.

This payback strategy is very aggressive and also could be discussed more moderate. Having a more moderate strategy the annual payment on capex payback could be at 82.957.841 €/Year. This is also with an equity share of 25% at an interest rate of 10% and a payback time of 20 years, while the debt is with a share of 75% with an interest rate of 5% and also with a payback time of 20 years. This is a possible or better optional reduction by more than 20% as a fall-back position. This will be also part of the discussion of the business case.

6.6 Business case economic calculations

With these assumptions on the cost side and the income side we can develop the balance of income and cost for the plant. The consumption and production values come from the operation analysis made in chapter 4 incl. three weeks of standstill in summer. The balance is listed in table 6-4. It can be assumed that the consumption and production are more or less very similar to equal each operational year.

Table 6-4: Income/cost balance for the first operational year

BALANCE (Y1)	Unit	Value/Year	EUR/Unit	2025 (Year 1)
Capital Cost				104.429.309 €
Fixed Cost				24.207.078 €
Fuel Cost BM	MWh	8.645.289	42,5	367.424.797 €
Fuel Cost NG	MWh	280.868	41	11.515.605 €
Var MW-firing	MWh	8.926.158	1,26	11.270.770 €
Var MeOH	t	76.163	14,4	1.098.203 €
Total				519.945.762 €
Steam	t	10.121.232	42,0	424.787.025 €
Power	MWh	759.872	75,0	56.990.399 €
Methanol	t	76.163	510	38.843.200 €
Total				520.620.624 €
Balance in €				674.863 €
Balance in % of Equity				0,28%

With this data also a net present value can be made for 15 years and the result is shown in figure 6-10. In addition, it must be seen that an additional earning is the gain in the balance sheet, which is positive for the company value as well.

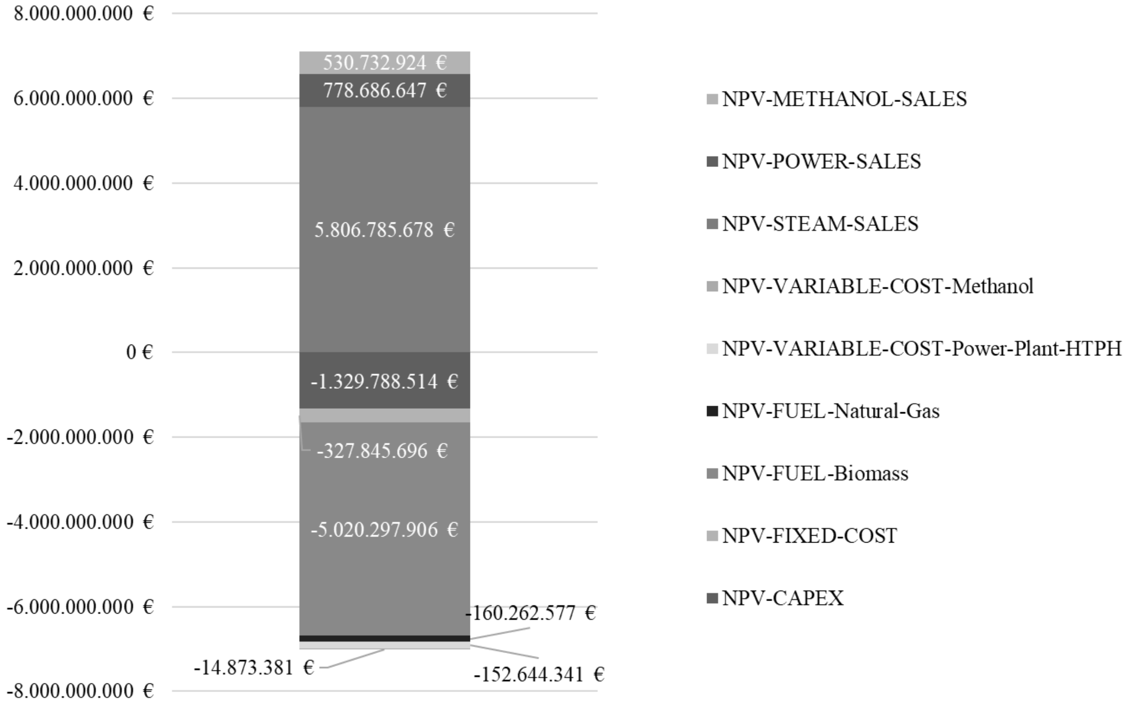


Figure 6-10: Net present value analysis of 15 years with the balance of table 6-4

Of course, the economics are not static and certain and so it has to be looked in the sensitivity of this business case, what is done in the following sub-chapter. The calculation method is assumed to be familiar to the reader and is taken from common economic literature [168].

6.7 Economic sensitivity

For this sensitivity analysis several values have be varied to find out about the impact on the business case. This was done in the balance of one year as shown in table 6-4. The effect of CAPEX variation is permanent and others will have only a temporary impact as e.g. from variations on fuel or power prices. The result is shown in figure 6-11. The diagram also includes two comparison lines, where one is shift of the annual CAPEX cost payment to the moderate scenario and the other one is the line, where the equity investors renounce on their interest rate payments, but not on any payback. This second comparison shall be for the option that in a year of crisis investors might reduce their expectation for a short period.

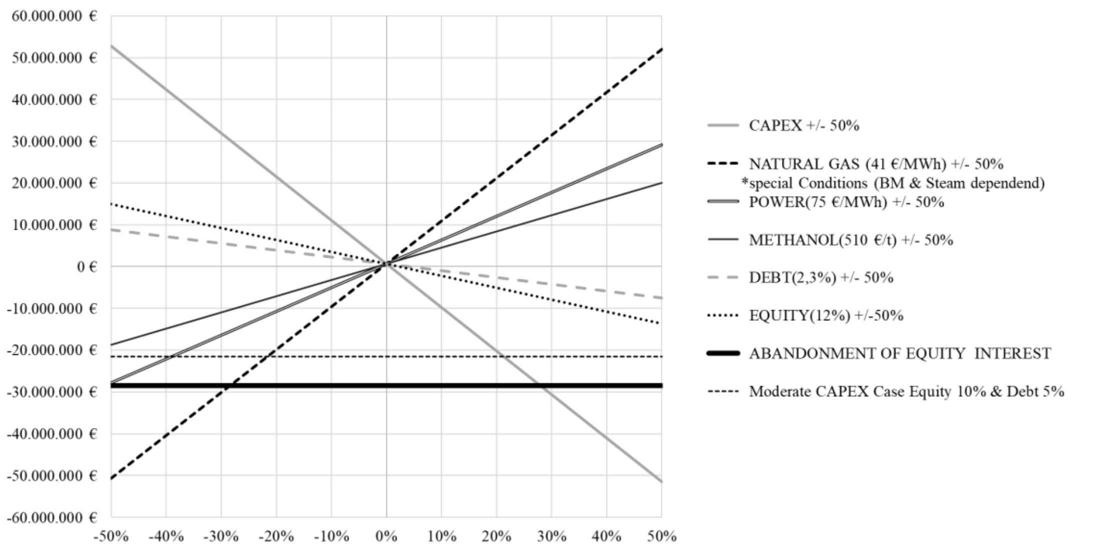


Figure 6-11: Sensitivity analysis of the chosen business case

The sensitivity is showing more or less expected results. A rise in the capital expenditure (CAPEX) as the permanent effect is dropping the reachable income from the investment, but it can be seen that an overrun of 20 % or about 190.000.000 € can be covered if the investors go to a more moderate scenario, which also covers that no state financing is available. Such a capital expenditure overrun can be avoided by a good planning of such a project and the risk can be widely mitigated.

The variations on the product sales side, which are expected to be only of temporary nature, always can be covered by an also temporary renouncing of the investors on their interest and this is more or less a common part of business. A rise for the debt interest rate can be covered by a drop in the investors interest expectations and also this is a part of the standard project development procedure.

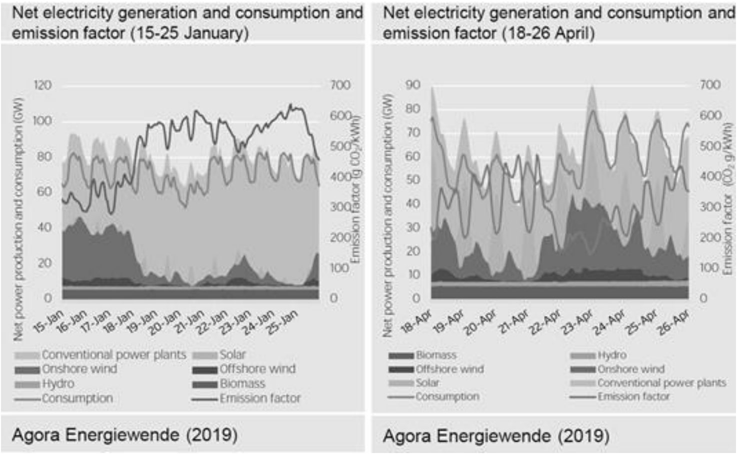
The most interesting effect is that the fuel side is strong sensitive to low natural gas pricing. Here are more effects expected, which are bound to each other. If the natural gas price drops also the biomass pricing is expected to drop and at the same time the income from the steam sales will drop, as the steam price is bound to the fuel pricing. Here now the effect takes place that any highly efficient but also high-price investment is getting in trouble, because of the fact that than the production is getting more and more dependent on the needed capital expenditure.

This is not new. Always in history low fuel prices favoured less efficient technologies and so it can be stated that this is more a political issue. In today´s world with its climate change, energy and especial low carbon energy is driven by political boundary conditions. Low carbon technologies are always depended on governmental help, either in financing or in legal boundary condition. One of this boundary conditions is to rise the fuel pricing as e.g. done political by the carbon certificates fee of the European emission trade system (ETS).

There is no mitigation option of the investors on this side, but having a today´s view on Germany and the EU with the actual legislation and jurisdiction the author is positive about this. The EU passed the new and ambitious act on climate action [22] and in Germany the climate policy is forced by the Federal Constitutional Court (Bundesverfassungsgericht) to review their policy until 2022 to be more social equal with the future generations [23]. Having this trust in policy we shall discuss the conclusion for this technology in the final chapter.

6.8 Discussion of additional benefits for the electricity generation system

Refurbishment of the electric grid at all levels is necessary in the future to serve the necessary flexibility of the grid [169]. The analysis of the renewable power generation in the grid shows that high flexibility is needed [170]. The use of biomass more or less in baseload in the power market also cannot be the best use of its value for the energy change. These points are very good expressed in the following figure.



Net electricity generation and consumption and emission factor (15-25 January)

Net electricity generation and consumption and emission factor (18-26 April)

Agora Energiewende (2019)

Agora Energiewende (2019)

Figure 6-12: To time periods with a) low and b) high renewables in the grid

The proposed plant is flattening flexible renewable generation to a 200 MW base load power with low carbon footprint and is constantly supplying heat and fuel also with low carbon footprints. In cases the gird needs more power as in this base-operation the plant has the capacity to deliver 200 to 240 MW more electricity by ramping up to 100% firing and reducing the methanol production to either 50% or even zero. This can be supplied in the speed needed for primary and secondary control energy. Sizing-up the methanol production part also the negative control capacity can be extended. This makes the plant interesting in many ways: For the highly efficient use of biomass, for methanol production with low carbon footprint and for flexibility in power production.

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[22] https://ec.europa.eu/clima/policies/eu-climate-action_en

[23] https://www.bundesverfassungsgericht.de/SharedDocs/Pressemitteilungen/DE/2021/bvg21-031.html

7 Conclusions

Today´s companies operating coal fired power plant of an age of less than 30 years are hit hard by the political developments of the past. The here shown technique is giving an option to a second life of solid fuel fired steam power plants, which is today a serious topic in the EU with their program "Re-purposing Coal Power Plants during Energy Transition" [24].

7.1 Future usability of the power plant integration concept

As shown in the thesis the technique is capable to be economically be operated today and in the future. As the used example is a combined heat and power plant for process steam generation it is a good option for many plants operated in refineries or chemical parks, but it is not limited to such plants. The principle can also be transferred to district heat power plants as e.g. the in the begin mentioned power plant of Avedoere, but as well e.g. power plant Moorburg in Hamburg. Due to the reason that such a power plant with the integration of heat pumps and methanol production has a higher heat output due to its higher heating value use and energy efficiency, it can also avoid the operation of a second block as it is today the case in the two mentioned sites. The principle also is not limited to methanol. It could either also only produce hydrogen, or as well methane or via methanol other fuels and chemicals as dimethyl ether, gasoline or kerosine.

Extending the common understanding of combined heat and power it can be shown, that the technique is capable to reach a more than 14% reduction of primary energy, so even if only a low carbon fossil fuel as natural gas is used, or another fuel mix from coal, natural gas and biomass, with a carbon footprint comparable to natural gas, the overall carbon emission balance is positive for this triple generation.

In all this in addition the technique is strongly supporting the flexible production of electricity and so the technique is the perfect partner to the fluctuation renewable electric energy sources as on- and off-shore wind and photovoltaic solar generation.

It is of course obvious due the resource limitation of sustainable biomass the technique is no silver bullet for the generation of everything, but for sure it can also help to use the source biomass more efficient. As shown the average annual fuel utilisation is more that 90% and reviewing the energy balances of e.g. Germany [25] the today´s utilisation of the biomass for heat and power generation is far away from this point. Today´s utilisation of biomass is less than 40% and as also obvious from figure 6-12 its electric generation is mainly used in base load. This solution gives an option to biomass to be used highly efficient and supporting the generation with necessary control electric generation.

The described possibilities in the cost reduction in the electric hydrogen generation will even do its own work in future as discussed it will not lead to a better fuel utilisation, but understandable it will lead to the fact that the needed capital expenditure will drop and support the business case.

The same counts for the integrated heat pump bay for higher heating value use. Starting investments in large scale high temperature heat pumps will lead to a price drop of the compressors and the design standardisation will in the opinion of the author lead to a drop of more than 30% in the needed capital expenditure.

The use of higher efficient carbon capture systems as e.g. the mentioned KM-CDR® process of Mitsubishi gives the possibility to shift the fuel efficiency of the entire process more to the electric use side, what gives as well a small but important energy saving gain for the primary energy savings.

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[24] https://www.recpp.eu/ (Grant Agreement number: 899512 – RECPP – RFCS-2019)

[25] https://www.ag-energiebilanzen.de/, (Energy flow diagram 2019)

Summing up the possible developments to cost savings the capital expenditure can be dropped by more than 100.000.000 € for the described case and for sure the retrofit of newer power plants as the one used in the example are possible also for less than 30% of the new-build-cost. I the opinion of the author this gives the technique a high potential in the future.

7.2 Comparison with other "green" methanol generation cost scenarios

In the already mentioned MefCO2 research project an economic investigation was made for the "green" generation of methanol and its cost (figure 7-1). Reviewing these findings, it is clear that the generation via the described case is more cost efficient. In the described business case, a methanol price of 510 €/t was assumed. In the findings of the MefCO2 project this only can be reached as well by either nuclear or hydro generation of electricity. The biomass case there is much higher estimated, with a minimum generation cost of approx. 800 €/t. This identifies the technique as a high potential green methanol source with a better economic potential.

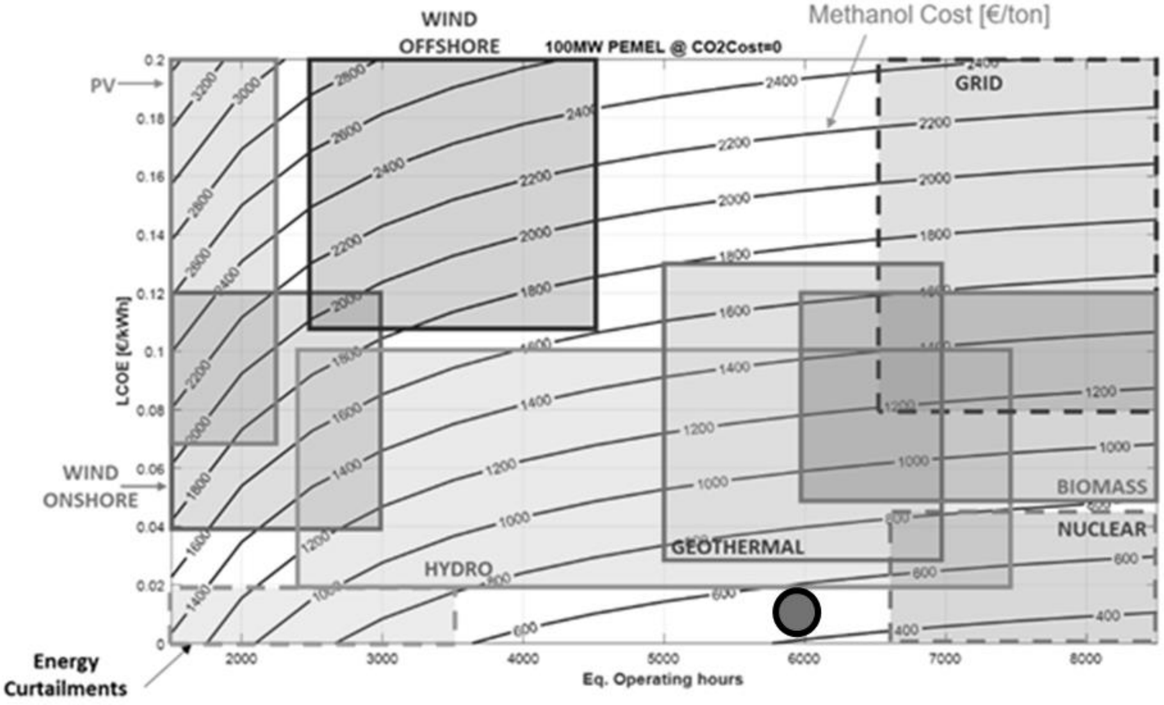


Figure 7-1: Economic findings in MefCO2 on methanol generation cost from low carbon electricity

7.3 Conclusion for other hydrogen and carbon dioxide sources

As shown in figure 5-10 it is obvious that an alkaline electrolysis in the described plant can be easily exchanged by an chlor-alkali electrolysis gaining the same advantages in the combined generation. This has the advantage that in several possible sites for such an installation one of the main investments is already taken.

As well is from the same chapter 5 obvious that using biomass for pure power generation needs absolute low carbon biomass, which is usual not available in large amounts as described before. This concluded to the fact, that biomass in not a good source, if it is used without combined generation.

It is as well shown that methane pyrolysis as hydrogen source needs as well as possible low carbon electricity sources, but if those are available it is a good hydrogen source for low carbon methanol generation.

This count as well for “blue” hydrogen based on steam methane reforming with carbon capture and storage, but the past showed that this has its challenges in the public acceptance produced in Europe.

For the alternative carbon sources it can be stated that the described sources are all workable for such low carbon methanol generation without major changes in the process, but of course here is the option for the cogeneration only given for the waste to energy case, because it is in basis a steam power plant as well.

7.4 Future work

From the conclusion mentioned above it is clear that also a lot of future work can be done in this field. To fulfil e.g. the options for the capital expenditure reduction alone several research options are open to reduce costs on the triple generation. These shall be due to their major impact the cost reductions for the alkaline electrolysis, discussed in chapter 2, and the cost reduction on heat pump compressors for industrial heat generation, of course including sub-systems of the heat pumps. In this course also the mentioned usage of chlor-alkali electrolysis for the combine generation is a cost saving alternative to be discussed.

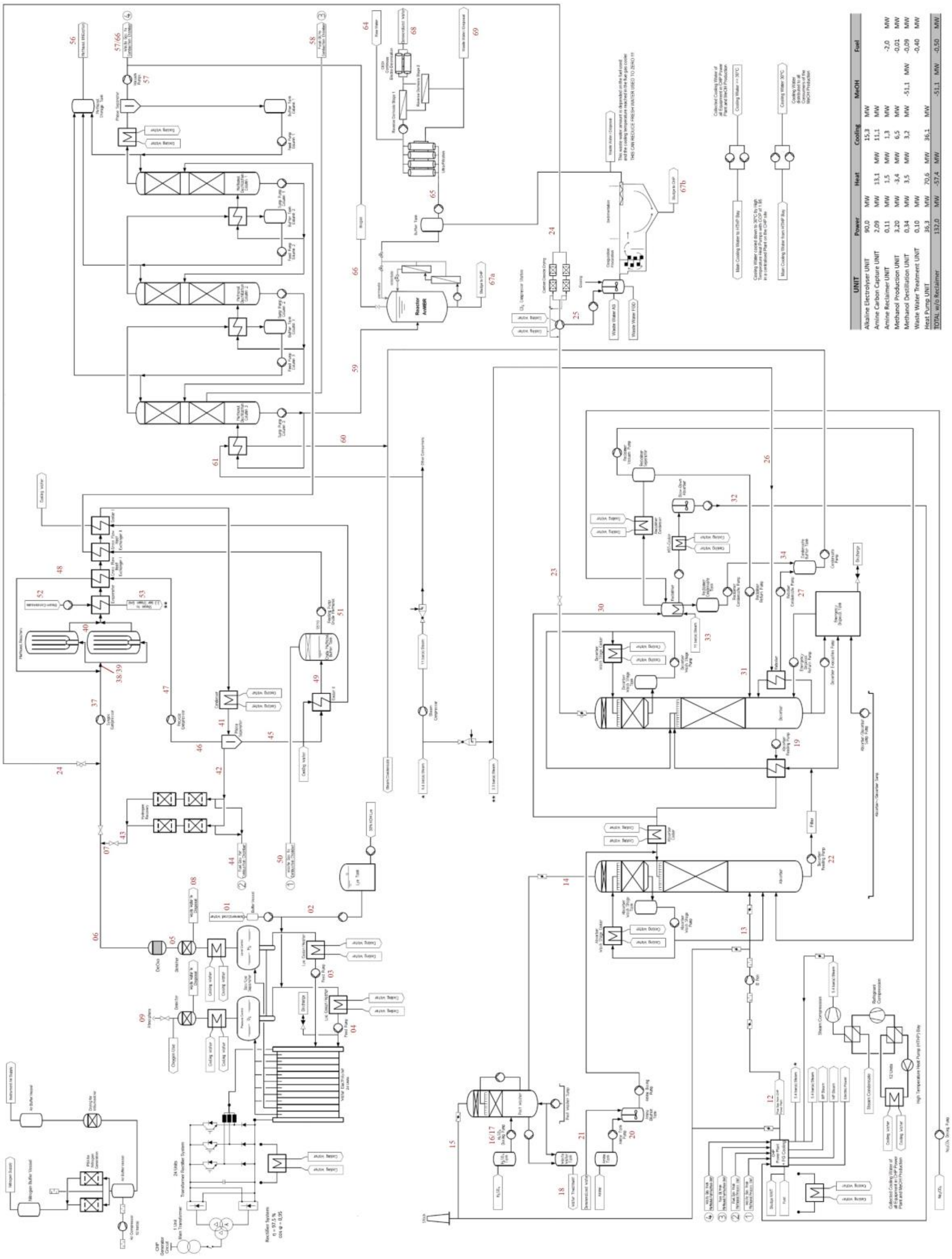
Also the operational expenditure must be deeper investigated in execution more variations for the main energy consumers, which are the electrolysis and the carbon capture unit, which both are available with better efficiencies, but then restricted to selected suppliers, which was avoided in this thesis. This work must be executed recursive with the capital expenditure optimisation mentioned above.

It is also techno-political important and necessary to put more efforts in the carbon footprint analysis of the overall process. The here started discussion only can be an ethereal flame of wider discussion which needs to lead finally to a certification of the calculation approach with the used extended Finish method. Therefore, the discussion between industry, science, notified bodies and the authorities has to be initialised and finalised. This will be essential for the technology usage.

Last but not least it is also necessary to investigate more deeper techno-economical on the business case options still hidden in the technology. Further investigations shall include more control electricity generation and the options of the use of the technology in smaller cogeneration plant as e.g. waste to energy plants or other similar. Also the relative up-sizing of the methanol generation plant must be investigated to find the real optimum size corresponding to the steam generator size. All in all a lot of techno-economical questions raised here, where it was not possible to discuss all of them.

8 Attachments

8.1 Attachment A: Process Flow Diagram Methanol Process



UNIT	Power		Heat		Cooling		MeOH		Fuel	
Alkaline Electrolyser UNIT	90,0	MW			15,3	MW				
Amine Carbon Capture UNIT	2,09	MW	13,1	MW	11,1	MW				
Amine Reclaimer UNIT	0,11	MW	1,5	MW	1,3	MW			-2,0	MW
Methanol Production UNIT	3,20	MW	-3,4	MW	6,5	MW			-0,01	MW
Methanol Destillation UNIT	0,34	MW	3,5	MW	3,2	MW	-51,1	MW	-0,09	MW
Waste Water Treatment UNIT	0,10	MW							-0,40	MW
Heat Pump UNIT	36,3	MW	70,6	MW	36,1	MW				
TOTAL w/o Reclaimer	132,0	MW	-57,4	MW			-51,1	MW	-0,50	MW

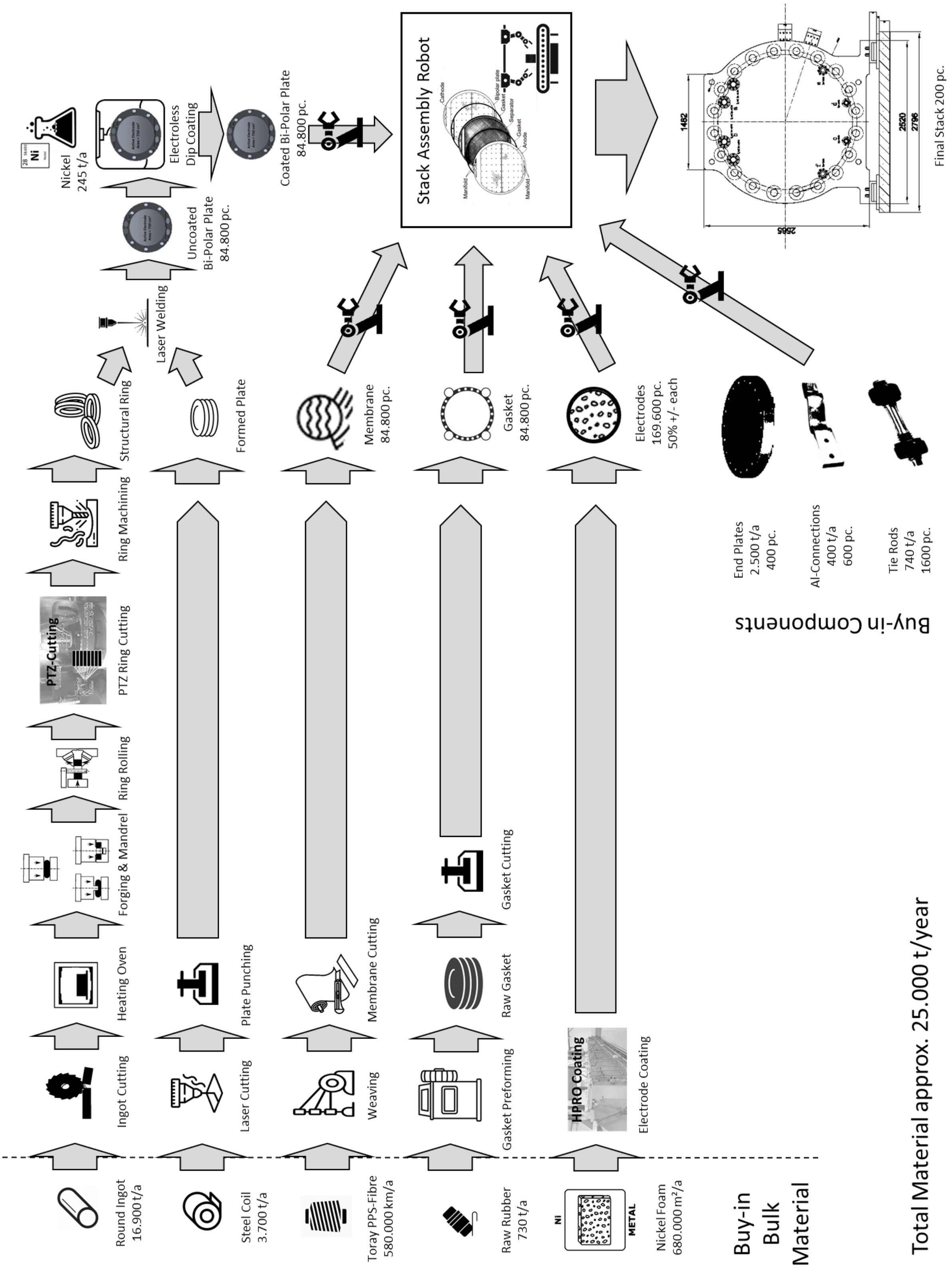
8.2 Attachment B: Mass Balance of the Process

Alkaline Electrolyser UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
Demin Water to AEL	S2110	01	5	25	liquid	kg/h							15.871,9							see Comment	VGB-S-010-T-00;2011-12
KOH Lye to AEL	S2115	02	5	25	liquid	m³/h							0.0					0.0			85°C operattion temperature of AEL
KOH Lye on H2-Side	S2117	03	32	79.9	liquid	m³/h							122.0					52.0			Flow per AEL unit of 24 units with 824 Nm³/h
KOH Lye on O2-Side	S2118	04	32	79.9	liquid	m³/h							122.0					52.0			Flow per AEL unit of 24 units with 824 Nm³/h
Hydrogen from AEL	S2120	05	30	40	gaseous	Nm³/h			19.747,3	39,5	1,8		2,1					traces		Oxygen	70,02 MW(HHV); 87,02 MW(DC); 89,25 MW(AC)
Hydrogen after DeOxo	S2150	06	30	46	gaseous	Nm³/h		traces	19.852,5	4,6	1,8	0,001	71,9							Oxygen	Water Loss from Condesation
Hydrogen from Recovery	S2125	07	30	44,9	gaseous	Nm³/h	0,01	0,01	175,1		0,002	0,001	0,0								
Wastewater from AEL (disposal)	S2140	08	30	40	liquid	m³/h							0.8					0.0			Attention: "high D2O content"
Oxygen from AEL	S2130	09	30	40	gaseous	Nm³/h			34,6	9.873,6	0.9		1.1								
CW in	S2001	10	7	30	liquid	m³/h							1.328,4								
CW out	S2002	11	6	40	liquid	m³/h							1.328,4								15,3 MW cooling (90% recovery)
Amine Carbon Capture UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
FG from CHP-PP	S3110	12	1,01	37	gaseous	Nm³/h		15.348,3		5.116,1	75.718,2		6.139,3							SO2, NOx, FH, HCL	uncritical for PCC process: 15 % CO2
FG after ID-Fan	S3210	13	1,15	40	gaseous	Nm³/h		15.348,3		5.116,1	75.718,2		6.139,3								
FG after Absorber	S3310	14	1,05	40	gaseous	Nm³/h		2.302,2		5.116,1	75.718,2		6.139,3								
FG after Afterscrubber (AS)	S3320	15	1	41	gaseous	Nm³/h		2.302,2		5.116,1	75.718,2		6.462,2				traces				
H2SO4 to AS (50wt%)	S3321	16	1	25	liquid	m³/h											1,0				
Water to AS	S3322	17	1	25	liquid	m³/h							1-2								Potable Water
Waste Water from AS	S3323	18	1	40	liquid	m³/h											2-3		Floculant		
Amine Solvent Flow to Absorber (lean)	S3230	19	1,1	120	liquid	kg/h							67.930,7		27.433,6	15.733,4				HSS; NH3 ; TVOC	Dry: NH3 < 0,3 mg/Nm³ ; TOVC < 0,5 mg/Nm³
Pure Amine Make-up	S3232	20	1,2	25	liquid	kg/h									10,5				<<2%		Dosing for anti foaming
Demin Water to PCC	S3234	21	1,5	25	liquid	kg/h							24,5								
Amine Solvent Flow to Desorber (rich)	S3236	22	1,5	43	liquid	kg/h							67.930,7		18.298,9	31.457,0				HSS; NH3 ; TVOC	
CO2 from Desorber	S3410	23	1,2	40	gaseous	Nm³/h		6.588,9			1,3		329,4							N2, NH3 as N2	1,1 MW(el) Compression
CO2 after Compression	S3450	24	30	50	gaseous	Nm³/h		6.556,1			0,9		6,6		traces					N2, NH3 as N2	
Waste Water from Compression	S3440	25	1	40	liquid	kg/h		64,9			0,5		271,2		traces				Floculant		
Steam to Desorber	S3420	26	3,3	150	gaseous	kg/h		19.569,1												see Comment	13,1 MW Heat; VGB-S-010-T-00;2011-12
Steam Condensate	S3430	27	85	3	liquid	kg/h		19.569,1												see Comment	VGB-S-010-T-00;2011-12
CW in	S3001	28	7	30	liquid	m³/h							970,0								
CW out	S3002	29	6	40	liquid	m³/h							970,0								11,1 MW Cooling (85% Recovery)
Amine Reclaimer UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
Amine Solvent to Reclaimer	S6010	30	2	40	liquid	kg/h							1.415,2		571,5	327,8			NaCO3	HSS	Reclaimer all 1 68 OPH (24hours)
Amine Solvent from Reclaimer	S6020	31	3	40	liquid	kg/h							1.233,2		498,0	285,6					Please review data carfilly in operation
Reclaimer Waste	S6015	32	3	40	liquid	kg/h							182,0		73,5	42,2				HSS	approx. 33% of Solvent Loss - Rest NH3 Loss
Steam to Reclaimer	S6003	33	11	200	liquid	kg/h							2.661,7								1,8 MW Heat
Condensate from Reclaimer	S6004	34	3	85	liquid	kg/h							2.661,7								
CW in	S6001	35	7	30	liquid	m³/h							115,0								
CW out	S6002	36	6	40	liquid	m³/h							115,0								1,5 MW Cooling (80% Recovery)
Methanol Production UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
Feed to MeOH Process	S4130	37	81,0	146,6	gaseous	Nm³/h	2,0	6.556,1	19.852,5	4,6	2,6		37,0								1,5 MW(el) Compression
Reactor Feed	S4210	38	81,0	144,1	gaseous	Nm³/h	477,1	8.379,3	191.228,5	4,6	1.781,5	627,7	164,3								
Reactor Feed after E-Heater	S4212	39	80,4	144,1	gaseous	Nm³/h	477,1	8.379,3	191.228,5	4,6	1.781,5	627,7	164,3								
Procuct after Reactor	S4310	40	78,0	207,1	gaseous	Nm³/h	475,8	1.837,7	171.591,8		1.781,5	7.170,7	6.715,0								
Cooled Product	S4318	41	74,5	45,0	gaseous	Nm³/h	475,8	1.837,7	171.591,8		1.781,5	7.170,7	6.715,0								
Purge stream	S4330	42	74,0	44,9	gaseous	Nm³/h	0,6	2,2	205,9		2,1	0,8	0,2								
Hydrogen from PSA	S2125	43	72,0	44,9	gaseous	Nm³/h	0,0	0,0	175,1		0,0	0,0	0,0								
Waste Gas to CHP	S4335	44	24,0	30,0	gaseous	Nm³/h	0,6	2,2	30,9		2,1	0,8	0,2								
Liquid Product 1	S4340	45	74,5	45,0	liquid	kg/h		24,5	0,7		0,5	9.351,9	5.294,8								
Recycle to Compression	S4410	46	74,0	44,9	gaseous	Nm³/h	475,2	1.823,2	171.376,1		1.778,9	627,7	127,3								1,6 MW(el) Compression
Recycle from Compression	S4418	47	81,8	59,6	gaseous	Nm³/h	475,2	1.823,2	171.376,1		1.778,9	627,7	127,3								
Recycle after Heating	S4420	48	81,0	144,0	gaseous	Nm³/h	475,2	1.823	171.376		1.779	628	127,3								
Liquid Product 1 after Throttle	S4510	49	10,0	44,9	liquid	kg/h		25	1		0,453	9.352	5.294,8								
Waste gas from Flash 2	S4610	50	10,0	44,9	liquid	Nm³/h		21,23	0,64		0,39	1,17	0,6								0,01 MW(LHV) S4335+S4610
Liquid Product 2	S4520	51	10,0	44,9	liquid	kg/h		3,3	0,1		0,061	9.350,1	5.294,0							see Comment	acc. IMPCA Standard 001-14
Steam Condensate in	S4003	52	4,0	85,0	liquid	kg/h							5.266,6							see Comment	VGB-S-010-T-00;2011-12
Steam out	S4004	53	3,3	150,0	gaseous	kg/h							5.266,6							see Comment	VGB-S-010-T-00;2011-12
CW in	S4001	54	7,0	30,0	liquid	m³/h							563,0								
CW out	S4002	55	6,0	40,0	liquid	m³/h							563,0								6,5 MW Cooling (95% Recovery)
Methanol Destillation UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
IMPCA Standard MeOH	S5520	56	1,0	35,0	liquid	kg/h						9.245,4	0,1 (wt)								acc. IMPCA Standard 001-14
Waste gas to CHP	S5540	57	1,0	35,0	gaseous	Nm³/h		3,3	0,1		0,1	1,7	0,9								0,01 MW(LHV)
Fussel Oil to CHP expr. as MeOH	S5170	58	8,0	35,0	liquid	kg/h						14,4	7,2								0,08 MW(LHV) : Ethanol, Alcohols and Eathers
Waste Water to Treatment	S5190	59	1,5	45,0	liquid	kg/h						87,7	5.286,9						Phosphor		
Steam Condensate out	S5003	60	6,0	140,0	liquid	kg/h							5.266,6								
Steam in [5,4 bar(a) compressed]	S5004	61	11,0	263,0	gaseous	kg/h							5.266,6								3,5 MW Heat (242 kW(el) Steam Compression)
CW in	S5001	62	7,0	30,0	liquid	m³/h							275,0								
CW out	S5002	63	6,0	40,0	liquid	m³/h							275,0								3,2 MW Colling (90% Recovery)
Waste Water Treatment UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
Raw Water to Treatment	S7100	64	1,0	25,0	liquid	kg/h							12.992,6								Raw Water from Well Head
Mixed Waste Water from Process	S7150	65	1,0	30,0	liquid	kg/h						up to 72	7.142,8								
Bio-Gas to CHP	S7130	66	1,0	37,0	gaseous	Nm³/h	1,8	19,6		0,5	10,0		0,3	39,9							0,4 MW(LHV)
Sludge to CHP	S7110	67	1,0	30,0	liquid	kg/h							65,0							+10% Solids	
Deminwater to Process	S7200	68	12,0	30,0	liquid	kg/h							15.896,4								
Waste Water to Disposal	S7300	69	1,0	20,0	liquid	kg/h							4.239,0								
Heat Pump UNIT	Stream	#	p in bar(a)	T in °C	Aggregate	UNIT	CO	CO2	H2	O2	N2	CH3OH	H2O	CH4	C2H7NO	C3H7NO3	H2SO4	KOH	Dosing	Contaminats	Comment
Steam Condensate in	S8003	70	7,0	85,0	liquid	kg/h							105.509,5								
Steam out	S8004	71	5,4	170,0	gaseous	kg/h							105.509,5								70,6 MW
CW in	S8001	72	7,0	40,0	liquid	kg/h							3.136,4								
CW out	S8002	73	6,0	30,0	liquid	kg/h							3.136,4								36,2 MW Cooling

Attachment C: Time Balance for 200 AEL-stacks/year manufacturing

Volume MW (2600 A/m²)	Cells/Stack	Stacks/Module	Modules	# of Rings	Time (min) / Ring	Hours/year	Days	Month
1136	424	2	100	84800	6,0	8480	353,3	11,6
			Steel	ca. 21.000 t/year	Nickel	ca. 245 t/year		
Machine		# of Machine	# of Rings	set-up time	Machining	Total per Ring	Time (min) / Ring	Comment/Link
Ingot Cutting	17	1	14	10	74	84	6,0	Saw
Heating oven	17	2	14	10	157	167	6,0	
Base Rind Forging	17	1	14	5	79	84	6,0	Forging Machine
Base Rind Intending	17	1	14	8	76	84	6,0	Forging Machine
Ring Rolling	17	1	14	24	60	84	6,0	Roller Mill
Ring Cutting	17	2	14	30	138	168	6,0	PTZ-Saw
Ring Machining	236	11	1	5	61	66	6,0	Milling Cutter
Sheet Cutting	236	2	1	2	10	12	6,0	Laser Cutter
Sheet Punching	236	1	1	4	1	5	6,0	Punching Machine
Sheet Welding	236	4	1	4	20	24	6,0	Laser Welder
Bipolar Plate Coating	236	2	70	60	780	840	6,0	Electroless Ni-Coat
Machine	m²	# of Machine	mm/min	m Width	m²/h	Total hours	Hours/year	Comment/Link
Membrane (Torray)	339.200	3	120	2	14,4	23.556	7.852	Weaving Machine
Weaving calculation	Fequenz of waeving	Fiber thickness	Weaving speed	Weaving speed	Wrap	Weft	Total Fiber	Spinning Frame
Figure	3,33	0,6	2,0	120	24.240	24.240	576.720.773	6,8
Unit	sch/s	mm	mm/s	mm/min	m/h	m/h	m/year	m/s
Machine	# per day	# of Machine	# of Rings	set-up time	Machining	Total per Ring	Time (min) / Ring	Comment/Link
Membrane Cutter	263	2	1	5	5	10	5	Cutting
Machine	m²	# of Machine	m²/Dip	Dips/min	m²/h	min/Dip	Hours/Year	Comment/Link
Electrodes Coating	612.256	6	3,6	0,06	0,433	17	7.852	Anode and Cathode
Machine	# per day	# of Machine	# of Rings	set-up time	Machining	Total per Ring	Time (min) / Ring	Comment/Link
Gasket Cutter	263	2	1	5	5	10	5	Cuting
Machine	kg/Stack	# of Machine	# of Rings	Finisching	Machining	Total per Stack	Time (min) / Ring	Comment/Link
Assembly Robot	87.535	2	424	721	3.604	4325	5,10	Robot
Modules per year 6 Days per week	max.	104	Days/Stack	0,5	2,5	1,5		plus other parts Ends, rods, etc.

8.3 Attachment D: Flow sheet for 200 AEL-stacks/year manufacturing



8.4 Attachment E: Equipment lists of entire process incl. power consumption

#	**Carbon Capture MEA-Solvent Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	Crude Flue Gas Dampers	4	Double Flap Dampers	104.000 €	5	5	kW
2	FID-Fan with Silencers	1		380.000 €	260	182	kW
3	Absorber Column with Internals	1		2.124.000 €			
4	Absober Head Cooling Pumps	2		28.000 €	70	42	kW
5	Absorber Head Cooler	1		23.000 €			
6	Absorber Head Buffer Tank	1		9.200 €			
7	Absorber Bottom Solvent Pumps	2		42.000 €	140	84	kW
8	Solvent Solid Filters	2		14.000 €			
9	Emergency Emtying Tank	1		49.000 €			
10	Solvent Return Pump	1		20.000 €	0	0	kW
11	Main Cross Flow Solvent Heat Exchanger	1	Hot Side Inconel	48.000 €			
12	Desorber Column with Internals	1	2 bar(a) Vessel	2.761.200 €			
13	Desorber Head Cooling Pumps	2		17.200 €	70	42	kW
14	Desorber Heat Cooler	1		39.000 €			
15	Desober Head Buffer Tank	1		8.600 €			
16	Desober Emptying Pumps	2		36.000 €	0	0	kW
17	Carbon Capture Sump Pumps	2		34.000 €			
18	Main Solvent Recirculation Pumps	2		53.000 €	160	96	kW
19	Main Lean Solvent Cooler	1		62.000 €			
20	Main Steam Control Valves	3		42.000 €			
21	Reboiler Systems	3	Natural Criculation Type	322.500 €			
22	Condensate Pumps	2		42.000 €	30	18	kW
23	Condensate Collection Tank	1		7.500 €			
24	Main Condensate Pumps	2		39.000 €	55	33	kW
25	Clean Flue Gas Dampers	2		67.600 €			
26	After Scrubber incl. Internals	1		81.000 €			
27	After Scrubber Recirculation Pumps	2		33.000 €	30	21	kW
28	H2SO4 Sosing Pump	2		15.800 €	2	2	kW
29	Waste Water Buffer Tanks AS	1		6.400 €			
30	Waste Water Pump	1		11.500 €			
31	AS Sump Pump	1		11.500 €	0	0	kW
32	H2SO4 Storage Tank	1		12.500 €			
33	Amine Storage Tank	1		19.300 €			
34	Amine Solvent Dosing Pump	2		28.000 €	10	6	kW
35	Solvent Mixing Tank incl. Agitator & Dosing	1	incl. Anti-Foam & Anti-Corrosion	16.300 €	8	8	kW
36	Solvent Supply Pumps	2		37.000 €			
37	Reclaimer Batch Vessel	1	Cattle Type	136.000 €			
38	Steam Valve	1		17.500 €			
39	Condensate Buffer Tank	1		8.600 €			
40	Reclaimer Condensate Pump	1		13.500 €	0	0	kW
41	Reclaimer Waste Pump 1	1		13.500 €	0	0	kW
42	Reclaimer Waste Cooler	1		6.800 €			
43	Recoverd Solvent Cooler	1		7.800 €			
44	Recoverd Solvent Tank	1		6.300 €			
45	Reclaimer Vacuum Pump	1		18.600 €			
46	Reclaimer Waste Tank incl. Agitator	1		12.700 €	5	5	kW
47	Reclaimer Waster Pump 2	1		11.400 €	0	0	kW
48	Na2CO2 Dosing Pump	1		11.400 €	0	0	kW
49	4 Stage CO2-Compressor System 2 x 50%	2		2.196.835 €	1.100	715	kW
50	Compressor Cooling Heat Exchangers	3	Inlet Guide Vale Control 30 bar(a)	279.000 €			
51	CO2-Drying System	1		436.000 €	40	30	kW
52	CO2-compressor Waste Water Pump	2		24.600 €	5	5	kW
					1.990	1.294	kW
	Engineering & Project Management		20%	1.969.127 €			
	Piping & Valves		35%	3.445.972 €			
	EMSR Equipment		25%	2.461.409 €			
	Transport, Erection & Comissioning		25%	2.461.409 €			
	Structural Steel & Civil Works incl. HVAC		25%	2.461.409 €			
	Overhead		20%	4.528.992 €			
	TOTAL			27.173.954 €			

#	**Alkaline Electrolyser Unit**	pc. of Equ.	Comment	Cost	Power 100%	Power 50%	Unit
1	Main Transformer	1		450.000 €	887	405	kW
2	Transformer Rectifier Sytsems	12		18.450.000 €	433	198	kW
3	Power Electronics Water Cooler System	1		288.000 €	1.731	791	kW
4	AEL-Stacks (20.000 Nm^3/h @ DC 4,375 kWh/Nm^3)	24	Active Ø 1,75m 2,4 m^2 424 cells; 31 bar(a)	22.200.000 €	86.527	39.555	kW
5	Hydrogen Gas Separator Vessel	12		1.104.000 €			
6	Oxygen Gas Separator Vessels	12		1.104.000 €			
7	Hydrogen Gas Coolers	12		216.000 €			
8	Oxygen Gas Coolers	12		216.000 €			
9	Hydrogen Mist Eleminators	12		84.000 €			
10	Oxygen Mist Eleminators	12		84.000 €			
11	Hydrogen DeOxo Reactors	12		468.000 €			
12	Hydrogen Lye Coolers	12		235.200 €			
13	Oxygen Lye Coolers	12		235.200 €			
14	Hydrogen Lye Pumps	12		228.000 €	168	101	kW
15	Oxygen Lye Pumps	12		228.000 €	168	101	kW
16	Demin Water Pumps	12		168.000 €	78	47	kW
17	Demin Water Buffer Vessel	6		99.000 €			
18	KOH-Lye Supply Pumps	6		90.000 €	15	15	kW
19	KOH-Storage Tank	1		67.000 €			
20	KOH-Unloading Pumps	2		44.000 €	4	4	kW
					90.010	41.217	kW
	Engineering & Project Managemnt		5%	2.302.920 €			
	Piping & Valves		10%	4.605.840 €			
	EMSR Equipment incl. Gas Monitoring		10%	4.605.840 €			
	Transport, Erection & Comissioning		20%	9.211.680 €			
	Civil Works incl. HVAC		15%	6.908.760 €			
	Overhead		20%	14.738.688 €			
	TOTAL	982 €		88.432.128 €			

#	**Methanol Reactor Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	4 Stage Syngas Compressor 2 x 50%	2	Inlet Guid Valve Control 81 bar(a)	1.883.002 €	1.450	943	kW
2	Tube Cooled Converter Methanol Reactors	2	Davy TCC Type	3.246.000 €			
3	Catalyst for Reactors	2	Clariant Type MegaMax 800®	4.153.000 €			
4	StG Feed Water Pumps	2		76.000 €	140	84	kW
5	Recycle Steam Generator	1		176.000 €			
6	Cross Flow Recycle Heater	1		136.500 €			
7	Cross Flow MeOH Preheater	1		138.500 €			
8	Cross Flow Recycle Cooler	1		132.000 €			
9	Recycle Cooler	1		121.000 €			
10	Phase Separator	1		84.500 €			
11	Prodcut Cooler	1		77.500 €			
12	Main Crude MeOH Pumps	2		33.000 €	55	33	kW
13	2 Stage Recycle Copressor 2 x 50%	2	Inlet Guid Valve Control 81 bar(a)	1.647.627 €	1.515	985	kW
14	Hydrogen Recovery Pressure Swing Absober	1		423.000 €	40	40	kW
					3.200	2.084	kW
	Engineering & Project Management		15%	1.849.144 €			
	Piping & Valves		25%	3.081.907 €			
	EMSR Equipment		20%	2.465.526 €			
	Transport, Erection & Comissioning		30%	3.698.289 €			
	Structural Steel & Civil Works incl. HVAC		25%	3.081.907 €			
	Overhead		20%	5.300.880 €			
	TOTAL			31.805.281 €			

#	**Methanol Purification Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	LP Destillation Column	1	Vacuum	330.000 €			
2	LP Heater	1		33.500 €			
3	LP-Head Cooler	1		23.500 €			
4	Phase Separator	1		12.400 €			
5	Vacuum Pumps	2		37.200 €	35	21	kW
6	MP Destillation Collumn	1	5 bar(a)	495.000 €			
7	MP Heater	1		41.875 €			
8	HP Destillation Column	1	10 bar(a)	742.500 €			
9	HP Steam Heater	1		52.344 €			
10	Cloumn Buffer Tanks	3	equal for better Spare Parts Handling	19.500 €			
11	Column Bottom Pumps	6	equal for better Spare Parts Handling	62.400 €	30	18	kW
12	Colum Circulating Pumps	6	equal for better Spare Parts Handling	55.500 €	30	18	kW
13	2 Stage HP-Steam Compressor	1	Spilling type for 11 bar(a) Steam	198.000 €	240	156	kW
14	Steam Conditioning Unit	1		22.300 €			
15	Methanol Storage Tank	1	15000 m^3	436.000 €			
16	Methanol Loading Station	1		89.000 €	5	5	kW
					340	218	kW
	Engineering & Project Management		30%	795.306 €			
	Piping & Valves		35%	927.857 €			
	EMSR Equipment		25%	662.755 €			
	Transport, Erection & Comissioning		40%	1.060.408 €			
	Structural Steel & Civil Works incl. HVAC		40%	1.060.408 €			
	Overhead		20%	1.431.550 €			
	TOTAL			8.589.301 €			

#	**Waste Water Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	Waste Water Collection Tank incl. Agitator	1		166.000 €	3	3	kW
2	Dosing System for Waste Water	1		48.500 €	1	1	kW
3	Floculation and Setelment System	1		248.000 €	5	5	kW
4	AnMBR Reactor incl. Membrane Cycle	1		366.000 €			
5	AnMBR Recirculation Pumps	2		37.000 €	10	10	kW
6	Buffer Tank	1		19.800 €			
7	Filter Pump	2		64.000 €	25	25	kW
8	Ultrafiltration Unit	1		232.500 €			
9	Reverse Osmosis Pump	2		76.800 €	30	30	kW
10	Reverse Osmosis 1st Stage	2		142.500 €			
11	Reverse Osmosis 2nd Stage	2		118.600 €			
12	CEDI System	2	Continous Electro De-Inonisation	193.000 €	26	26	kW
					100	100	kW
	Engineering & Project Management		40%	685.080 €			
	Piping & Valves		35%	599.445 €			
	EMSR Equipment		20%	342.540 €			
	Transport, Erection & Comissioning		30%	513.810 €			
	Structural Steel & Civil Works incl. HVAC		40%	685.080 €			
	Overhead		20%	907.731 €			
	TOTAL			5.446.386 €			

#	**Balanced of Plant Installations**	pc. of Equ.	Comment	Cost	Power		Unit
1	Nitrogen and Instrument Air Supply Unit	2	Partwise Operation	372.000 €	75	75	kW
2	Main Cooling Water feed pumps	2		73.000 €	125	88	kW
3	Main Cooling Water return pumps	2		76.000 €	125	88	kW
					325	250	kW
	Engineering & Project Management		50%	260.500 €			
	Piping & Valves		60%	312.600 €			
	EMSR Equipment		20%	104.200 €			
	Transport, Erection & Comissioning		30%	156.300 €			
	Structural Steel & Civil Works incl. HVAC		40%	208.400 €			
	Overhead		20%	312.600 €			
	TOTAL			1.875.600 €			

#	**Overall add. Project Costs**	pc. of Equ.	Comment	Cost	Power		Unit
1	Coordination Engineering & Project Management		EPCM Cost	11.793.115 €			
2	Office Building & Control Room	1		1.550.000 €	65	65	kW
3	Fire Fighting, Roads and Parking			3.345.000 €	20	20	kW
					85	85	kW
	Overhead		20%	3.337.623 €			
	TOTAL			20.025.739 €			
	TOTAL for entire MeOH Production			183.348.389 €	96.000	45.198	kW
	Specific Price per kW Consumption			1.910 €			€/kW

#	**High Temperature Heat Pump Pool Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	Compressors incl. Motor & Control	12	7,25 m€ first System 21,6 MW(el) other 70% of Cost	63.075.000 €	260.092	239.022	kW
2	Heat Exchangers sets (5 pc.)	12		13.104.000 €			
3	E-Heater	12	Start-up heater only	576.000 €			
4	Pumps	24		432.000 €	5.308	4.878	kW
5	Throttle & plus Water Injection System	12		2.940.000 €			
6	Flare System	1	Emergency System	198.000 €			kW
7	Drain Tank incl. Vacuum Pump	1	Emptying only	286.000 €			
8	Insulation			864.000 €			
					265.400	243.900	kW
	Engineering & Project Management		10%	8.147.500 €			
	Piping & Valves		10%	8.147.500 €			
	EMSR Equipment		5%	4.073.750 €			
	Transport, Erection & Comissioning		15%	12.221.250 €			
	Structural Steel & Civil Works incl. HVAC		20%	16.295.000 €			
	Overhead		20%	26.072.000 €			
	TOTAL			156.432.000 €			

#	**Flue Gas Cooling Unit**	pc. of Equ.	Comment	Cost	Power		Unit
1	Flue Gas Dampers	4		720.000 €	10	10	kW
2	Regenerative Gas/Gas Heater (RGGH)	1		2.730.000 €	30	30	kW
3	Crude Gas Ducts		2.000.000 Nm³/h	3.450.000 €			
4	Cooling Vessel incl. Internals	1	acc. FGD Absorber	12.950.000 €			
5	Recirculation Pumps	3		705.000 €	2.250	2.250	kW
6	Mist Eleminator Wasing Pumps	2		76.000 €	90	90	kW
7	Heat Exchangers	2		636.000 €			
8	Cooling Water Pumps	2		178.000 €	320	320	kW
9	NaOH Tank	1		48.000 €			
10	NaOH Loading	2		36.000 €	10	10	kW
11	NaOH Dosing	2		18.000 €	5	5	kW
12	Waste Water Pumps	2		72.000 €	85	85	kW
13	Clean Gas Dampers	4		140.000 €			
14	Clean Gas Ducts		110.000 Nm³/h	1.560.000 €			
					2.800	2.800	kW
	Engineering & Project Management		8%	1.865.520 €			
	Piping & Valves		12%	2.798.280 €			
	EMSR Equipment		10%	2.331.900 €			
	Transport, Erection & Comissioning		30%	6.995.700 €			
	Structural Steel & Civil Works incl. HVAC		20%	4.663.800 €			
	Overhead		20%	8.394.840 €			
	TOTAL			50.369.040 €			

#	**CHP Power Plant 1500 MW Fuel -New-Build- Unit**	pc. of Equ.	Comment	Cost	SC-Power		Unit
1	Coal Yard	1	commonly not used	20.000.000 €	0		kW
2	Biomass Yard	1		30.000.000 €	200		kW
3	Gas supply	1		10.000.000 €	100		kW
4	Steam Generator	1	incl. FWStT 17 MW(mech. by Steam)	180.000.000 €	9.600		kW
5	Turbine	1	acc. FGD Absorber	110.000.000 €	1.500		kW
6	Flue Gas Cleaning (SCR, ESP, FGD)	1		50.000.000 €	3.800		kW
7	Cooling Tower	1		20.000.000 €	600		kW
8	Water Preparation	1		5.500.000 €			
9	Steam Extraction	1		4.500.000 €	100		kW
10	Balance of Plant incl. Habour, Storages etc.	1		15.000.000 €	200		
					16.100		kW
	Engineering & Project Management		10%	44.500.000 €			
	Piping & Valves		20%	89.000.000 €			
	EMSR Equipment		10%	44.500.000 €			
	Transport, Erection & Comissioning		25%	111.250.000 €			
	Structural Steel & Civil Works incl. HVAC		35%	155.750.000 €			
	Overhead		20%	178.000.000 €			
	TOTAL			1.068.000.000 €			

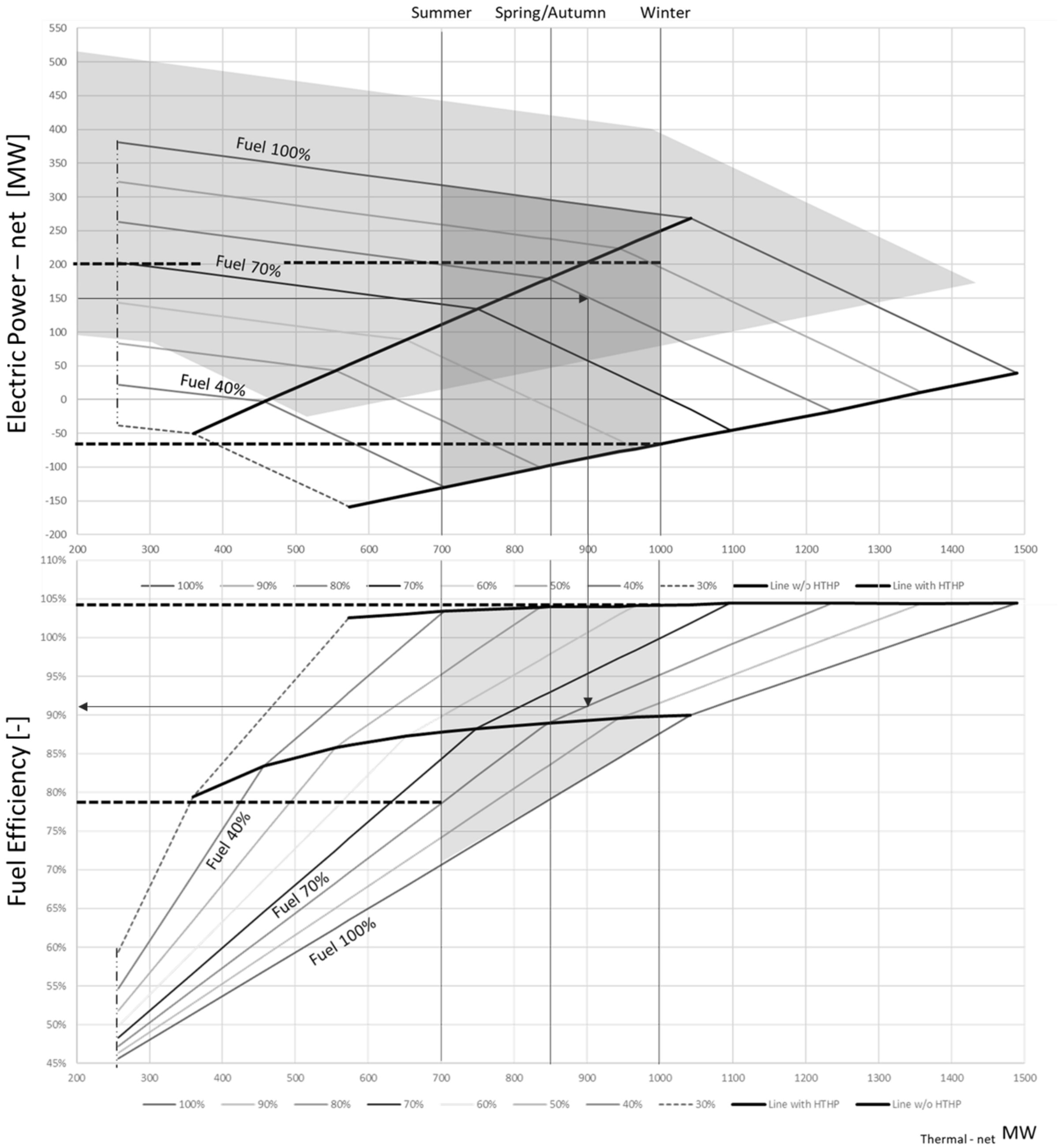
#	**CHP Power Plant 1500 MW Fuel -New-Build- Unit**	pc. of Equ.	Comment	Cost	SC-Power		Unit
1	CHP Power Plant	48%	100% ... or Retrofit of existing Power Plant (45-50%)	512.640.000 €	16.100		kW
2	Flue Gas Cooler for HTHP´s and Methanol Unit	1		50.369.040 €	2.800		kW
3	High Temperature Heat Pump Pool	1		156.432.000 €	265.400		kW
4	Methanol Generation	1	incl. FWStT 17 MW	183.348.389 €	96.000		kW
5	Risk Pool	5%	acc. FGD Absorber	45.139.471 €			
			Fuel Consumption (LHV)		1.512.000		kW
			Brutto Power Generation		-418.800		kW
			Total Heat Generation		-1.490.000		kW
			Methanol Generation		-51.100		kW
	TOTAL	% of Power Plant new Build	89%	947.928.900 €	-67.600		kW
			Power Plant in HHV Use		228.000		kW
			Specific Price for total kW generated @ 100% Load Rating	600 €	per kW		

8.5 Attachment F: Main diagram of plant with use description

The production of methanol in the cases is constant with 51,1 MW-fuel output. Follow the example by the red drawn arrows and use the diagram in two steps:

Step 1: Choose an electrical and thermal load point, as e.g. 150 MW-electrical and 900 MW-thermal, in the power diagram

Step 2: Go down in the efficiency diagram to the same iso firing line, as e.g. here the 70% line and read out the related fuel efficiency of the load case



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