Analysis and evaluation of decarbonization measures in synthetic resin production

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Vienna, September 2023

Michael Steiner

Abstract

The goal of this thesis is the identification of suitable alternatives to replace natural gas at temperatures, of 290 °C. Natural gas is used to supply process heat for synthetic resin production, as well as to recycle the resulting process waste. Furthermore, alternative ways to treat the process waste should be found. In addition, potentials for reducing CO_2 emissions by analyzing the production process have to be identified. At the beginning of the thesis a special focus will be given to the analysis of the currently used technologies and the batch production. This allows identification and quantification of the process waste, which is generated. In addition, the calculation and presentation of the different required energy sources is carried out. A time-related representation of the necessary thermal energy during the production process enables further investigations. These include measures for waste heat utilization and for the storage of thermal energy during the production process. This could save up to 15 % of the total natural gas. The treatment of the process wastes with the thermal oxidizer is another vital portion, it consumes about 10 % of the total natural gas. Therefore, the investigation of various technologies for the decomposition of the generated process wastes during synthetic resin production is carried out. An essential part of the work is the identification of alternative ways to provide process heat. For this purpose, a technology screening is carried out, identifying electricity, hydrogen and the pyrolysis of powder coating residues as promising methods. Based on the created overview of the different technologies and possibilities to reduce CO_2 emissions, further decisions can be made by the industrial company.

Kurzfassung

Das Ziel dieser Masterarbeit ist die Identifikation von passenden Alternativen um Erdgas bei Temperaturen von 290 °C zu ersetzen. Erdgas wird verwendet, um Prozesswärme zur Kunstharzproduktion bereitzustellen, sowie zur Verwertung der anfallenden Prozessabfälle. Des Weiteren sollen alternative Möglichkeiten zur Behandlung der Prozessabfälle gefunden werden. Außerdem sollen durch Analyse des Produktionsprozesses Potentiale zur Reduzierung der CO_2–Emissionen ermittelt werden. Zu Beginn wird ein besonderer Fokus auf die Beleuchtung der aktuell verwendeten Technologien und die Analyse der Batch-Produktion gelegt. Dadurch können die anfallenden Prozessabfälle identifiziert und quantifiziert werden. Außerdem erfolgt die Berechnung und Darstellung der verschiedenen benötigten Energieträger. Eine zeitliche Darstellung der benötigten thermischen Energie während des Produktionsprozesses ermöglicht weiter Untersuchungen. Diese beinhalten Maßnahmen zur Abwärmenutzung und um die Speicherung von thermischer Energie während des Produktionsprozesses zu realisieren. Dadurch könnten bis zu 15 % des gesamten Erdgases eingespart werden. Die Behandlung der Prozessabfälle in der thermischen Nachverbrennungsanlage benötigt in etwa 10 % des verbrauchten Erdgases. Daher werden verschiedene Technologien zur Nachbehandlung der anfallenden Prozessabfälle untersucht. Ein wesentlicher Teil der Arbeit ist die Identifizierung von alternativen Möglichkeiten zur Bereitstellung der Prozesswärme. Dazu wird ein Technologiescreening durchgeführt, dabei werden Strom, Wasserstoff und die Pyrolyse von Lackresten als vielversprechende Methoden erkannt. Auf Basis des geschaffenen Überblicks über die verschiedenen Technologien und Möglichkeiten zur Reduzierung der CO_2–Emissionen, können vom Industriebetrieb weitere Entscheidungen getroffen werden.

Contents

Nomenclature

Acronyms

AEM	anion exchange membrane
AOP	advanced oxidation process
BTF	biotrickling filter, filtration
COP	coefficient of performance
HHV	higher heating value
HTF	heat transfer fluid
LHV	lower heating value
MBR	membrane bioreactor
MBTF	moving-bed trickling filter
MIBK	methyl isobutyl ketone
NPG	neopentyl glycol
P2H	power-to-heat
PBTES	packed bed thermal energy storage
PCO	photocatalytic oxidation
PEM	proton exchange membrane
SCWO	supercritical water oxidation
STR	stirred-tank reactor
SWOT	strenght, weakness, opportunity, threat
TES	thermal energy storage
TO	thermal oxidizer
TOC	total organic carbon
VOC	volatile organic compound

WHR	waste heat recovery

Subscripts

avg	average
batch	per batch
H	heating
in	input
max	maximal
ng	natural gas
pcr	powder coatings residues

Roman symbols

E	energy	kW h
m	mass	kg
Q	heat quantity	J
T	temperature	°C
V	volume	L
$\dot{V}$	volume flow	$\mathrm{L\,h^{-1}}$
W	work	J

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1 Introduction

The climate change affects our daily lives and the world around us. Weather extremes occur more frequently and cause damage that affects wildlife, vegetation and humanity. Intervention is necessary to limit the effects and ensure continuity. To stop, or slow down global warming, greenhouse gas emissions must be reduced. In particular CO_2 emissions must be drastically cut. Otherwise, irreversible and destructive effects on our planet could be the result.

Energy demand continues to increase every year, and large parts of the required energy are provided by fossil fuels, such as natural gas, oil and coal. Only a small piece is covered by renewable resources. The use of fossil fuels results in high CO_2 emissions. This again leads to the fact that the earth surface temperature rises further and further. Figure 1 shows the change of the global temperature throughout the years, with increasing industrialization.

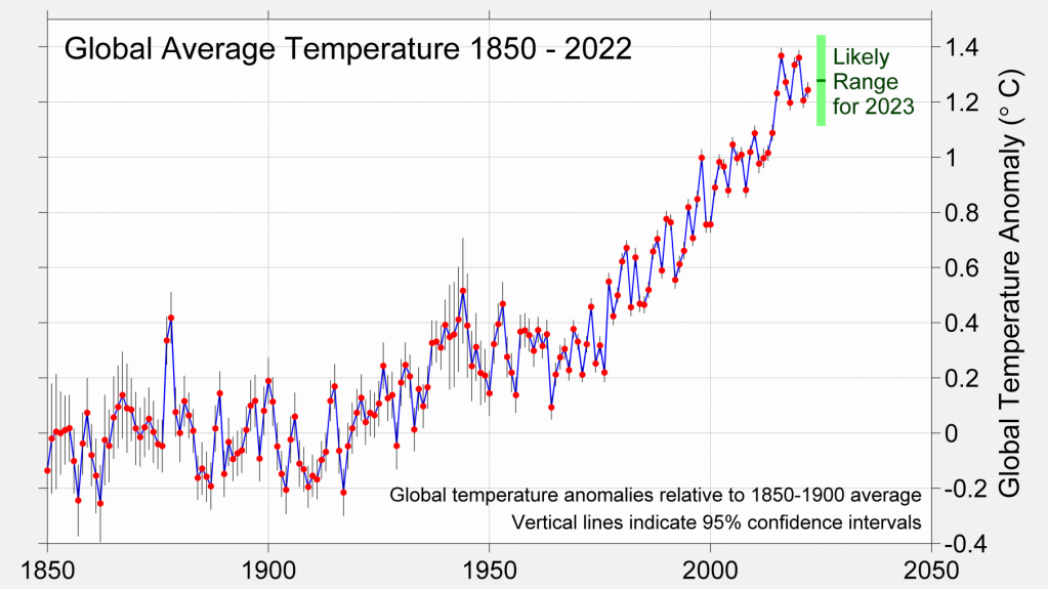

Figure 1: *Global average temperature from 1850–2022 [1].*

In order to prevent a further steep rise of the earth's surface temperature, several factors play a decisive role. As already mentioned, fossil fuels must be successively replaced by renewable ones. This can be done mainly through the use of renewable generated electricity and hydrogen.

As reported by Agora *et al.* [2], especially in the chemical industry, the implementation of a circular economy is a crucial aspect to enable an efficient and resource-saving production. Another important factor is the enormous waste heat recovery (WHR) potential in the industrial sector. The efficient implementation of WHR can lead to a significant reduction of the energy consumption and thus to a reduction of CO_2 emissions. In batch processes, the implementation of a direct WHR is often not possible due to a time mismatch between the availability and demand of energy. Therefore, a lot of energy is often lost in such processes. Thermal energy storage (TES) systems can be used to store this energy. These systems also play a decisive role on the way to an energy-efficient industry [3].

This thesis is carried out in cooperation with an industrial company. They spare no effort to reduce CO_2 emissions. The company's vision for the future includes the plan to be independent of fossil fuels by 2040. Currently, natural gas is used to provide process heat for the production. Therefore, it is essential to replace natural gas with renewable energy sources.

1.1 Scope of work

The main task of this thesis is to find low carbon alternatives for natural gas at high temperatures. In the course of this, a broad technology screening will be conducted. Furthermore, measures to reduce CO_2 emissions in synthetic resin production will be investigated. In general, three main subjects are dealt with in this work, which are:

- Analysis and quantification of the energy flows of the whole process
- Identification of suitable alternative technologies, which lead to reduction of the CO_2 emissions
- Consolidation and presentation of the alternative technologies

At the beginning, the energy flows of the entire process are analyzed and quantified. The energy flows are brought together and presented clearly in order to carry out further investigations. The synthetic resin manufacturing process and the technologies currently used are explained. The possibility of substituting energy sources is being investigated, for example electricity or hydrogen instead of natural gas. In addition, alternative technologies for cleaning process wastes are being explored.

An important factor is to maximize the energy efficiency, this can be achieved through various measures. The possibility of WHR from the exhaust gas is being investigated. The integration of TES systems can lead to savings in natural gas.

Finally, the technologies, the potential for energy savings and the associated advantages and disadvantages are brought together. So that further decisions for the future of the company may be supported by this.

2 System analysis

As mentioned above, this work is done in collaboration with an industrial company, whose main products are powder coatings. The powder coatings are produced on the basis of various synthetic resins, which act as the binding agent. These synthetic resins are manufactured at the company's site. Two plants for the production of various synthetic resins are operated there. A third production plant is being completed, which has almost double the capacity of the other two plants combined. Over 95 % of the resins produced, are used for the company's own further processing.

2.1 Synthetic resins production

Synthetic resins are produced in batches. Batch production is a discontinuous production process, as it is often used for the synthesis of chemicals. Since chemical reactions take place, they need several hours to be completely finished. In this process various stages are carried out step by step in a reaction vessel. At the end of the process, the finished product is removed. After that, the next batch can start.

According to Günther *et al.* [4], a typical batch process takes place in the following order:

- Filling of the reaction vessel with the starting materials (reactants)
- Reaction of the reactants to products
- Discharging of the reaction vessel and transporting it for further processing
- Preparation of the reaction vessel for the next filling (cleaning, maintenance)

Batch production brings some advantages over continuous production processes. However, it also presents some challenges that impact the various systems throughout the whole production process. These advantages and disadvantages are listed below.

+ High flexibility, different products can be manufactured with the same production plant
+ Comparatively simple plant design
– Different requirements during the various process phases (heat demand, cooling water)
– Complex plant control
– Difficult management of process waste, due to discontinuous operation
– Low production volumes

According to DIN EN ISO 4618:2015-01, synthetic resin is produced by chemical reactions (e.g. polymerization, polycondensation and polyaddition) [5]. Synthetic resin production takes place in a discontinuously operated stirred-tank reactor (STR) by melting-condensation-processes, of di- or polyhydric alcohols and dicarboxylic acids, at high temperatures. Polycondensation involves the elimination of a low-molecular component, which is water. The released water must be continuously removed, otherwise the polycondensation stops (Le-Chatelier). Therefore, the reactor performance depends on how fast the process condensate is removed from the polyester melt. With increasing reactor size, the necessary mass transfer becomes more difficult. For this reason, a so-called entraining agent is added to accelerate the transport of the water out of the reactor. Since the entraining agent used has limited water solubility, a mixture of water and entraining agent is formed, hereinafter referred to as process condensate.

2.1.1 Production process

The produced resins form the main component of the powder coatings, up to 60 %, so they are largely responsible for the properties of the final coating. Therefore, certain demands are required from the binders. The softening temperature should be $\geq 80\,°C$, so the binders must have a comparatively high glass transition temperature of $\geq 55\,°C$. Otherwise, the grinding of the powder coatings is not possible. Another consequence is caking during storage at room temperature. [6]

Figure 2 shows a schematic of a production plant for the manufacture of polyester resins. The whole process is carried out in an inert gas atmosphere, for which nitrogen is used. The thermal energy required for the process is provided by thermal oil, which is heated by natural gas burners. This achieves the necessary temperatures of up to 240 °C. The reaction time is between 16 and 24 hours, depending on the resin produced [6]. The liquid storage tank is filled with neopentyl glycol (NPG), which is the most important diol for the production of polyesters for the coatings industry. The liquid storage tank is heated to 80 °C with thermal oil and kept at this temperature. The solid storage tank is also heated, to a temperature of 50 °C.

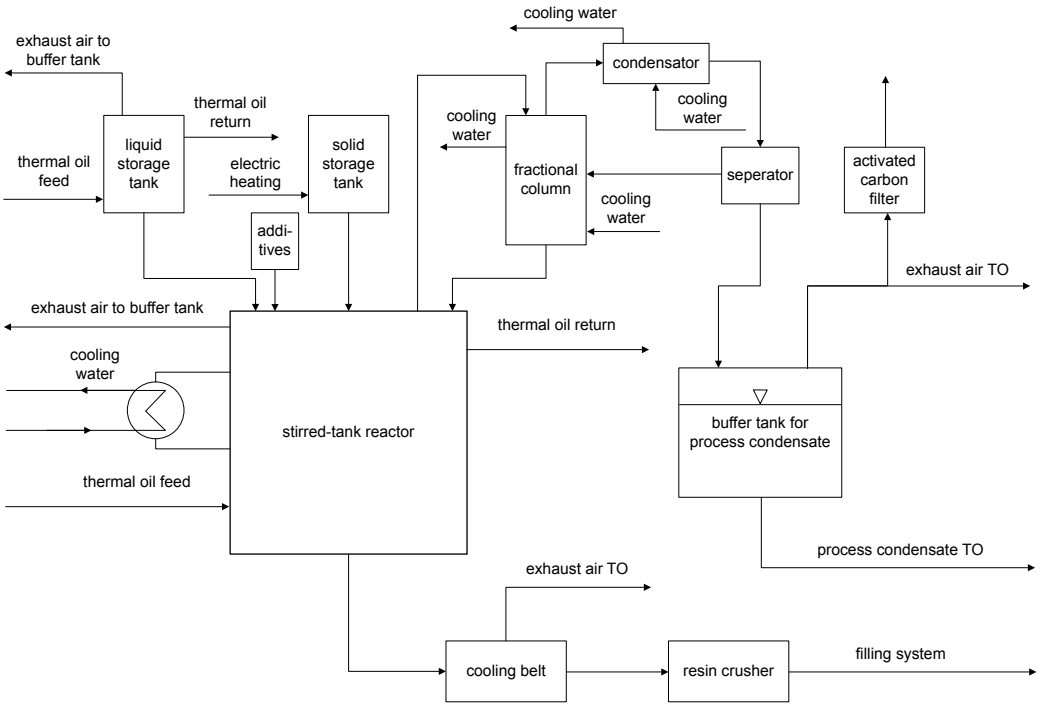

Figure 2: *Schematic representation of the polyester resin production process.*

Figure 3 shows the change of the temperature in the STR througout the production process. The first step of the process is the transfer of the liquid and solid feedstocks, according to the formula of the produced resin, to the STR. Various additives, (like e.g. antifoam), are also added to achieve the desired properties. The actual manufacturing process starts with the first heating stage of the feedstocks up to 240 °C in the STR, which lasts up to ten hours. From a temperature of about 125 °C the entraining agent is injected. The entraining agent used is methyl isobutyl ketone (MIBK), which is required to achieve the desired gas-liquid exchange in the fractional column. During the entire process, the produced process condensate is continuously discharged. This is done by separation in the fraction column and subsequent condensation. The liquid mixture of water and MIBK is then separated. The MIBK is then returned to the fractionation column. The resulting process condensate and process exhaust gases are then collected in the buffer tank and subsequently fed to the thermal oxidizer (TO), where they are decomposed. The progress of the reaction is monitored via the quantity of produced condensate. For safety reasons, an activated carbon filter system must be provided. In order to have an alternative possibility for exhaust gas cleaning in case of failure of the TO.

The first cooling phase begins, during which the STR is cooled down with thermal oil to 200 °C. This takes about one and a half hour. Afterwards, solids are again fed from the solid storage tank. The second heating stage, which lasts about five hours,

brings the reactor up to 240 °C. Meanwhile the entraining agent is injected in the same way as in the first stage. The second cooling phase then starts, during which the boiler is again cooled down to 200 °C over a period of two hours. Depending on the resin produced, it is then also treated under vacuum. The total process time for the production of a common resin is approximately 24 hours. Then the finished resin is pumped onto the steel-cooling-belt. There it is cooled with water, to a temperature of ≤ 30 °C, until a solid resin plate is formed on the belt. In order to enable further processing and storing, the resin is crushed with the resin crusher. It is then stored in silos or bags until further processing.

Figure 3: *Tmeperature profile of the STR during the synthetic resin production over the duration of one batch.*

2.2 Process waste

During the production of synthetic resins, various pollutants are produced which are discharged in the form of process waste. These are liquid and gaseous wastes, the so-called process condensate and process exhaust gas. The formation and composition of these process wastes will now be explained in more detail.

2.2.1 Condensate

The process condensate generated during the production process consists mainly of water, but is contaminated with organic impurities. Therefore, it cannot be discharged into the sewer system and must be subjected to secondary treatment. The exact composition of the process condensate is not known. But the main fraction of pollutants is formed by the entraining agent MIBK, which is dissolved in the water. In addition, NPG is also present in the process condensate, which is lost due to carryover in the production process.

Table 1 shows the values of the average volume flow and the total amount of process condensate generated in one batch over 24 hours. The amount of process condensate produced by plant three is twice as large as that generated by plants one and two, due to the double production capacity. This means that the following quantities of process condensate to be treated are produced in one batch in the respective production line. In fact, constant amounts of condensate do not accumulate during the production process. In some process phases, quantities are up to twice as high as the average quantities. However, there are also phases where no process condensate is produced at all (e.g. cooling phases). This inconstancy is compensated by intermediate storage in the buffer tank, see Figure 2. The process condensate is then fed to the TO and decomposed.

Table 1: *Process condensate volume flow and quantity per batch generated by the production plants 1, 2 and 3.*

Production plant	$\dot{V}_{\mathrm{avg}}/\mathrm{L\,h^{-1}}$	$V_{\mathrm{batch}}/\mathrm{L}$
Plant 1 and 2	200	4800
Plant 3	400	9600
Total	600	14 400

Since **Methyl isobutyl ketone** (MIBK) is the main pollutant in the process condensate, this substance will now be examined in more detail. MIBK is a ketone, which is produced from acetone. In the production of synthetic resins it is used as an entraining agent. MIBK belongs to the group of the volatile organic compunds (VOC), the collective term for organic substances that change into the gas phase at room temperature by evaporation. Table 2 shows the relevant substance properties of MIBK, according to Friedrich [7]. At room temperature, MIBK is liquid but has a very high vapor pressure. Therefore it quickly breaks down to acetone, formaldehyde, and isobutanal if released under ambient conditions. The low flash point means that highly flammable vapor/air mixtures can easily form. When MIBK is heated, ignition may occur, as a result, the combustion produces CO and CO_2.

Table 2: *Substance properties of MIBK [7].*

Paramter	Value	Unit
State of matter	Liquid	-
Melting/freezing point	−84	°C
Boiling point	114	°C
Flash point	15	°C
Ignition temperature	448 to 460	°C
Water solubility at 20 °C	14.1	$\mathrm{g\,L^{-1}}$
Vapor pressure at 20 °C	2093	Pa
Density at 20 °C	797.8	$\mathrm{kg\,m^{-3}}$

During synthetic resin production at the company site, approximately 8000 L of MIBK are required per batch for all production plants combined. The loss during the production process is about 3.2 kg per ton of processed resin. The production capacity of plant one and two is eleven tons each. Production plant three reaches a capacity of 40 tons. The loss of MIBK is mainly due to the solubility of $14.1\,\mathrm{g\,L^{-1}}$ in water. So MIBK dissolves when it is mixed with water and therefore enters the process condensate. MIBK must not simply be discharged into the sewage system, or into the environment, although in principle it can be easily biodegraded under certain conditions.

2.2.2 Exhaust gas

The process exhaust gas generated during the production process contains various impurities. To gain a better understanding of the waste gases produced, a gas measurement was commissioned by the industrial company on the raw gas side of the TO. The measurements were carried out from 19.02.2019-22.02.2019.

Table 3 shows the results of the continuously measured parameters, these are carbon monoxide (CO), oxygen (O_2) and total organic carbon (TOC). TOC is a parameter, which describes the concentration of the organic carbon in a sample. It thus excludes the inorganically bound carbon, like CO_2. So TOC allows conclusions to be drawn about the contamination with foreign substances. The measurement results were given as half-hour averages, based on standard temperature and pressure, 0 °C and 1013 mbar. The non-representative measurement results, due to the operating conditions of the production plant were removed. Then an average value was formed from the remaining measured values.

Table 3: *Continuously measured parameters on the raw gas side of the TO.*

Paramter	Avg. value	Unit
CO	1565.0	$\mathrm{mg\,m^{-3}}$
O_2	16.6	Vol.-%
TOC	1463.0	$\mathrm{mg\,m^{-3}}$

Table 4 shows the discontinuously measured parameters, which display the measuring conditions. The values shown are averaged values from 17 measurements over the entire measurement period. The measurements were made over different periods of time, ranging from 45 min to 2 h 15 min. The temperature of the measured exhaust gas is almost room temperature. Due to the fan for transport to the TO, a flow velocity is established. Furthermore, the exhaust gas is loaded with dust and has only low humidity.

Table 4: *Discontinuously measured parameters on the raw gas side of the TO.*

Paramter	Avg. value	Unit
Temperature	24.5	°C
Total dust	22.0	$\mathrm{mg\,m^{-3}}$
Exhaust air velocity	2.4	$\mathrm{m\,s^{-1}}$
Humidity	14.0	$\mathrm{mg\,m^{-3}}$

Table 5 shows the values of the average volume flow and total amount of process exhaust gas produced in one batch over 24 hours. The amount of process exhaust produced by plant three is twice as large as that produced by plants one and two.

The following quantities of process exhaust gas to be treated are produced in a batch in the respective production line. The same general conditions apply as for the process condensate, described in Section 2.2.1. So there are again no constant amounts, therefore the exhaust gas is also temporarily stored in the buffer tank, see Figure 2. Then it is fed to the TO and decomposed.

Table 5: *Process exhaust gas volume flow and quantity per batch generated by the production plants 1, 2 and 3.*

Production plant	$\dot{V}_{\mathrm{avg}}/\mathrm{N\,m^3\,h^{-1}}$	$V_{\mathrm{batch}}/\mathrm{N\,m^3}$
Plant 1 and 2	500	12 000
Plant 3	1000	24 000
Total	1500	36 000

2.3 Process waste treatment

The occurring process wastes are treated thermally, which is very common in the chemical industry. Since the exact composition and the pollutant loading of the process waste is often not known. There are different technologies for the thermal treatment of liquid and gaseous wastes. The thermal oxidation of process waste gases and the thermal waste water incineration are discussed below. After the process, the main constituents of the treated wastes are water vapor, nitrogen, carbon dioxide and oxygen. Depending on the pollutant composition of the raw waste stream being incinerated and on the operating conditions of the thermal oxidiser.

2.3.1 Thermal oxidation of waste gas

According to Brinkmann *et al.* [8], thermal oxidation, also often referred to thermal incineration, is the oxidation process of combustible gases in a waste gas stream, by heating a mixture of contaminants with air above its auto ignition point in a combustion chamber. The temperature is maintained at a high level for sufficient time to complete combustion. Equation (1) describes the exothermic process involved in the combustion of such a composition, as reported by Vatavuk *et al.* [9]. The VOCs are decomposed into carbon dioxide and water vapor with the addition of oxygen and fuel. If there are other pollutants in the exhaust gas, different compounds may also be formed, e.g. nitrogen oxides. Additional secondary treatment of the exhaust gases is then also necessary.

$$C_xH_yO_z + \left[x + \frac{1}{4}\,y - \frac{1}{2}\,z\right]\,O_2 \rightarrow x\,CO_2 + \frac{1}{2}\,y\,H_2O \tag{1}$$

As reported by Neuwahl *et al.* [10], the following advantages and disadvantages are associated with the treatment of waste gas by thermal oxidation.

+ Good and constant performance
+ Simple principle
+ Reliable in operation
+ Process integration of waste heat, steam generation or thermal oil heating is possible
– Emission of carbon monoxide and nitrogen oxides
– Risk of dioxin formation, when chlorinated compounds are incinerated
– Additional fuel needed, at least for start-up operations and VOC concentration below auto-ignition point (not cost effective with low concentrations and high flow)

2.3.2 Waste water incineration

Thermal waste water incineration is the oxidation of organic and inorganic waste water containments and the simultaneous evaporation of the aqueous part. It takes place at normal pressure and at temperatures between 730–1200 °C. The reaction products are carbon dioxide, water and other inorganic compounds. It is only self-sustaining if the organic load is sufficient to ensure adequate energy support for the vaporisation and heating of the water. With a low organic load, the incineration plant needs to be operated with supporting fuel. There is a high demand for the stability and corrosion resistance of the plant material, so combustion chambers are mostly built in ceramics. Incineration is often the treatment of choice to treat waste waters from chemical multi-product plants with toxic waste water streams, which cannot be routed to a conventional waste water treatment plant. The achieved TOC removal rates of such plants are typically in the order of > 99 %. [8]

According to Neuwahl *et al.* [10], the advantages and disadvantages associated with thermal waste water incineration are as follows.

+ High organic content will be nearly completley removed
+ Elimination of pollutants also possible with high salt concnetration
+ Waste heat can be used
– Low organic concentrations need supporting fuel
– Solid waste (bottom and fly ashes) need to be disposed of
– Incineration of sulphur and halogenated compounds might demand flue-gas treatment, causing waste water and solid waste

2.3.3 Combined system for liquid and gaseous wastes

There are systems which are suitable for the treatment of both, liquid and gaseous wastes. The TO, which is used at the company site for the treatment of the process condensate and process exhaust gas, works according to this principle. Figure 4 shows the design of such a typical incineration chamber. A common application of an incineration chamber is in the chemical industry for the incineration of liquid and process waste gas [10]. The basic design for the incineration chamber depends on temperature, gas residence time, turbulence and the availability of oxygen. These factors all affect the rate and efficiency of the combustion process. The operational temperature is chosen to ensure good destruction of the wastes fed to the chamber. Normally it is operated with a temperature from 900–1500 °C. The chamber is equipped with a burner, usually powered by natural gas. Since the combustion chamber must withstand high temperatures it is lined with ceramic. The gaseous and liquid waste is fed in via multiple inlets. The incineration chamber is fed with preheated primary air, to transport the fuel to the burner and to supply some of the combustion air. The added secondary air is recirculation air, which provides the necessary oxygen to complete the combustion. In addition, secondary air can

reduce nitrogen oxide (NO_x) formation during combustion. Since this air has less oxygen, local reducing zones are created. This leads to the breakdown of nitrogen monoxide (NO) in the exhaust gas by reduction to nitrogen (N_2). A heat exchanger is integrated directly into the combustion chamber, which is simply a pipe that is arranged around the chamber. Usually there is process steam generated or thermal oil is heated from access heat. After that, the approximately 350 °C hot exhaust gas is led out of the combustion chamber.

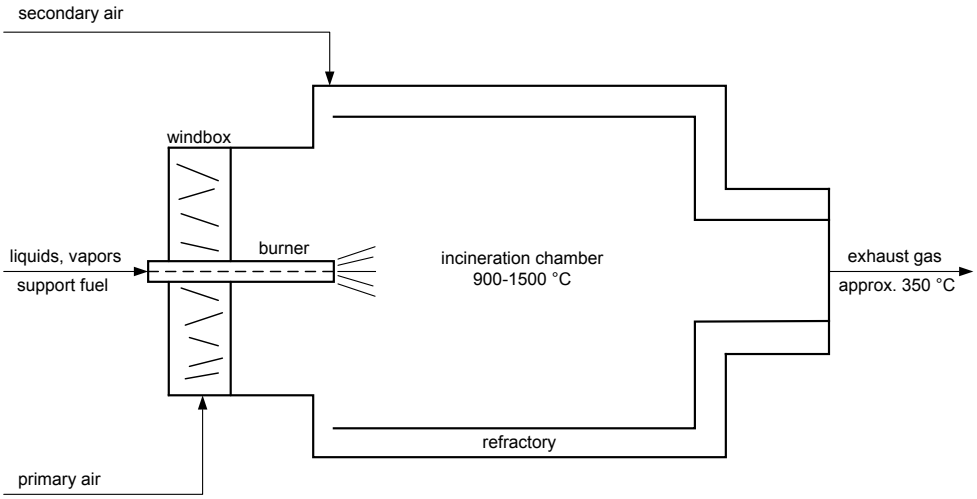

Figure 4: *Typical design of an incineration chamber for liquid and gaseous wastes, according to Neuwahl* et al. *[10].*

2.3.4 Thermal oxidizer

Two different TOs are operated, one for production plant one and two, the other for production plant three. The TO is also used to heat the thermal oil, thus partial recovery of thermal energy can be achieved. To ensure complete decomposition of the pollutants a temperature of at least 950 °C is required in the combustion chamber. The TO must always be in operation and may only be shut down for maintenance work. Therefore, the TO can be operated with variable power, nevertheless the temperature must not fall below the minimum temperature.

Table 6 shows the technical data of the two operated TOs. They essentially do not differ. The TO for production plant one and two has a power of 1162 kW. The minimum power, at which the TO can be operated is 150 kW. Of course the TO for production plant three is much bigger. It has a power of 3000 kW, but can only provide a maximum thermal oil heat output of 2000 kW. The natural gas consumption shows that the TO needs one tenth of the maximum flow, when operating with minimum thermal oil power of 205 kW. Both can reach temperatures up to 1150 °C.

Table 6: *Technical data of the TOs of the production plant 1, 2 and 3.*

Paramter	Plant 1,2	Unit	Plant 3	Unit
Volume combustion chamber	1300	L	19 792	L
Power	1162	kW	3000	kW
Combustion temperature	950–1150	°C	950–1150	°C
Gas residence time	2	s	2	s
Exhaust gas temperature	350	°C	350	°C
Max. thermal oil power	1162	kW	2000	kW
Min. thermal oil power	150	kW	205	kW
Min. natural gas volume flow	-	-	30	$N\,m^3\,h^{-1}$
Max. natural gas volume flow	-	-	300	$N\,m^3\,h^{-1}$

The industrial company must perform emission measurements of the exhaust gas annually, where several parameters are recorded, see Table 7. The sampling location is inside the 20 m high non-insulated steel chimney, after the exhaust gas cleaning system, at a height of 12.7 m, see Figure 5.

Table 7: *Average values and limits of the measured parameters during the emission measurement of the exhaust gas.*

Paramter	Avg. value	Unit	Limit value	Unit
Temperature	160	°C	-	-
O_2	5.2	Vol %	-	-
CO	24	$mg\,m^{-3}$	100	$mg\,m^{-3}$
NO_x	68	$mg\,m^{-3}$	150	$mg\,m^{-3}$
TOC	2	$mg\,m^{-3}$	20	$mg\,m^{-3}$

At the measuring point the exhaust gas has an average temperature of of 160 °C. But it still, continues to cool down during the discharge. According to official regulations, condensation of the vaporous substances in the exhaust gas must not occur in the chimney. In consequence the temperature may not drop below the dew point temperature, of 100 °C.

The comparison of the measured exhaust gas values with the values on the raw gas side, see Table 3, shows the separation efficiency of the TO. The CO and TOC levels can be drastically reduced, this ensures compliance with the specified limit values, given in Table 7.

2.4 Thermal oil circuit

Thermal oil is used as the heat transfer medium to provide the thermal energy required for synthetic resin production. Thermal oil is a heat transfer fluid (HTF) based on hydrogenated mineral oils. Table 8 shows the temperature range specified by the manufacturer at which the thermal oil can be used. For the production of synthetic resins a supply temperature of 290 °C is required.

Table 8: *Operating temperature range of the thermal oil, according to FRAGOL AG [11].*

Paramter	Value/°C
Min. Temperature	−18
Max. Temperature	325
Start of boiling	380

Figure 5 shows the piping and instrumentation of the thermal oil circuit of production plant three. Basically the structure of plant one and two are the same. This figure is used because there are the most accurate and recent records on plant three. The main part of the thermal oil circuit is the TO. It is fed with natural gas and preheated air to provide the necessary oxygen for combustion. The preheated air is provided by a heat exchanger working as preheater, which is fed with exhaust gas at 350 °C inlet temperature from the TO. Downstream the preheater the exhaust gas has a temperature of around 180 °C. Subsequent, it is discharged to the environment through the chimney at a temperature of 150 °C. The return temperature of the thermal oil is 265 °C, with the the heat exchanger inside the TO it is brought to the feed temperature of 290 °C. After that, the heated thermal oil is distributed to the different consumers by means of the thermal oil distributor, see Section 2.1.1. The maximum flow rate of thermal oil that can be supplied for plant three is 150 $m^3\,h^{-1}$. There is also a buffer tank which can store up to 5000 L thermal oil. Due to safety regulations, an expansion tank and a control cooler with at least one third of the capacity of the thermal oxidizer must also be provided. To prevent overheating of the system or of the thermal oil in the event of a malfunction. The blue lines in Figure 5 show an additional thermal oil heater, which could optionally be integrated into the system.

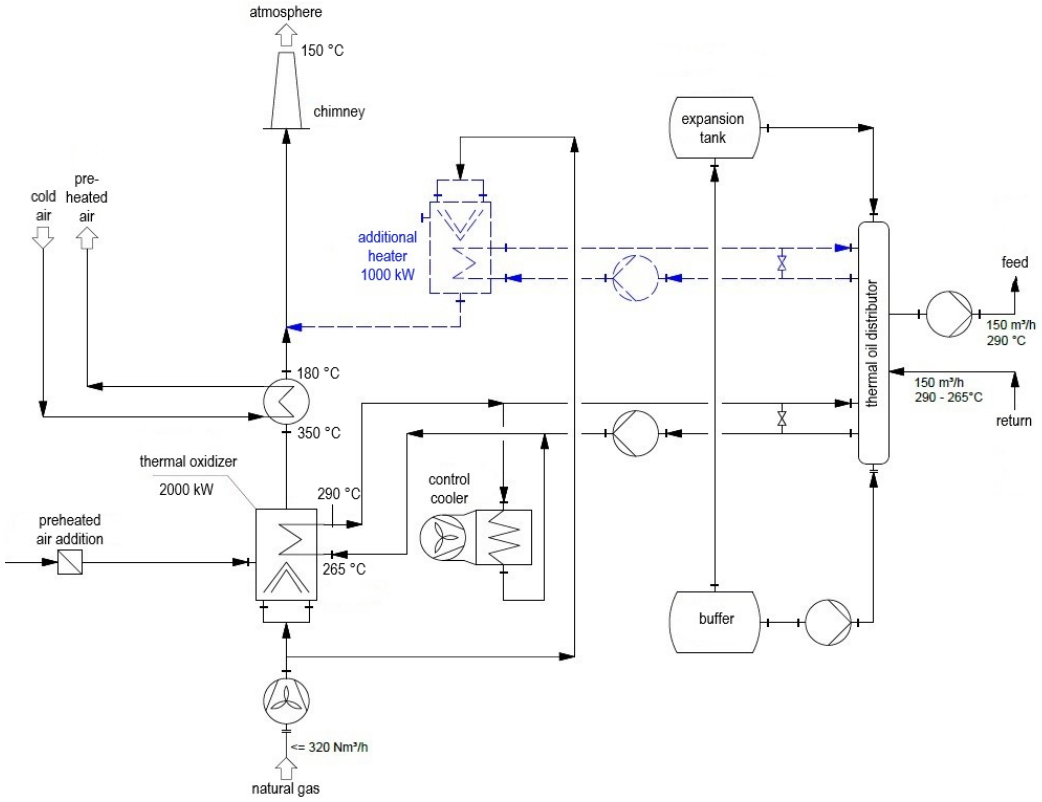

Figure 5: *Piping and instrumentation of the thermal oxidizer of production plant 3.*

2.4.1 Additional heater

There is an additional thermal oil heater to ensure the thermal energy supply of production plant one and two. This is a natural gas boiler with an output of 1250 kW. This additional heater is necessary because in some process phases more thermal energy is required than can be provided by the TO. If the feed temperature of the thermal oil falls below 275 °C, the additional heater switches on automatically, and switches off again when it reaches 285 °C.

For production plant three, the possibility of installing an additional heater was also provided during the planning stage. This will be realized at a later stage, as it is attempted to operate the plant without an additional heater. The possibility of providing the energy through alternative measures is also to be kept open.

2.5 Energy flow analysis

In order to identify potentials for energy saving and select alternative energy sources, it is essential to present the current energy consumption. The three main energy sources required are thermal energy for heating and cooling, as well as electrical energy. The thermal energy for heating required at the company site for synthetic resin production is provided by natural gas. The electrical energy required, is mainly for the plant control system, lighting, pumps and electric motors. The thermal energy for process cooling is provided by several water wells.

In the following, the determination of these energy flows is explained and also their magnitude is shown. The industrial company records the consumption of electricity and natural gas at their site at monthly intervals, since 2013. Based on this, the energy consumption can be determined. All data presented below refer to production plants one and two. Since plant three is not yet in operation, there is no consumption data yet.

2.5.1 Natural gas

The consumers which are operated with natural gas are the TO and the additional heater for thermal oil. The operating conditions and characteristics of the two gas boilers can be found in Section 2.3.

With the beginning of the year 2020, two gas meters were installed, which record the gas consumption for the TO and the additional heater. Therefore, only the data from 2020 onwards will be used. These gas meters record the natural gas consumed in cubic meters. A conversion factor of $1\,\mathrm{m}^3 \mathrel{\widehat{=}} 11\,\mathrm{kW\,h}$ has been set in the company. The meter readings are recorded once a week, so very accurate consumption data is available. In addition, it was documented when there was a malfunction or repair work, therefore non-representative data can be filtered out very well. After removing the non-representative data, the obtained consumption per week was added. This was used to calculate an average for the monthly gas consumption of the TO and the additional heater. The weekly consumption could then be converted to an average monthly and annual consumption. The time period considered was 01.01.2020–31.08.2022 to obtain the most recent data. The determined average consumption of the TO and the additional heater for thermal oil, of production plant one and two, are shown in Table 9.

Table 9: *Average natural gas consumption of production plant 1 and 2.*

Parameter	Monthly/kW h	Annual/kW h
TO	843 247.7	10 118 972.0
Additional heater	312 966.6	3 755 599.6
Total	1 156 214.3	13 874 571.6

This results in an average gas consumption of 13.87 GW h for one year. About 73 % of the consumption is accounted for the operation of the TO. The remaining 27 % is required by the additional heater for thermal oil.

2.5.2 Electrical power

The electricity consumers mainly include the lighting of the production halls, the plant control system, electric motors and pumps. In order to use the most current data, consumption from 2020 onwards will be used again. Unlike gas consumption, electricity consumption is only recorded on a monthly basis. The months in which were malfunctions or planned repairs are removed. An average value then could be formed over these monthly consumption. Thus, an average monthly and annual electricity consumption could be determined, the values are shown in Table 10.

Table 10: *Average electrical power consumption of the resin department.*

Period	Electrical power/kW h
Monthly	218 007.6
Annual	2 616 090.7

So the whole resin department consumes about 2.61 GW h electrical power per year. About 340 000 kW h are generated by the photovoltaic panels installed at the company site.

2.5.3 Cooling water

Cooling water is required for process cooling during the cooling phases in the manufacturing process, the condensator, the fractional column, the control cooler and for the cooling belt, see Section 2.1.1. It is provided by several water wells. It is also used in other departments at the company area. After use, it is returned to the ground through a percolation shaft.

The industrial company carried out a detailed cooling water evaluation in 2019. Average values for mass flow, inlet temperature and outlet temperature were determined there. These values could be used to determine the required cooling energy

consumption per hour. From this, the required cooling energy consumption for one month and one year could be determined, shown in Table 11.

Table 11: *Average cooling energy consumption of production plant 1 and 2.*

Period	Cooling energy/kW h
Monthly	487 923.8
Annual	5 855 085.9

The synthetic resin department receives the cooling water with maximum 15 °C. A temperature difference of 4.5 °C and 400 $m^3\,h^{-1}$ is available for cooling. The required cooling energy varies during the production process, on average the required cooling power is about 700 kW. There is a phase in the production process where cooling from 290 °C to 100 °C must be carried out in a time of 15 min, which requires about 1400 kW for a short time. During this phase it may happen that the 4.5 °C mark is exceeded, but on average the maximum difference must be respected.

2.5.4 Energy flow diagram

Based on the determined energy flows, a sankey diagram is created. By means of a sankey diagram, a clear presentation of the required energies can be achieved. Based on this, Section 3 identifies the potential energy savings and inefficiencies. The sankey diagram, Figure 6, shows the total consumption of thermal energy for heating and cooling, as well as electrical power. It also displays the thermal energy flow, but the exact process description can be found in Section 2.4.

The thermal energy for heating is provided by natural gas. The natural gas consumption is divided into two flows, one to the TO, which accounts for about 73 % and the other to the additional thermal oil heater, which includes the remaining 27 %. About 10 % of the natural gas is required to decompose the process waste in the TO. Another 10 % are dissipated by the control cooler to prevent overheating of the thermal oil. The remaining energy is needed to heat the thermal oil. The hot exhaust gas is used to preheat combustion air and then discharged into the environment. The thermal energy for cooling is supplied through cooling water, which is pumped from the water wells to the consumers of the first divison at the company site. After that it is stored in a cooling pool, where it has a temperature of about 15 °C. Starting from the cooling pool, the water is used for process cooling in the resin department. After use, it must have a temperature of max. 19.5 °C. Afterwards, the water is transported to the next division.

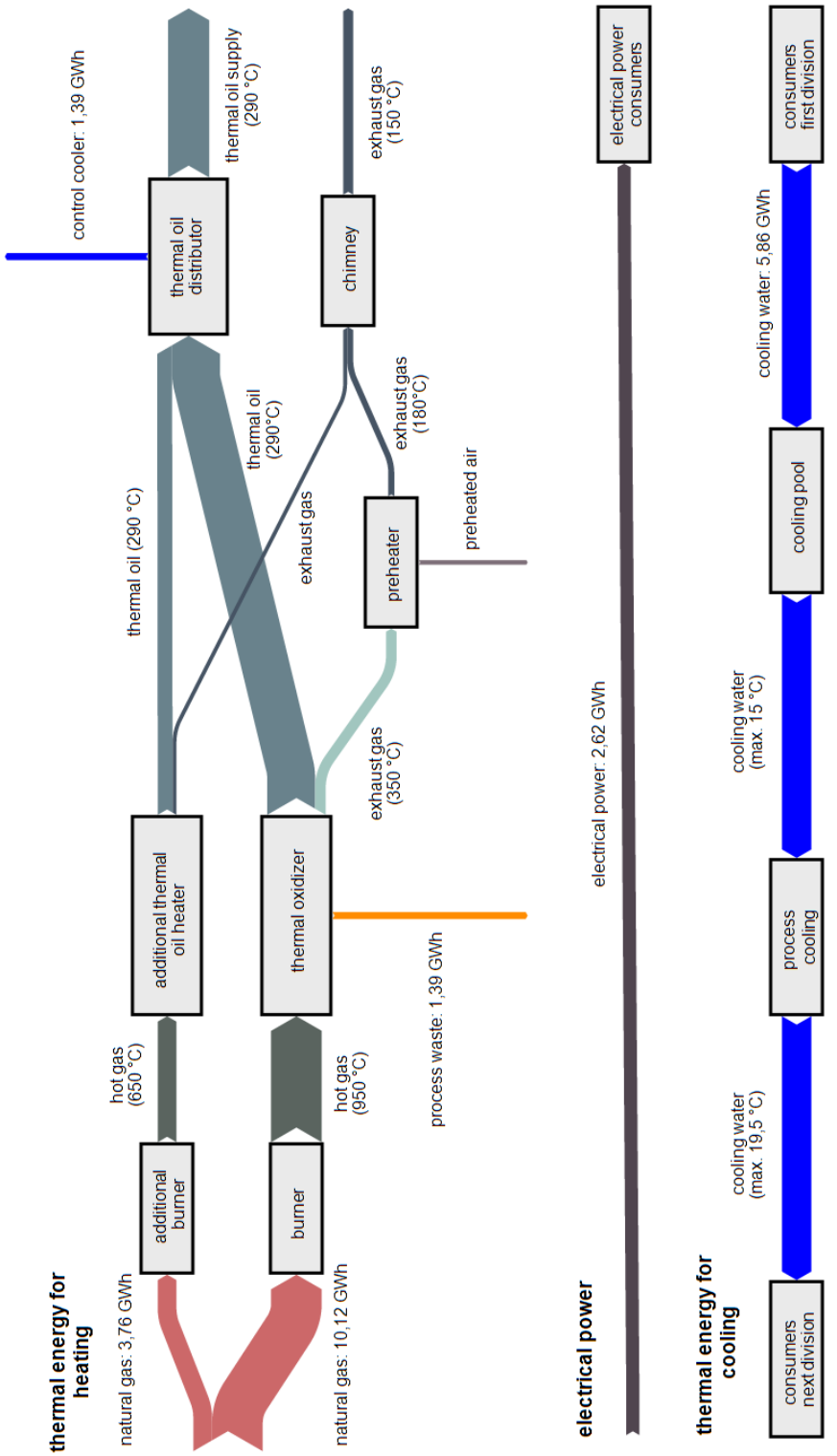

Figure 6: *Annual energy consumption of the resin department.*

3 Thermal energy optimization

In this section, the thermal energy required in the process is analyzed in more detail with the aim of identifying possibilities to increase the thermal energy efficiency. For this purpose, the batch process is examined closer in order to find the energy-intensive process phases. Furthermore, the possibility of WHR and the integration of TES systems are evaluated. Figure 7 shows a path with possible measures to minimize CO_2 emissions.

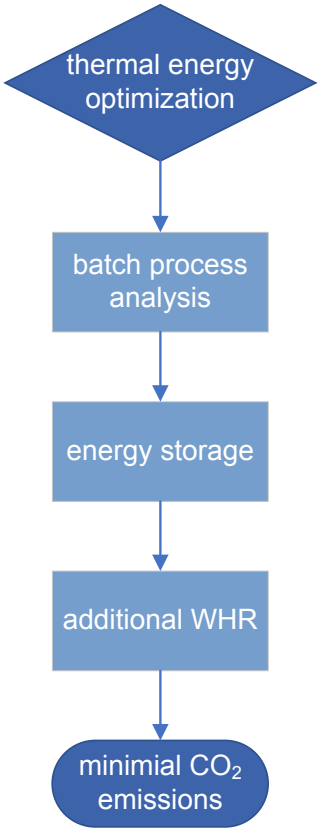

Figure 7: *Steps to optimize the thermal energy consumption and in consequence reduce the CO_2 emissions.*

3.1 Batch process analysis

Like described in Section 2.1 the synthetic resin production is carried out as batch production. Since it is a discontinuous process, there are phases where a lot of thermal energy is needed and phases where no thermal energy is needed at all.

The production process takes place in an STR, each plant has two. In both STRs, the same product is manufactured with a time delay. Figure 8 shows the thermal power demand of production plant three in the course of 24 hours. The diagram shows the thermal power demand in kilowatts over the elapsed process duration in minutes. The blue line in Figure 8 presents the thermal power consumption for the preheating of the liquid storage tank. The grey line includes various little consumers, which require a nearly constant amount of thermal power throughout the whole batch. Furthermore the thermal energy demand for STR one and two is displayed, it shows that the two reactors are operated in exactly the opposite way. There are two main heating stages during the production process. While the first heating stage is currently taking place in STR one, the second heating stage is underway in STR two. The reason for this is simpler plant operation and lower simultaneous thermal power consumption. After a short intermediate phase, the next batch starts, so this process repeats itself again.

Figure 9 shows the total thermal power demand of production plant three over the whole batch duration. For this, the graphs shown in Figure 8 are summed up. In addition, the minimal, 200 kW, and the maximal thermal output, 2000 kW, of the TO is presented. The maximum thermal output of the TO is reduced to 1820 kW, if large amounts of process condensate and process exhaust gas are simultaneously decomposed. The green line shows the required average thermal power over the entire process, which is about 1700 kW. Figure 9 shows, there are phases during the process where no thermal power is required at all, but the TO must still be in operation. The thermal oil circuit leads directly through the TO and oil is continuously pumped through, see Section 2.4. Because the circuit cannot be drained, the thermal oil would overheat during this phase and consequently start to crack. For this reason, the thermal oil must be cooled down with the control cooler, see Figure 5. There is a control cooler for production plant one and two, it has a capacity of 400 kW. The one for production plant three has a capacity of 800 kW. Both are designed as tube coolers and are fed with cooling water. The dissipated energy is lost in the process, as it is simply fed back into the ground with the cooling water, see Figure 6.

Figure 8: *Thermal power demand of the different consumers of production plant 3 during one batch of 24 hours.*

Figure 9: *Total thermal power demand of production plant 3 and thermal power output of the TO over one batch of 24 hours.*

3.2 Storage charging

In order to find suitable time slots for charging a TES system the data obtained in Section 3.1 is used. Sometimes the process needs very large amounts of thermal power, more than can be provided by the TO. At this time the required thermal power must be generated by the additional heater. For the entire batch there are about eight hours, where more than 2700 kW are required. Throughout the remaining 16 hours energy could be stored, because less thermal power is needed than could be generated by the TO. Figure 10 shows the thermal power which could be stored with a TES system, assuming the TO is operated with max. power during the entire batch. In addition, the thermal power which cannot be provided by the TO at peak times is displayed. The diagram shows, with the integration of a TES system, the additional heater could theoretically become redundant.

To get an overview how a TES system could be integrated into the existing production process another sankey diagram was created, see Figure 11. The already generated sankey diagram, see Figure 6, was used as reference. Figure 11 shows the integration of a TES system, could theoretically save approximately 2.18 MW h of natural gas per year, this corresponds to 15.7 % of the total consumption. Nevertheless, the same amount of thermal energy could be provided. The natural gas saved is made up of the energy dissipated by the control cooler, which could then be stored, and the elimination of the additional thermal oil heater.

Figure 10: *Theoretical max. thermal power which could be provided by a TES system and required power from the storage.*

Figure 11: *Expected annual natural gas consumption of production plant 1 and 2 with the installation of a TES system.*

3.3 Waste heat recovery

In this section, the possibility of additional WHR besides combustion air preheating is evaluated. This requires an understanding of the thermal oil circuit explained in Section 2.4. In addition, the data from the sankey diagram, see Figure 6, is used.

First the exhaust gas temperatures have to be examined. Like displayed in Figure 5, the temperature after the preheater is about 180 °C. This is an averaged temperature, because fluctuations occur during regular operation, due to the variable operating mode of the TO. This could lead to difficulties in implementation of WHR and must be taken into account in any case. The emission measurement, see Table 7, shows an average temperature of 160 °C at about halfway up the chimney. Further cooling in the chimney is assumed to be about 10 °C, until discharge into the environment. This results in an outlet temperature of 150 °C. Considering that condensation of steam in the exhaust gas can occur from 100 °C and therefore a maximum cooling down to about 110 °C would be practicable, a usable temperature difference of 40 °C results.

Figure 12 shows how a additional WHR unit could be integrated in the current production plant. The unused theoretical potential is about 0.6 MW h per year.

Figure 12: *Expected annual natural gas consumption of production plant 1 and 2 with a TES system and additional WHR.*

4 Alternative technologies

The identification of alternative technologies is essential to reduce the CO_2 emissions. Figure 13 shows the possible path from natural gas to zero emissions.

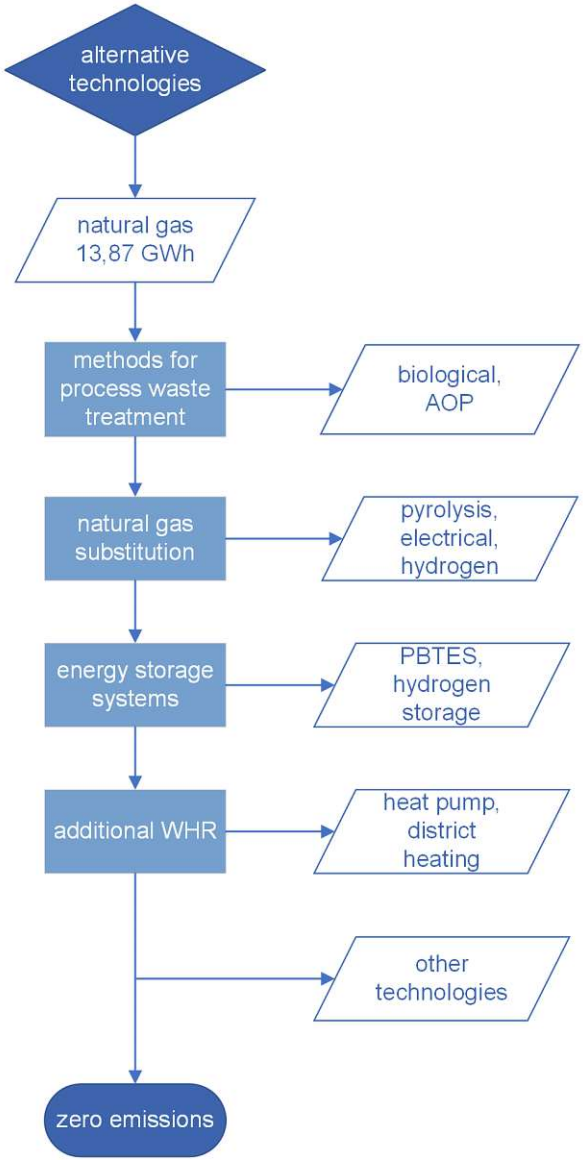

Figure 13: *Overview of the technologies that enable the path to zero emissions.*

To find alternative technologies a technology screening was carried out in the course of this thesis, which includes four main topics. The first one is about alternative technologies for process exhaust gas and condensate treatment. The next section discusses the options for providing process heat with other energy sources, in order to substitute natural gas. The third one covers various technologies for storing energy during the production process. The last section describes possibilities for additional WHR. All technologies mentioned in this chapter are discussed only theoretically, in order to be able to realize the actual implementation further investigations have to be done. In addition, there are other technologies that could be appropriate but are not covered in this thesis.

Currently, the process exhaust gas and condensate produced is treated with the TO. The natural gas required for this is about 10 % of the total demand, see Figure 6. The supply of the process heat has a much higher ratio. However, very high temperatures of min. 950 °C are required for the decomposition of the pollutants, see Section 2.3.4. Due to the high temperature for thermal decomposition, this method is comparatively energy intensive. Therefore, the identification of alternative ways to treat the process waste is crucial. The aim of the post-treatment is to remove the pollutants or to recover substances from the waste streams. In order to comply with the specified limit values and to enable discharge into the sewerage system, respectively the environment. According to Reineke *et al.* [12], the suitable processes for purification are basically based on adsorptive, absorptive, thermal, catalytic and biological mechanisms. Like explained in Section 2.2 the main pollutants are VOCs, especially MIBK.

4.1 Biological methods for waste treatment

There are methods for biological treatment of exhaust gas and condensate, the methods discussed in this section are biofiltration, bioscrubbling, biotrickling and membrane bioreactors. In general spontaneous changes in exhaust stream composition are unfavorable for biological systems, but there are methods which can cope with that.

There are fundamental requirements which must be fulfilled in order to enable biological purification. Firstly the pollutants must be micro-biologically degradable. For degradation of volatile substrates, they have to be present in dissolved form. So, the substances must have enough water solubility. The defining parameter for this is the Henry-constant. According to Sander [13], the Henry-volatility-constant of MIBK is $46\,\mathrm{Pa\,m^3\,mol^{-1}}$. The value of the constant decreases with increasing solubility. The different methods have specific ranges for which Henry-constants they can be used. To enable effective purification, a high mass transfer rate from the gas to the liquid phase is crucial. Therefore, the largest possible contact area between the gas phase and the liquid phase must be provided. Even with solid fillers in filters, a liquid film is present between the gas and solid phases in which the microorganisms grow. The working range for biological plants is the mesophilic area, from 20–40 °C [12]. For optimal performance of the microorganisms, the environmental conditions, like temperature, water supply and pH value must be respected. When the operating conditions of the plant change, adjustment times must be expected. Since the microorganisms are affected by changes in living conditions.

If, for process engineering, economic or ecological reasons, a system with only one purification system cannot be realized, then combinations of biological and other processes are used. According to Reineke *et al.* [12], for ensuring the suitability of biological purification methods, pilot plants must be operated for at least three months.

4.1.1 Biofiltration

Biofilters have a solid matrix on which the microorganisms in the biofilm multiply. It is the easiest way to clean waste gases biologically. Biofilters are designed as open or closed packed bed reactors and have a lifetime of several years. The packing consists of bulk layers with organic materials, like leaves, soil, wood chips, bark, compost or fibrous peat. To improve the structure some inorganic materials like polystyrene, expanded clay or volcanic slag are added. The organic substances of the bulk layers serve as nutrients for the microorganisms, thus the packing material is continuously degraded. A water and biofilm forms on the surface of the packing, where the biological degradation of the pollutants takes place. The waste gas is biologically oxidised to carbon dioxide, water, inorganic salts and biomass. [8], [12]

According to Reineke *et al.* [12], the used filter materials must fulfill specific conditions:

- The largest possible effective surface area, for mass transfer and microorganism colonization.
- Porosity and homogeneity, about 50 % air space, to ensure a good and uniform flow. The cost for operating the fans is thus kept limited, due to the associated pressure drop.
- High water retention capacity to prevent dehydration, as heat is generated by the biological reaction.
- Low degradation rate, so that service life of the filters is ensured.

Figure 14 shows the schematic of a typical biofiltration process. Biofilters can be divided into open and enclosed filters, with single- or multi-layers. To transport the exhaust gas through the filter, a fan is used for open ones, while a compressor is installed for closed ones. Open filters are supplied with the exhaust gas from the bottom to the top, the velocity is about 0.02–0.1 $\mathrm{m\,s^{-1}}$ [12]. The water soluble pollutants are transported into the aqueous phase on the surface of the filter material and so reach the microorganisms. A humidification device is arranged in ahead of the outlet of the purified gas. This is for providing the required water and simultaneous removal of degradation products of the filter. Water and other residues accumulate at the bottom of the filter, these must be removed. In areas with a cold climate, the suitability of open biofilters is restricted. An enclosed biofilter has a distribution system which supplies the waste gas stream uniformly to the filter. The waste gas stream flows from the bottom to the top or in reverse direction. Closed systems in the form of containers are often used for organic solvents. They allow better control of process parameters, such as humidity or temperature, and analysis of the cleaning performance. Due to the lower costs, mainly open biofilters have been used so far. However, they are also less efficient, so closed filter systems with controlled inlet and outlet of exhaust gases are preferable. [8], [12]

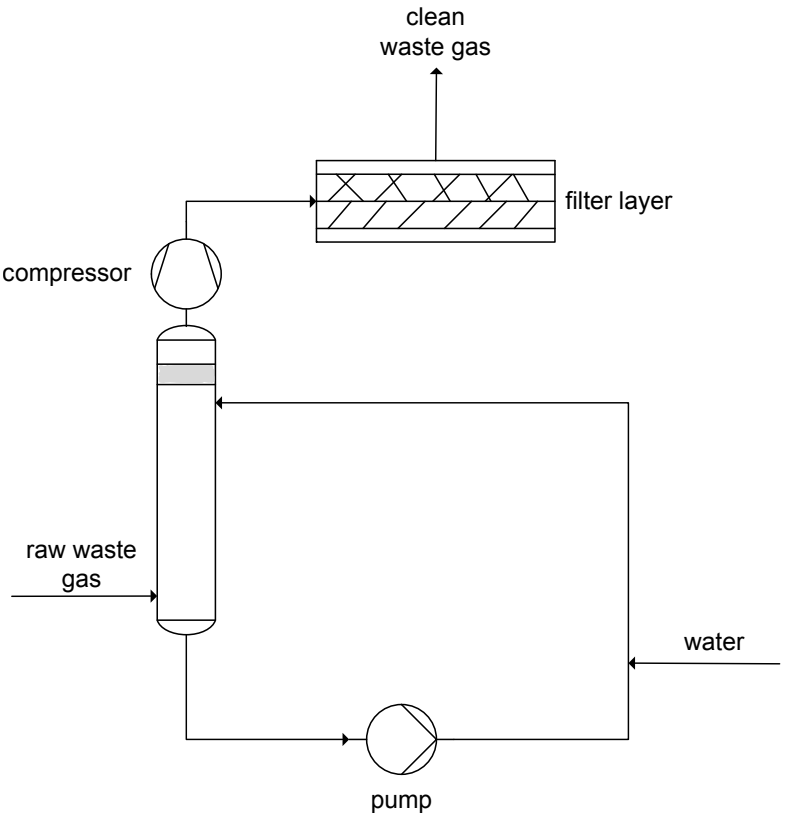

Figure 14: *Schematic of a biofiltration process with a closed biofilter, according to Angerer [14].*

The height of the filter material should be between 0.5–1.5 m, distributed over a maximum of three layers. Best practices show that the filter material should be at least 1 m. The residence time for an effective abatement depends on the pollutant concentration, but should be at least 30–60 s. The reached specific load of the filter bed is about 100–500 $\mathrm{N\,m^3\,h^{-1}}$ per $\mathrm{m^2}$ of filter surface. [8]

For regulation of the moisture balance in the filter, a humidifier or a gas scrubber is used. To avoid clogging the relative humidity should be kept below 60 %. If the waste gas stream has a temperature higher than 38 °C, cooling is necessary. This can be done by mixing with cold air or with a heat exchanger. The filter material has a lifetime of about 0.5 to 5 years, depending on the composition of the gases. [8]

Typical parameters, which are associated with biofiltration are shown in Table 12.

Table 12: *Parameters associated with biofilters, according to Brinkmann* et al. *[8].*

Parameter	Value	Unit
VOC input concentration	200–2 000	$\mathrm{mg\,N^{-1}\,m^{-3}}$
VOC abatement efficiency	75–95	%
$\dot{V}$ exhaust gas	100–200 000	$\mathrm{N\,m^3\,h^{-1}}$
Temperature	15–38	°C
Temperature, thermophilic bacteria	50–60	°C
Pressure	Atmospheric	-
Pressure drop	5–20	mbar
Oxygen content	near ambient level	-
Relative humidity	> 95	%
Water consumption	5	$\mathrm{m^3}$ per $1000\,\mathrm{N\,m^3}$
Energy consumption	< 1	$\mathrm{kW\,h}$ per $1000\,\mathrm{N\,m^3}$

The following advantages and disadvantages can be connected with biofilters, as reported by Brinkmann *et al.* [8].

+ Low investment and operating costs
+ Simple construction
+ In combination with adsorption and absorption, also suitable for barely soluble compounds
+ High efficiency for biodegradable compounds
+ Low amount of waste water and waste material
– Dried-out peat and compost filter beds are difficult to rewet
– Relatively bulky design
– Poisoning and acidification of the biomass has to be prevented
– Fluctuations in the exhaust gas stream conditions have a significant impact on the performance
– Packing is sensitive to dust clogging
– Limited control (including pH)
– Energy consumption for cooling, if the temperature of the incoming gas is too high

4.1.2 Bioscrubbling

A bioscrubber works according to the principle of physical absorption. A schematic of a typical bioscrubber is shown in Figure 15. The pollutants are dissolved in the absorbent and then degraded by the microorganisms. Unlike biofilters, the microorganisms are in a supension, which is added from the top of the reactor and then absorbs the pollutants in the waste gas. Bioscrubbers are designed as cylindrical plants, where the raw waste gas is injected into the reactor from the bottom. Due to the small specific gas-liquid mass transfer range, bioscrubbers are restricted to pollutants with low Henry-constant of lower than $25\,\mathrm{Pa\,m^3\,mol^{-1}}$. So bioscrubbling is not suitable for the degradation of MIBK, but for further investigation it is necessary to explain the method. The degradation of the pollutants takes place in a separate tank. Bioscrubbers have larger degradation capacities per reactor volume compared to biofilters because of the higher organism density. [12]

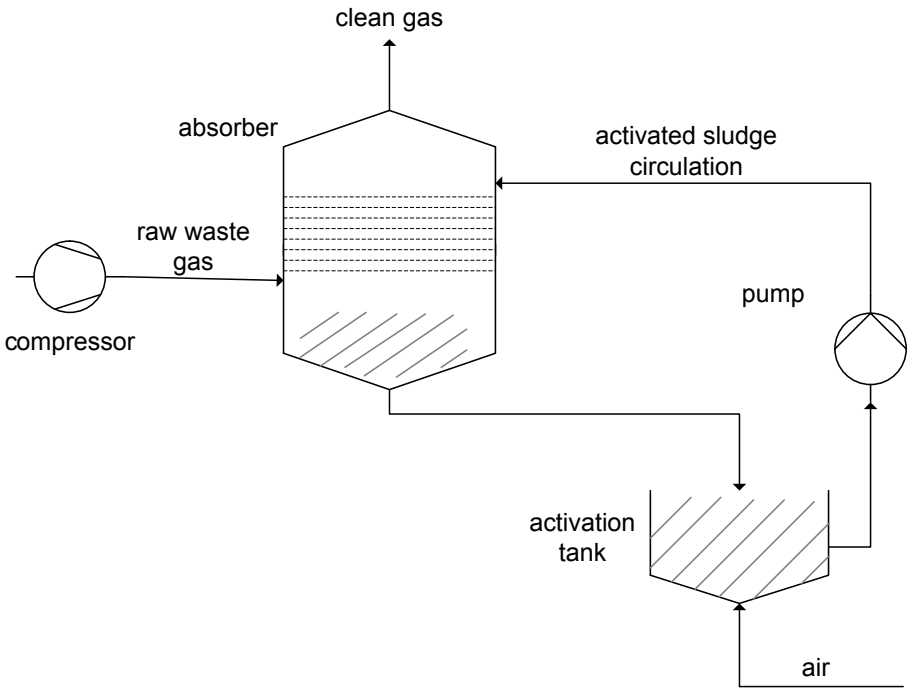

Figure 15: *Schematic of a bioscrubber, according to Brinkmann* et al. *[8].*

4.1.3 Biotrickling filter

The design of a biotrickling filter (BTF) corresponds to a bioscrubber with packed beds. Biotrickling is a method used for exhaust gas purification. Figure 16 shows a biological trickle-bed reactor. The aqueous phase is continuously circulated through the bed of inert material, which consists of irregular bulk material, like rings, saddles, or structured packing.

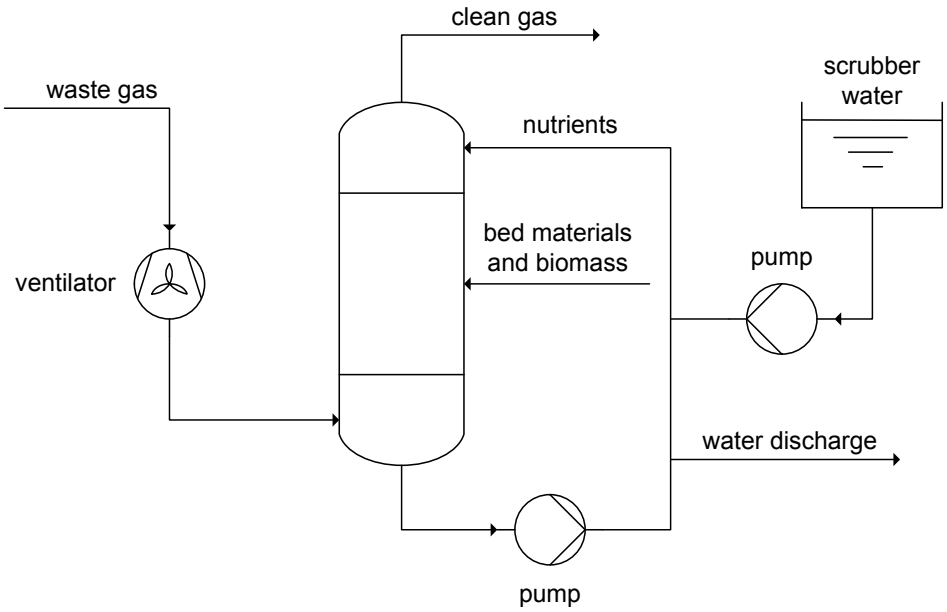

Figure 16: *Schematic of a typical biotrickling process, according to Auweraert* et al. *[15].*

The water in the system has two tasks, the solvent function and its action as a rinsing medium. For maintaining the humidity balance for the microorganisms the packing is sprayed with a liquid film. During the trickling down, the pollutant-absorbing water is regenerated at the same time. The waste gas is fed from the bottom, where it is added into the washing solution. The washing solution is sprayed on to the packing and afterwards circulated. For well soluble and degradable compounds, the contact time of gas and liquid is about 5–20 s. For more difficult degradable components, the contact time must be significantly higher [12]. The biological activities in the bioscrubber increase the salt concentration in the circulation water. It must therefore be discharged when the salt concentration becomes too high and disposed of. Afterwards, fresh water is fed into the system again. Depending on the contaminants or degradation products, surplus activated sludge has to be disposed of, e.g. by incineration. Typical parameters, which are connected with the operation of BTFs are shown in Table 13.

Table 13: *Parameters associated with biotrickling, according to Brinkmann* et al. *[8].*

Parameter	Value	Unit
VOC input concentration	400–4 000	$mg\,N^{-1}\,m^{-3}$
VOC abatement efficiency	70–99	%
$\dot{V}$ exhaust gas	1 000–500 000	$N\,m^3\,h^{-1}$
Temperature	15–40	°C
Pressure	Atmospheric	-
Pressure drop	1–10	mbar
Microorganism concentration	$>$ 15	$g\,L^{-1}$ dry matter
Energy consumption	$<$ 1	kW h per $1000\,N\,m^3$

As reported by Brinkmann *et al.* [8], the following advantages and disadvantages are linkable with BTFs.

+ Biodegradation of absorbed compound
+ Suitable for medium concentrations of acidifying compounds which contain sulphur, chlorine and nitrogen
+ Low pressure drop
+ Small pH corrections are possible
+ Average investment and operating costs
+ Compact construction and reasonable space requirements
+ Low energy consumption and thus limited CO_2 emissions
+ Little use of additives
+ Better reliability than a biofilter
– Fluctuations, of type and concentrations of the pollutants, in the intake air stream conditions have a significant impact on effectiveness
– Poorly soluble compounds are more difficult to abate
– High concentrations of toxic and acidifying substances should be prevented
– The biomass can obstruct the packing
– More complex to construct than a biofilter
– Production of waste water, depending on the compounds abated

4.1.4 Moving-bed trickling filter

The moving-bed trickling filter (MBTF) is a modification of the BTF, it is used for the combined treatment of process exhaust gas and condensate. A schematic of a typical MBTF is shown in Figure 17.

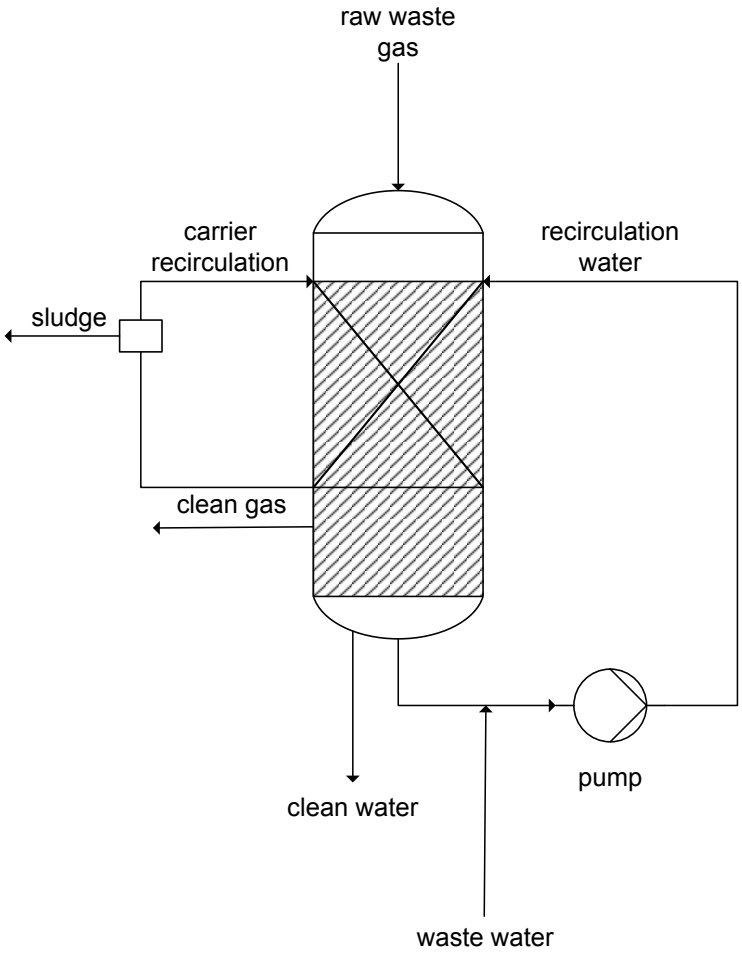

Figure 17: *Schematic of a typical MBTF process, according to Auweraert* et al. *[15].*

The main component of the MBTF is a tank, which is filled with 50–150 m^3 of specially shaped synthetic balls. These balls are grooved, microorganisms grow in and on them and decompose the incoming pollutants. The waste water is pumped to the top of the reactor where it is sprayed over the filter bed. As the waste water trickles through the filter bed, it is purified of pollutants. Afterwards, the treated water is collected in a buffer tank so that any particles present can deposit. The raw waste gas is injected into the reactor together with the waste water trough a fan. Special sections of the sieve plate at the bottom of the reactor ensure good separation of air and water. Afterwards, the cleaned air can be discharged into the environment. As with any biological treatment, some of the pollutants are

converted into biomass. This increases the amount of biomass in the reactor, which can cause clogging in the trickling filter. To avoid clogging in the MBTF, a part of the bioballs are pumped to the upper section of the reactor, where they are cleaned by a cyclone. The cleaned balls are then returned to the process and the separated sludge is disposed of. In order to determine the effectiveness of the MBTF, the gas feed and outlet concentrations are measured. The composition of the absorbing water is monitored by continuous measurement of the parameters pH, temperature, oxygen concentration and conductivity. Typical parameters, which are associated with MBTF are shown in Table 14.

Table 14: *Parameters associated with MBTF, according to Brinkmann* et al. *[8].*

Parameter	Value	Unit
VOC input concentration	100–10 000	$\mathrm{mg\,N^{-1}\,m^{-3}}$
VOC abatement efficiency	80–95	%
$\dot{V}$ exhaust gas	5 000–40 000	$\mathrm{N\,m^3\,h^{-1}}$
$\dot{V}$ condensate	$<$ 200	$\mathrm{m^3\,h^{-1}}$
Temperature	10–45	°C
Pressure	Atmospheric	-
Pressure drop	1–10	mbar
Energy consumption	1–5	kW h per $1000\,\mathrm{N\,m^3}$

Confirming to Brinkmann *et al.* [8], the following advantages and disadvantages are connected with MBTF.

+ Combined or seperate treatment of exhaust gas and condensate is possible, leading to a compact installation
+ Can handle very large loads
+ Free of clogging
+ Suited for gas streams with very fast and large variations of concentration
+ Barley sensitive to acidification when processing nitrogen, sulphur or chlorine compounds
– Investment costs depend to a great extent on the prices of raw materials
– Less suited for small gas streams, lower than $5000\,\mathrm{N\,m^3\,h^{-1}}$, no limitation when processed simultaneously with condensate
– Construction height up to 20 m

4.1.5 Membrane bioreactor

The membrane bioreactor (MBR) process is an option for biological waste gas and water treatment for many domestic and industrial applications. They are particularly well suited for the purification of air contaminants that are difficult to dissolve in water, e.g. dichloroethane, benzene, xylene [8], [12].

In Figure 18 the schematic of a MBR is shown, it is the combination of a membrane process, e.g. microfiltration or ultrafiltration, with a bioreactor. There are two types of typical setups. Vacuum-driven membrane units, which are embedded in the aerated part of the bioreactor and pressure-driven membrane systems located outside the bioreactor. The membranes used are made of a wide variety of composite materials. They have different chemical properties, like solubility and selectivity. And also various physical properties, like mechanical strength, thickness, porosity. A reactor consists of several hundred hollow fibers, which are packed to bundles, to achieve the largest possible exchange area. These hollow fibers are flushed with microorganisms in a nutrient solution. The lipophilic substances are dissolved in the membranes and then degraded on the outside by the microorganisms. The nutrient solution with the organisms is pumped around, so that the cells are supplied with oxygen. The degradation products, like CO_2 are discharged. [12]

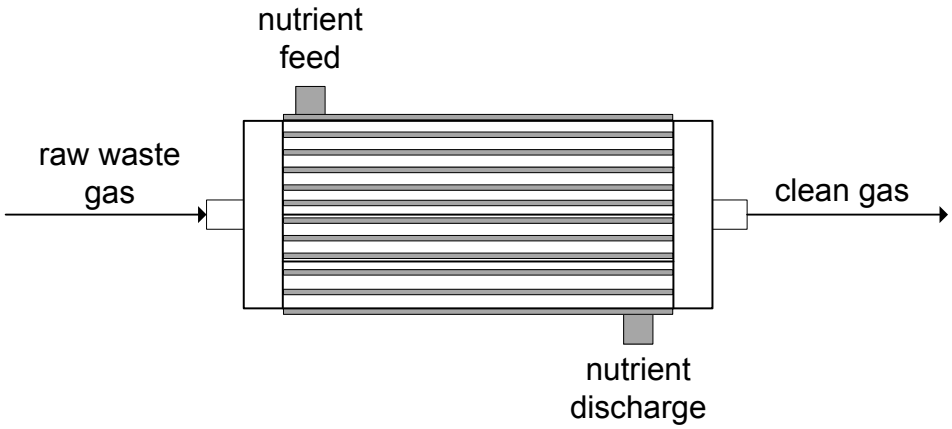

Figure 18: *Schematic of a MBR, according to Reineke* et al. *[12].*

The following advantages and disadvantages can be associated with MBRs, as reported by Brinkmann *et al.* [8].

+ Small space requirements
+ Reduced amount of sludge, compared to conventional activated sludge system
+ MBRs can keep a good efficiency with inlet concentration variations, whereas keeping the same performance with a conventional activated sludge plant requires larger equalisation tanks than with MBRs
+ Can operate at much higher solids concentrations, 8000–12 000 $\mathrm{mg\,L^{-1}}$, compared to the conventional activated sludge system, 3000–6000 $\mathrm{mg\,L^{-1}}$
+ Once abrasion and pressure variations are under control, ceramic membranes have constant performance without aging loss
– High energy consumption because of the large pressure drop and high air-flushing rate required for the operation
– Membranes are sensitive to abrasion
– Silicones in the influent must be prohibited as they rapidly plug the membranes
– Pressure variations must be controlled as membranes are quite sensitive

4.2 Advanced oxidation processes for waste treatment

This section discusses advanced oxidation processes (AOPs) for treating process exhaust gas and process condensate. The examined methods include photocatalytic oxidation with titanium dioxide, wet oxidation with hydrogen peroxide and supercritical water oxidation.

AOPs are genuinely efficient in treating various toxic organic pollutants. In general the efficiency depends on the physical and chemical properties of the pollutant as well as on the operating conditions. The costs for installing AOPs are low, but the operating costs are high, due to the chemicals and energy required. To limit the costs, AOPs are often used for pretreatment combined with biological processes. Also the combination of different AOPs is a possibility to enhance the removal of pollutants while reducing the costs. There are many methods classified under the definition of AOP. An advanced oxidation normally uses strong oxidizing agents, catalysts and irradiation, separately or in combination. The processes are carried out at low temperatures and pressures. [16]

4.2.1 Photocatalytic oxidation with titanium dioxide

Photocatalytic oxidation (PCO) is a method for degradation of pollutants, like VOCs, in waste gas and water. A two-step reaction process with a catalyst, like titanium dioxide (TiO_2), and an irradiation system, to activate the catalyst, takes place. For the activation of the catalyst ultraviolet rays or sunlight can be used.

Due to the simultaneous effect of UV rays and TiO_2, a part of the water vapor in the air is transformed into two strong oxidizing agents. Which are hydroxyl radicals ($HO\cdot$) and superoxide ions (O_2^-), these decompose the organic impurities to carbon dioxide. When illuminating a photocatalytic surface with UV light, a positive hole (p^+) and an electron (e^-) are formed. Through the positive hole, either the pollutant is oxidized directly, or water is oxidized to OH-radicals. While the electron reduces the oxygen adsorbed on the photocatalyst (TiO2). As reported by Thiruvenkatachari *et al.* [17], PCO works according to the mechanism shown in Equations (2)–(6).

$$TiO_2 \xrightarrow{hv} e^- + p^+ \tag{2}$$

$$e^- + O_2 \rightarrow O_2{}^- \tag{3}$$

$$p^+ + Organic \rightarrow CO_2 \tag{4}$$

$$p^+ + H_2O \rightarrow HO\cdot + H^+ \tag{5}$$

$$HO \cdot + Organic \rightarrow CO_2 \tag{6}$$

The system is suitable for both, continuous and batch operation, and can be scaled according to throughput requirements. Either a suspended or an immobilized photocatalyst can be used. The advantage of a suspended catalyst is that it can be recovered. But on the other hand with an immobilised catalyst, the process is clearly simpler, whether a batch or a continuous flow is used. When treating waste gas, the process is especially effective with low pollutant concentration, up to $30\,\mathrm{g\,m^{-3}}$, and low volume flows, $1500\,\mathrm{m^3\,h^{-1}}$. Maximum efficiency is achieved at a relative humidity of 40 %. [8]

As reported by Brinkmann *et al.* [8], high destruction efficiencies of more than 99 % were recorded for the treatment of waste water. As an example, a plant treating $15\,\mathrm{m^3}$ per week would require about 24 kW h of electrical power. Table 15 shows the advantages and disadvantages associated with PCO when using TiO_2 slurry and immobilised.

Table 15: *Advantages and disadvantages of different catalysts, according to Brinkmann* et al. *[8].*

Photocatalyst	Advantages	Disadvantages
TiO_2 slurry	• Readily available • Relatively inexpensive • Highly photoactive • Higher surface area, $50\,\mathrm{m^2\,g^{-1}}$ • No mass transfer effects	• Need to remove slurry afterwards • Can coagulate and lose activity
TiO_2 immobilised	• No replacement of catalyst afterwards • No coagulation • Easy to replace	• Not readily available • Lower surface area than slurry • Adherence and robustness problems

Coronado *et al.* [18] have studied the PCO of ketones, including MIBK, with TiO_2 in more detail. It was found that water can strongly increase the PCO rate. Therefore, in the treatment of gases, the efficiency is strongly dependent on the relative humidity.

There are also recent research results on PCO with TiO_2. Assadi *et al.* [19] have conducted a study with the aim of investigating the photocatalytic degradation of VOCs of the ketone group, such as MIBK, in a fluidized bed photoreactor. The strong influence of humidity was also found there. He *et al.* [20] have studied the treatment of waste gas from a paint plant by the combination of a BTF and PCO. It was observed that the VOC degradation by the combination of BTF and PCO is very effective. The removal rates of the VOCs ranged from 79.4–99.8 %.

4.2.2 Wet oxidation with hydrogen peroxide

Wet oxidation with hydrogen peroxide is used to remove organic pollutants from waste water. The aim is to reduce TOC, as well as to increase the biodegradability of the pollutants in the waste water. The method is based on the Fenton reaction. The organic pollutants contained in the waste water are oxidized by hydroxyl radicals. The radicals are produced by a reaction of hydrogen peroxide (H_2O_2) with a ferrous ion catalyst, like $Fe_2{}^+$. The reaction is carried out in acidic conditions, typical reaction parameters are listed in Table 16.

Table 16: *Typical reaction parameters for wet oxidation with hydrogen peroxide, as reported by Brinkmann* et al. *[8].*

Parameter	Range	Unit	Comment
Temperature	100–150	°C	-
Pressure	2–5	bar	-
pH	1–5	-	Typically 2–4
H_2O_2	1–3	%	-
Residence time	30–60	min	-
Catalyst	10–100	$mg\,L^{-1}$	Fe, Cu, Mn

The most efficient way of the technique is achieved when used as pretreatment, followed by a biological process. A process schematic of a typical plant for wet oxidation with hydrogen peroxide is shown in Figure 19.

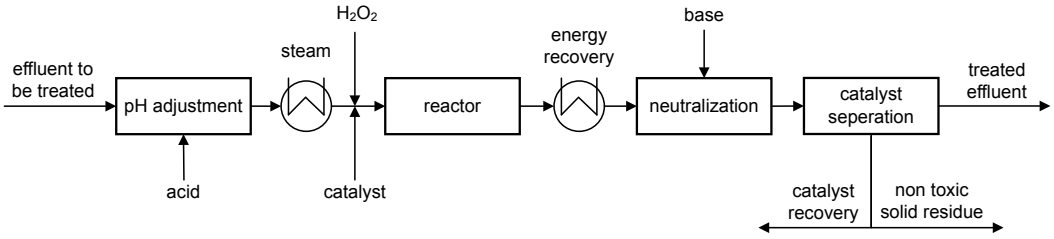

Figure 19: *Process schematic of wet oxidation with hydrogen peroxide, according to Brinkmann* et al. *[8].*

First, acid is added to the waste water to adjust the pH value to the required level. Then the medium is heated to a temperature of at least 100 °C by a heat exchanger. The heat exchanger is fed with steam or an other heat transfer medium. After the addition of H_2O_2 and the catalyst, the reaction takes place in a continuous STR. The necessary residence time is about 30–60 min. With another heat exchanger a partial energy recovery can be reached. Now the secondary treatment of the waste water follows. The pH value is adjusted to a slightly alkaline level in order to flocculate and recover the catalyst. Precipitation takes place in the decanter by adding flocculation agent. Finally, the waste sludge is separated from the purified

water with a centrifuge or a filter press. Parameters, which are associated with the operation of a plant for wet oxidation with hydrogen peroxide are shown in Table 17.

Table 17: *Parameters associated with wet oxidation with hydrogen peroxide, as reported by Brinkmann* et al. *[8].*

Parameter	Value	Unit
TOC ranges	100–20 000	$mg\,L^{-1}$
TOC abatement efficiency	70–99	%
MIBK input concentration	11 000	$mg\,L^{-1}$
MIBK abatement efficiency	99	%

For TOC concentrations higher than $10\,000\,mg\,L^{-1}$, a multi reactor system is needed, because not more than 4 % of H_2O_2 can be added per reactor vessel. The energy consumption of the process depends on the amount of TOC to be removed and on the amount of H_2O_2 used. If more than 2 % of H_2O_2 are added, or the TOC concentration is higher than $3000\,mg\,L^{-1}$, the process surpasses the autothermal area. Then the excess heat can be used.

According to Brinkmann *et al.* [8], the following advantages and disadvantages are related to wet oxidation with hydrogen peroxide.

+ Compared to other bulk oxidants, hydrogen peroxide is inexpensive and easy to handle
+ Large flow rate fluctuations can be managed
+ Short residence time, therefore small vessel volume
+ Easy to integrate in existing plants
+ Can be integrated with other treatments, e.g. biological
– Limitations mainly from need of pH control and sludge generation
– Hydrogen peroxide requires an appropriate storage and handling to avoid risk of explosive decomposition
– Sludge formation

4.2.3 Supercritical water oxidation

The supercritical water oxidation (SCWO) takes place in the supercritical region of water. That means at temperatures higher than 374 °C and pressures above 22.1 MPa [8]. Figure 20 shows a schematic of an SCWO plant. The waste water is caught in a tank, then a high-pressure pump brings the water to supercritical pressure. Afterwards the feed is preheated in the economiser. At start-up, or if the waste water has less than 4 % organic fractions, the feed has to be heated further, through a gas fired boiler, to reach the supercritical temperature. With the addition of liquid oxygen, the temperature in the reactor increases to about 600 °C. The

reactor effluent is used for the preheating in the economiser. The remaining thermal energy is used for the operation of a recovery steam generator. Finally, the water is returned to atmospheric conditions with a cooler and a valve. Then liquid and gas separation is possible. So the organic waste water content is reduced to carbon dioxide, nitrogen and water.

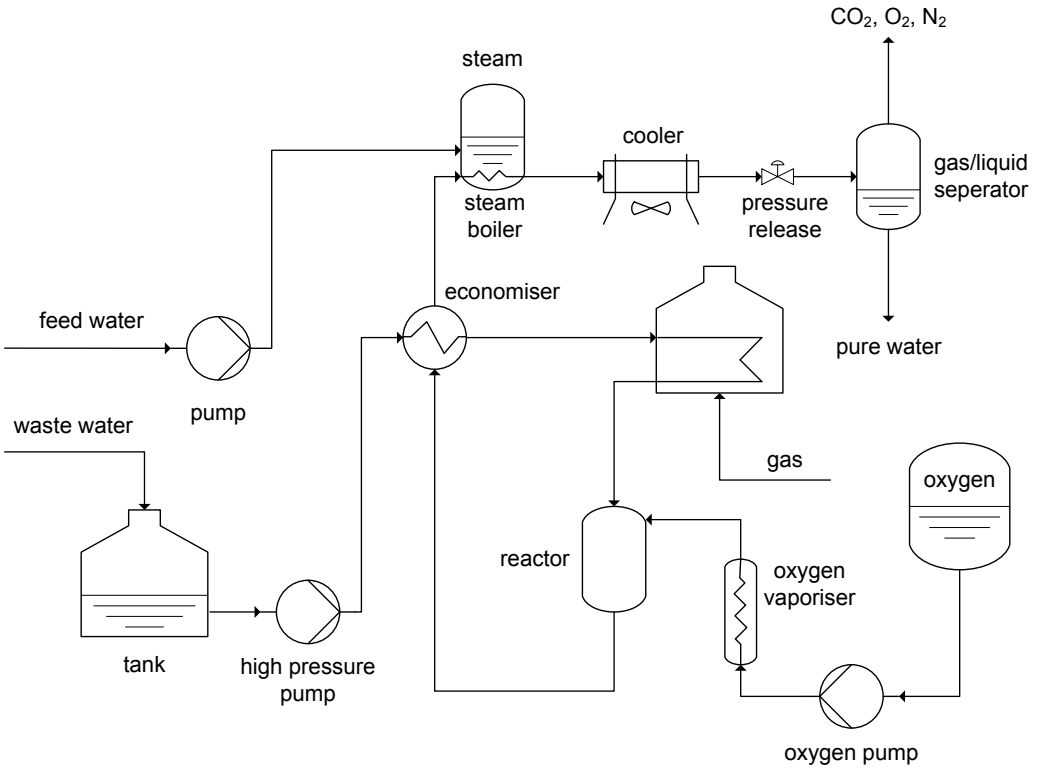

Figure 20: *Schematic of a SCWO plant, according to Brinkmann* et al. *[8].*

Depending on the components of the treated waste water, other compounds may also be formed. These must then be treated in waste gas purification plants. During the whole process a monitoring of the operating parameters, like pressure, temperature and oxygen content is necessary. Table 18 shows some parameters which are required when operating a SCWO plant.

Table 18: *Parameters associated with SCWO, as reported by Brinkmann* et al. *[8].*

Parameter	Range	Unit
Temperature	400–600	°C
Pressure	25	MPa
Reaction time	30–60	s
TOC abatement efficiency	> 99	%

According to Brinkmann *et al.* [8], the following advantages and disadvantages are related to SCWO.

+ All organic substances are destroyed regardless of its content
+ Very high destruction efficiency is achieved at relatively low temperatures, resulting in NO_x-free emissions
+ No dioxins are generated
+ Very short reaction time is necessary
+ Can be combined with other downstream treatments
– Traces of nitrous oxide (N_2O) and acetic acid are likely to be found
– Inorganic solids precipate and might cause corrosion
– Elevated chloride concentrations lead to increased corrosion thereby requiring specific types of steel

4.3 Supply of process heat

Currently, fossil fuels, in the form of natural gas, are used for thermal energy supply at the industrial company. Especially for high-temperature processes, the use of fossil energy is still common. To minimize CO_2 emissions, another energy source must be identified. Therefore, a technology screening is being conducted to find opportunities to replace fossil fuels. Three different technologies are discussed, which could supply the required temperature of 290 °C. These are electrical power, hydrogen, and the pyrolysis of powder coating residues.

4.3.1 Electrical power

Providing thermal energy with the help of electrical power is one way to replace fossil fuels, such systems are called power-to-heat (P2H). There are different ways to generate thermal energy with electrical power. The two most common technologies are heat pumps and electric boilers. Due to the required temperature level of 290 °C, heat pumps are currently out of the question. Since according to Agora *et al.* [21], a maximum of 200 °C can be achieved with so-called "very high temperature heat pumps".

Electric boilers are used to bring a heat transfer medium to a high temperature with electrical power. The boiler is filled with a heat transfer medium, e.g water, steam or thermal oil. The boiler is equipped with one or more heating electrodes, which are brought directly in contact with the heat transfer medium. The heating electrodes are fed with electrical power and thus heat up the transfer medium. According to Agora *et al.* [21], in combination with downstream electric superheaters, temperatures of about 500 °C can be reached. The efficiency of electric boilers is almost 100 %.

As reported by Agora *et al.* [21], the following advantages and disadvantages are related to the operation of electric boilers.

+ Low investment costs
+ No waste heat source needed
+ High efficiency
+ Easy to integrate in existing plants
– Electric grid infrastructure required
– Very high electrical power requirement
– Max. 500 °C can be reached

Combination of P2H and TES allows electrical energy to be converted into thermal energy and stored at the same time. Thus, flexibility can be created and peak loads can be balanced. There are market-ready technologies for this purpose. These systems basically all work according to the same principle. Thermal energy

is generated from electrical energy with the help of a P2H module. This is mainly done by means of a heat pump or electric boiler. The thermal energy generated can be used immediately. If less or no thermal energy is needed, it can be stored by integrating a TES system. The TES system is charged by a hot HTF and, if required, discharge can take place in an analogous way. There are different types of TES systems, see Section 4.4.1. With the combination of P2H and TES, temperatures of up to 1000 °C and storage periods of up to 2 weeks can currently be achieved. This allows electrical energy to become an alternative to gas, oil and coal.

4.3.2 Hydrogen

Hydrogen will play a crucial role in the energy transition toward renewable sources. However, there are different approaches for which areas hydrogen should be used. Especially for the supply of high-temperature heat, the use of hydrogen is controversial, according to Agora *et al.* [22]. Because the direct electrification would be possible, some ways to do this are discussed in Section 4.3.1. Hydrogen is needed especially where it serves as a reagent or raw material, such as for steel and plastics production. Since hydrogen production requires a lot of electricity and entails losses of about 30 %. [22]

There are some advantages and disadvantages associated with the use of hydrogen as an energy carrier, to substitute natural gas.

+ Can replace natural gas directly
+ Existing infrastructure can continue to be used
+ Green hydrogen is CO_2 neutral
– Electric grid infrastructure required
– Very high power requirement
– Comparatively high losses
– Limited storage options

Electrolysis is the splitting of a chemical compound through the use of electrical power. The process is carried out in an electrolyzer. This requires two electrodes, anode and cathode, a direct current source and an electrolyte, e.g. water or alkaline compounds. During electrolysis of water, two hydrogen molecules and one oxygen molecule are obtained from two water molecules, see Equation (7).

$$2\,H_2O_{\,(l)} \rightarrow 2\,H_{2\,(g)} + O_{2\,(g)} \tag{7}$$

As reported by Shiva Kumar *et al.* [23], currently four different processes for water electrolysis are known, these differ mainly in the electrolyte used and the operating conditions. These are alkaline, anion exchange membrane (AEM), proton exchange membrane (PEM) and solid oxide water electrolysis. The principle of operation is

the same for all four processes. Table 19 and 20 show the characteristics and the advantages and disadvantages of the different types of water electrolysis.

Table 19: *Technical characteristics of the different water electrolysis technologies, according to Shiva Kumar* et al. *[23].*

	Alkaline	AEM	PEM	Solid oxide
Voltage range	1.4–3.0 V	1.4–2.0 V	1.4–2.5 V	1.0–1.5 V
Temperature	70–90 °C	40–60 °C	50–80 °C	700–850 °C
Cell pressure	< 30 bar	< 35 bar	< 70 bar	1 bar
Efficiency	50–78 %	57–59 %	50–83 %	89 %
Lifetime	60 000 h	$> 30\,000$ h	up to 80 000 h	20 000 h
Development status	Mature	R&D	Commercial	R&D

Table 20: *Advantages and disadvantages of the electrolysis technologies, as reported by Shiva Kumar* et al. *[23].*

Technology	Advantages	Disadvantages
Alkaline water electrolysis	• Well established • Commercial for industry • Noble metal-free catalysts • Relatively low cost • Long-term stability	• Limited current densities • Crossover of gases • High conc. electrolyte
AEM water electrolysis	• Noble metal-free catalysts • Low conc. electrolyte	• Limited stability • Under development
PEM water electrolysis	• Commercial • Higher current densities • Higher gas purity • Compact system design • Quick response	• Cell costs • Noble metal catalysts • Acidic electrolyte
Solid oxide water electrolysis	• High working temperature • High efficiency	• Limited stability • Under development

Shiva Kumar *et al.* [23] have summarized in the study the suitability for industrial application and the development status of the four technologies for water electrolysis.

Alkaline water electrolysis is a well established technology for green hydrogen production. It is commercial in the industry up to the multi-megawatt range. Nevertheless, challenges such as current density, cell efficiency and crossover of the gases need to be improved. In order to store and transport the hydrogen, it must be com-

pressed. Therefore, the low pressure in the cell results in high energy consumption for compression. But for now the alkaline water electrolysis is a favorable system for large-scale applications.

AEM water electrolysis is the latest developed technology, aiming to overcome the disadvantages of alkaline and PEM water electrolysis. The major advantages of this technology are the lower cost of catalyst and electrolyte. To make AEM water electrolysis interesting for large-scale applications, the limited lifetime and efficiency must be improved.

PEM water electrolysis is commercial for industrial applications and has a few advantages compared to alkaline water electrolysis. These include high operating current density, high purity of gases and higher outlet pressure. However, the major challenge are the costs of the components, e.g for the noble metal catalysts.

Solid oxide water electrolysis is a technology in development stage. It has similar major benefits to other electrolysis technologies. The high operation temperature reduces the power consumption for splitting water into hydrogen and oxygen drastically, which results in much higher efficiency. It does not require the use of noble metal catalysts. However the low lifetime is a big issue, for industrial application it needs to be improved.

4.3.3 Pyrolysis of powder coating residues

The industrial company is currently conducting a feasibility study on the further utilization of powder coating residues. These are residues that are surplus during the application of the coatings. The waste is collected and transported to their site. There, synthesis gas could be generated by pyrolysis of the powder coating residues. Typical pyrolisis plants can treat waste volumes of up to $1000\,\mathrm{kg\,h^{-1}}$.

An analysis was carried out to determine the suitability for pyrolysis of the powder coating residues. Table 21 shows the results of the elemental analysis of the powder coating residues. The main component is with more than 65 % organic carbon.

Table 21: *Element analysis of the powder coating residues.*

Element	Value/ wt%
Carbon	65.3
Oxygen	27.6
Hydrogen	5.9
Nitrogen	0.8
Chlorine	0.1
Others	0.3

Table 22 shows the higher heating value (HHV) and lower heating value (LHV) of the powder coating residues and, for comparison, natural gas. The powder coating residues have only a slightly smaller HHV as well as LHV than natural gas.

Table 22: *HHV and LHV of the powder coating residues and natural gas.*

Component	HHV/kW h kg^{-1}	LHV/kW h kg^{-1}
Natural gas	8.80	7.93
Powder coating residues	7.30	7.00

Furthermore, a pyrolysis test has already been carried out, which results are very promising. The synthesis gas produced could then be used to provide the necessary thermal energy. For this purpose, a special burner was developed for optimum combustion of the pyrolysis gases. The remaining coke after pyrolysis amounts to about 15 %, which must then be processed elsewhere.

The annual consumption of natural gas is 13.87 GWh, as calculated in Section 2.5. Equation (8) shows the theoretical amount of powder coating residues required to provide the same energy.

$$m_{\text{pcr}} = \frac{E_{\text{ng}}}{HHV_{\text{pcr}}} = \frac{13\,874\,571.6\,\text{kW h}}{7.3\,\text{kW h kg}^{-1}} = 1\,900\,626.2\,\text{kg} = 1900.6\,\text{t} \tag{8}$$

According to the industrial company the available powder coatings residues mass is about 2500 t per year, so this would theoretically be enough to cover the demand. This process could create a sustainable circular economy and at the same time replace natural gas.

There are main advantages and disadvantages, which can be related to pyrolysis of powder coating residues.

+ Can replace natural gas directly
+ Existing infrastructure can continue to be used
+ Only other burner required
+ Circular economy
– Coke must be processed
– Powder coating residues must be collected from customers
– Permission for incineration

Agora *et al.* [2] has conducted a study on climate-neutral industry, it also discusses the pyrolysis and gasification of waste plastics. Pyrolysis is seen as an essential element for the development of a circular economy, in order to achieve a climate-neutral chemical industry. Under the condition, that 100 % electricity from renewable sources is used.

4.4 Energy storage systems

Energy storage systems are crucial in the transition to renewable energy. Since the production of electricity from e.g. solar and wind power is not constant, systems are needed to store the energy produced when it is not needed. This can be used to compensate power grid fluctuations and ensure a continuous supply. There are different types of energy storage systems, the most important ones are based on thermal, electrical and chemical principles. The implementation of an electrical energy storage system is currently not relevant for the industrial company, since the generated electrical power is consumed directly in the company. If it comes to the expansion of the own electrical power production, e.g. by further photovoltaic surfaces, then an electrical energy storage could be a suitable technology. So this section presents different technologies that could be used to store energy during the production process, which work on thermal and chemical principles.

4.4.1 Packed bed thermal energy storage

Especially TES are an important tool for the industry for waste heat utilization in an ideal way. There are three different types of TES systems, sensible heat, latent heat and thermochemical energy storage systems. They mainly differ by storage type and storage duration. Packed bed thermal energy storages (PBTES) belong to the group of sensible heat TES systems. Figure 21 shows a schematic of a typical PBTES system.

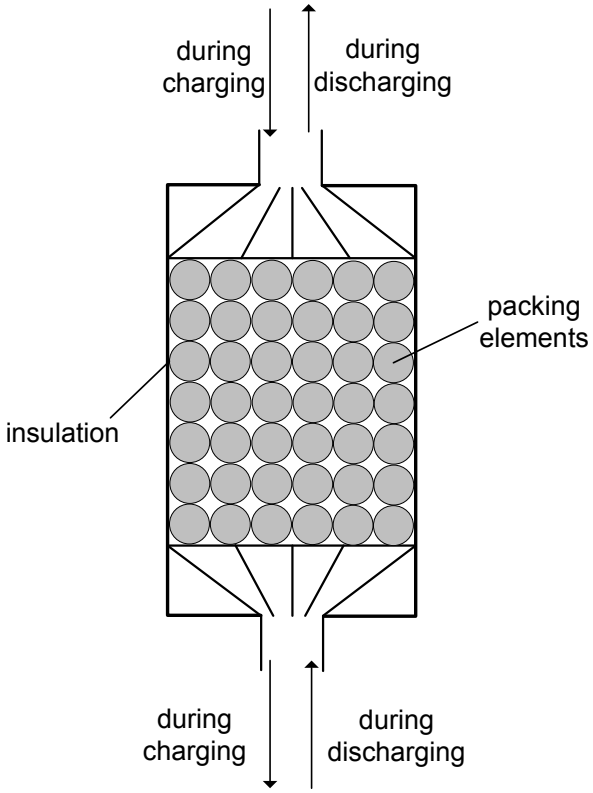

Figure 21: *Schematic of a PBTES system, according to Gautam* et al. *[24].*

PBTES consist of a insulated vessel, which is filled with loosely packed storage materials, like rocks or steel slag. The PBTES is charged with a HTF, which flows through the packed bed. Various substances can be used as HTF, gases, e.g. air, but also various liquids, like water. Normally, the flow direction during the charging process is from top to bottom. The energy from the HTF is stored by the storage medium. If the stored thermal energy is required, the cold HTF flows through the PBTES in the opposite direction. As a result, the stored thermal energy in the storage medium is transferred to the HTF.

Research and development of PBTES systems has primarily been focused on theoretical analysis and materials research. The experience with large-scale systems over

longer periods is very limited. Therefore, prior to any potential implementation of a PBTES, detailed studies must be conducted to determine suitability. The main advantages and disadvantages of PBTES systems are listed below, according to Trevisan *et al.* [25] and Schwarzmayr *et al.* [26].

+ High power rates
+ Wide temperature range
+ Low-cost storage material
+ Direct heat transfer between HTF and storage material
+ High maximum temperature
– Limited capacity due to mechanical constraints
– Reduced heat transfer efficiency over time due to corrision and settling
– Pressure loss of the HTF
– Thermocline degradation over longer storage periods

The main advantage of PBTES system is the possibility of using low-cost, unprocessed materials as storage medium. Some of these different storage materials are listed in Table 23.

Table 23: *Examples for different storage materials in PBTES systems, according to Adebiyi* et al. *[27], Esence* et al. *[28], Ortega-Fernández* et al. *[29], Schlipf* et al. *[30], Touzo* et al. *[31], and Zavattoni* et al. *[32].*

Material	Inventory	Unit	Capacity/MW h	T_{max}/°C
Rock	381.2	m^3	100	570
Basaltic pebbles	3.54	m^3	1.45	800
Steal slag	2300	kg	0.4	800
Bauxite rubble	16 000	kg	1.9	600
Silicia sand	10 560	kg	1.5	600
Zirconium dioxide	646	kg	-	1040

4.4.2 Hydrogen storage systems

If hydrogen production is constant, but demand is not constant, storage is necessary. The possibility of storage is also an effective way of compensating fluctuations in the power supply. If the electricity required for hydrogen electrolysis is produced in-house, this is often dependent on the time of day. For example, photovoltaic systems which produce electricity during the day. There are several ways to store hydrogen, basically following physical and chemical principles. The established ways to store hydrogen are physically, these are compressed and liquefied hydrogen storage.

Compressed hydrogen storage is the storing of hydrogen in a pressure vessel. In this process, the hydrogen is compressed with compressors up to 700 bar. Since hydrogen has high specific energy, of 33.3 $\mathrm{kW\,h\,kg^{-1}}$, but a very low energy density under normal conditions, see Table 24. The energy required for compression to 700 bar is about 12 % of the energy content of the hydrogen. [33]

Liquefied hydrogen storages are designed as kyro storages, where the hydrogen is converted into liquid form by cooling it to temperatures below the boiling point of −252.8 °C. The hydrogen is stored in special insulated vessels with liquid nitrogen jackets. The energy required for liquefaction is about one-third of the whole hydrogen energy content. [33]

Table 24: *Energy density of hydrogen under different conditions [33].*

Conditions	Energy density/$\mathrm{kW\,h\,L^{-1}}$	Comment
Normal	0.003	-
Compressed	1.3	to 700 bar
Liquified	2.4	at −253 °C

4.5 Technologies for additional waste heat recovery

Like explained in Section 3.3 there is still potential to use waste heat from the exhaust gas. But there are also special requirements for the possible technologies for additional WHR due to the changing exhaust gas conditions. The different technologies which might be considered are discussed below. This section is intended to show various options, but further detailed research must be conducted to determine the suitability of the technologies described.

4.5.1 Heat pump

The heat pump is a very efficient form of heat supply, since the heat source used only needs to have low temperatures. Electrical power is used to utilize energy from a cold medium to heat another medium. Figure 22 shows a schematic of a heat pump.

A heat pump essentially consists of three system elements, according to [34]:

- Heat source system, for extracting the energy from the heat source.
- Heat pump consisting of evaporator compressor, condenser and expansion valve.
- Heat boiler plant, responsible for using or feeding the heat brought to a higher temperature level by the heat pump.

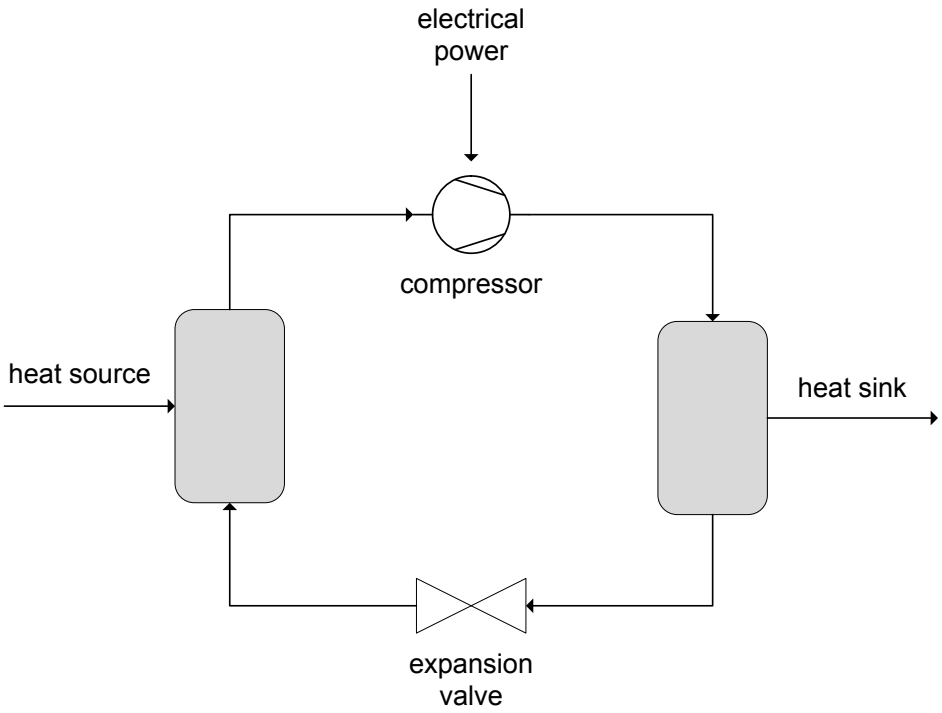

Figure 22: *Schematic of a heat pump.*

The heat pump operates according to a closed thermodynamic cycle in which there is a refrigerant. The refrigerant absorbs energy from the heat source at low pressure and temperature causing vaporization. The heat source can be industrial waste, but also environmental heat. The heated refrigerant is compressed, increasing the temperature. Now the heat can be transferred and utilized at high temperatures. After the heat has been released, the refrigerant is expanded with a expansion valve. This reduces the temperature and the pressure, the refrigerant condenses and is thus restored to its initial state. The cycle can then start again. Current systems can reach temperatures of about 150 °C, using a downstream compressor temperatures up to 200 °C can be generated [21].

The temperature difference between the heat source and the heat sink defines the efficiency of the heat pump. To evaluate the efficiency of a heat pump, the coefficient of performance (COP) is used, see Equation (9).

$$COP = \frac{|Q_{\mathrm{H}}|}{W_{\mathrm{in}}} = \frac{\text{Heat quantity output}}{\text{Work input}} > 1 \tag{9}$$

So the COP indicates how many kW h of heat output can be provided by one kW h of electrical power.

The Carnot efficiency describes the difference between the actual achievable efficiencies and the theoretical maximum. As reported by Agora *et al.* [21], current heat pump systems achieve a Carnot efficiency of 40–60 %. Figure 23 shows the achievable COPs depending on carnot efficiency and the temperature difference between heat source and sink.

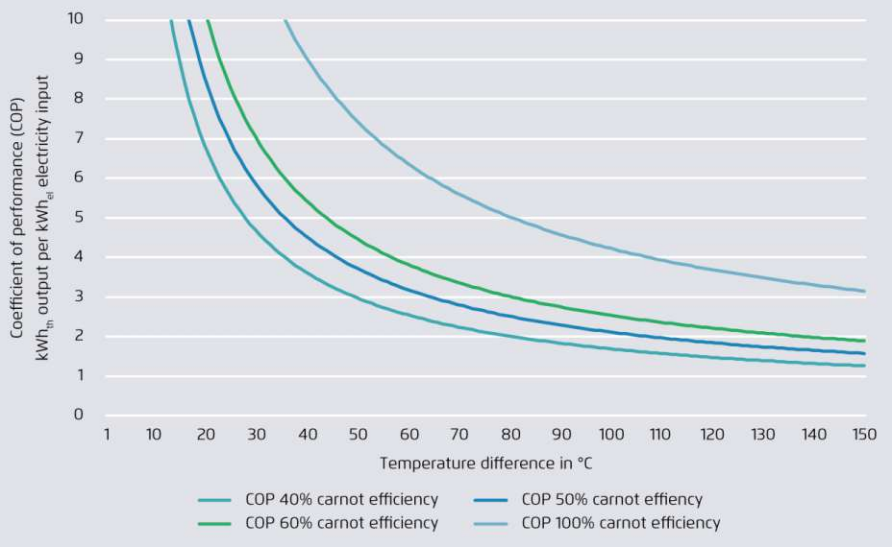

Figure 23: *COP of heat pumps, according to Agora* et al. *[21].*

4.5.2 Building/district heating

Currently, the building heating as well as the hot water for sanitary facilities at the company site is provided by district heating. The district heating is produced by the thermal waste incineration plant not far from the company site.

One possibility for additional WHR would be to feed the available energy into the district heating network. By installing an additional heat exchanger, the remaining energy from the exhaust gas could be used to heat water. This hot water could then be fed into the district heating network. Furthermore it could be an option, to use the generated hot water directly on site. Feeding it into the company's internal heating network would be an efficient solution for using the available energy.

4.5.3 Low temperature process heat

If hot water is generated, it could also be used internally to provide energy for other processes. Hot water is not required directly in the production of synthetic resins, but subsequent processes in the further processing of powder coatings could be considered for this.

5 Results and Discussion

This section provides an overview of the options available for the industrial company identified in this thesis. The major long-term perspective is to support the direction to independency of fossil fuels until 2040.

A strength, weakness, opportunity, threat (SWOT)–analysis is carried out to clearly present the various aspects of the identified technologies. This should serve as a starting point for further decisions. The results of this analysis are presented in Section 5.1.

5.1 SWOT-analysis

The SWOT analysis is a method of strategic planning, it is helpful when it comes to the use of new technologies. With the SWOT analysis, the advantages, disadvantages, opportunities and risks that can arise from the introduction of a new technology are presented.

Figure 24 shows the results of the performed SWOT-analysis. The SWOT analysis is divided into three subgroups, which are energy efficiency, waste treatment and process heat. The three subgroups contain the various identified methods that meet the requirements. First, the results of the energy efficiency group are discussed. It shows that the integration of a PBTES system is a very promising option, because of the high power rates and low costs. A big opportunity, which comes with the integration of a PBTES system is the replacement of the additional thermal oil heater. But a challenge will be the integration of the PBTES system into the existing plant. The additional WHR through various measures, such as heat pump, district heating or low temperature process heat, would need to be investigated in more detail. Especially the cost/benefit factor will play a major role. However, the additional WHR is also a crucial step for a zero emissions policy. The waste treatment sector shows, that biological methods, as well as AOPs may be a good way for post-treatment of process waste. On the one hand a big opportunity is that discharging of waste water into the sewerage system would be possible. On the other hand major modifications at the production plant would be required. So the integration of such a system is also associated with a significant investment. Especially a MBTF, see Section 4.1.4, and PCO, see Section 4.2.1, could fulfill the requirements very well. For the supply of process heat, pyrolysis of powder coating residues is a sustainable solution, which could also be realized in the near future. On a long-term basis, direct supply by electrical power has major advantages over

the use hydrogen for the provision of process heat.

The presentation of the results is now divided into three groups. On the one hand, measures to support short and mid-term scenarios to reduce CO_2 emissions. On the other hand, possibilities to enable a CO_2 neutral production in the future. These scenarios are then discussed in more detail in the following Sections 5.2–5.4.

	Strengths	Weaknesses	Opportunities	Threats
Energy efficiency				
PBTES	• Low costs • High power rates	• Integration in the plant • Pressure loss	• Replace additional heater for thermal oil	• No long term studies for large-scale systems
WHR	• Additional WHR • Energy savings	• Costs vs. benefit	• Higher energy efficiency • Lower CO_2 emissions	• Condensation of flue gas must be investigated in more detail
Waste treatment				
Biological	• Combination with other systems • High efficiencies • Low energy consumption	• Ambient conditions must be monitored and in the best case constant • Pilot plant necessary	• Sustainable method for waste treatment • Waste water discharging into sewerage system	• Major modifications would likely be required • No studies for operation in resins production
AOP	• Combination with other systems • Efficient destruction	• Sludge must be processed • Oxidants needed • Relatively complex plant designs	• Waste water discharging into sewerage system	• Major modifications would likely be required • No studies for operation in resins production
Process heat				
Electrical power	• High efficiency • High temperatures • Provides energy reliably	• Very high electrical power requirement	• Zero emissions, if renewable electrical power used • Independent if electrical power is self-produced	• Electrical grid infrastructure
Hydrogen	• Can replace natural gas direct • Existing infrastructure can be used	• High losses • Limited storage options • High costs for electrolysis	• Zero emissions with green hydrogen	• Hydrogen grid • Electrical grid infrastructure for electrolysis
Pyrolysis of paint residues	• Can replace natural gas direct • Existing infrastructure can be used	• Paint residues collection	• Circular economy	• Permission for incineration • Coke must be processed

Figure 24: *SWOT analysis for the different identified technologies.*

5.2 Short-term scenarios

In this section the procedures that support short-term scenarios, so in the course of about one to five years, are discussed. The main benefits that can be expected are a reduction of CO_2 emissions and an improvement of the energy efficiency. There are essentially two methods already presented in Section 4. The integration of a TES system, in the form of a PBTES and the additional WHR, which could be realized through different ways.

As already mentioned in Section 3.2, the integration of a TES system could probably replace the additional heater for thermal oil. If the TO, by intelligent control in the process phases in which little thermal energy is needed, is used to load a PBTES. In addition, theoretically max. 15.7 % of natural gas could be saved, since the energy dissipated by the control cooler could then be stored in the PBTES and the hot exhaust gas from the additional heater for thermal oil would no longer be discharged into the environment. The integration of a PBTES would be particularly suitable for production plant three, since the additional heater for thermal oil is not yet implemented in the first construction phase. A PBTES could then provide the required energy. The exact implementation of a PBTES into the process still needs to be investigated to ensure optimal utilization of the available energy. Basically, this is a very simple system, only the control of the charging and discharging cycles is a more complex matter. In addition, a suitable HTF would have to be identified if direct loading with the exhaust gas from the TO is not possible.

The additional WHR could be realized by different methods. Basically, there are two possibilities, firstly the integration of a heat pump and secondly a heat exchanger to provide hot water. With a heat pump, the temperature of the waste heat could be raised to a higher level and accordingly more usable energy is generated. However, this is also associated with a considerable investment, since the acquisition costs of a heat pump are high. In order to determine the economic viability, a cost/benefit analysis would likley to be carried out. The direct use of waste heat by means of a heat exchanger is associated with significantly lower investment and could therefore be a promising solution. A precondition for both methods is that the energy has a consumer, such as district heating or within the company.

5.3 Mid-term scenarios

In this section the options, which can help to reduce CO_2 emissions in mid-term are discussed. The timeline for implementing these measures would be approximately five to ten years. Some technologies are already commercially viable and can be integrated more quickly. However, independence from fossil fuels could also already be feasible. Two groups are discussed that meet these requirements, which are the pyrolysis of powder coating residues, see Section 4.3.3, to substitute natural gas and alternative technologies for waste treatment, see Section 4.1 and 4.2.

The production of synthesis gas by pyrolysis of powder coating residues is an option for substituting natural gas in the mid-term. One of the major advantages is that natural gas could be replaced directly without any significant changes to the production plant. Probably only the burner in the TO would have to be replaced. Furthermore, a circular economy could be achieved by the pyrolysis of powder coating residues. The theoretical calculation done in Equation (8) shows, the amount of powder coating residues would be sufficient to cover the energy demand for the production plants one and two. Further studies are needed to determine whether the energy required for production plant three could also be generated. One obstacle for the implementation of a plant for the pyrolysis of powder coating residues could be that permits for such processes are very complicated. Since this is formally a waste incineration plant. Another point is the CO_2 emissions caused by the collection of the coating residues from the customers, as they all have to be brought to the company site. In addition, the coke from the pyrolysis process has to be properly disposed of.

An important measure for the future and independence from fossil fuels is an alternative way for treating the process waste. Since it is currently decomposed in the TO at very high temperatures, which accounts for about 10 % of the total natural gas consumption. Two processes were considered particularly suitable for this purpose. These are, from the group of biological methods, the MBTF, and from the AOPs, the PCO. The MBTF, explained in Section 4.1.4, is a sustainable way to treat process waste. The main advantage is the simultaneous treatment of process exhaust gas and condensate. MBTF achieve high removal efficiencies of VOCs. They also require very little electrical energy to operate. The possibility of combination with other systems is another advantage of the technology. After treatment, the wastewater can be discharged into the sewer system, which is a crucial aspect. MBTFs can handle waste streams that have very fast and large variations of concentrations. Beside of that, major modifications would likley to be required at the production plant to implement a MBTF. The construction height can reach up to 20 m. A major drawback is that there are no studies on the use of MBTFs in synthetic resins production. The PCO, see Section 4.2.1 is an efficient way for treatment of process waste, which is also suitable for treatment of process exhaust gas and condensate. For the operation only a catalyst, like TiO_2, and

electrical power is needed. Also there are recent research results in the field of PCO. After treatment with PCO, the wastewater can be discharged into the sewer system. The combination with other treatment systems is also a possibilty. A disadvantage is that significant changes to the production plant would be necessary to enable the use of this process. Also there are no studies for operation in synthetic resins production. In order to find out which of the two mentioned processes is best suited for the treatment of the process waste, more comprehensive investigations would have to be carried out.

5.4 Long-term scenarios

This section discusses the long-term options for the industrial company in the direction to be fossil free by 2040. Direct production of process heat using electrical power has emerged as a possible solution. In principle, electrification has been found to have decisive advantages over the use of hydrogen. The biggest obstacle for both options is, that an appropriate electrical power grid is needed to implement these processes.

Hydrogen electrolysis is expected to have losses of about 30 % and storage at this stage is also very energy intensive, see Section 4.3.2. Therefore, the use of hydrogen only seems to be appropriate if direct supply via a hydrogen network is provided. On-site electrolysis is much less efficient than provision of process heat via electrical power.

Providing process heat via electrical power could be a solution for the future, if it is combined with a suitable system for process waste cleaning. This could save energy and at the same time achieve independence from fossil fuels. The main advantage of generating process heat with electrical power is the high efficiency. If renewable electricity is used, there are no CO_2 emissions during operation. In case the electrical power is generated on site, a self-sufficient production could be realized. For providing process heat there are currently two suitable methods, especially the combination of P2H and TES could fulfill the requirements very well, see Section 4.3.1. In addition, further research results and technologies will appear in this area in the next few years.

6 Conclusion and Outlook

In this thesis, a technology screening is carried out to identify low carbon alternatives for natural gas at high temperatures and alternative technologies for process waste treatment. Furthermore, the process of resin production at the site of the industrial company is analyzed in detail. Thereby possibilities are investigated to achieve a higher energy efficiency in order to reduce CO_2 emissions.

At first the energy flows in the production process are identified and brought together. Special attention was given to the analysis of the batch process in order to find suitable windows for storage charging.

Alternative possible technologies for process waste treatment consist of two major groups, which are biological methods and AOPs. MBTF was identified as a suitable biological possibility for treatment of the process waste. Simultaneous treatment of process exhaust gas and condensate is a major advantage of this process. In addition, MBTF copes well with changing waste compositions during the production process. PCO is also a method for treatment of process exhaust gas and condensate, out of the group of AOPs. With this technology, the resulting process waste could be efficiently decomposed using electricity and a catalyst.

Three different technologies are identified for substituting natural gas to provide high temperature process heat. Firstly, there is direct electrification, which could be implemented by two systems. An essential requirement for this is the electric grid infrastructure, since large amounts of electrical power are needed. This infrastructure is currently not available and will also determine the implementation of this measure, or the timing thereof. A disadvantage of this technology is that significant changes have to be made to the production plant. In contrast, a major advantage of the two following technologies is that the production plant would essentially not have to be changed. Hydrogen is found as a further alternative for energy supply. Hydrogen will play a decisive role in the decarbonization of industry in the future. However, opinions differ on whether it should also be used to provide process heat. Regardless, there are different scenarios for using hydrogen as an energy carrier. On the one hand, there is the possibility of a large hydrogen network transporting it via pipelines to the consumers in the future. On the other hand, hydrogen can be produced by various electrolysis processes. However, as with direct electrification, this requires large amounts of electrical power. In addition, losses during electrolysis are not negligible. The pyrolysis of powder coating residues and the production of synthesis gas from them is identified as a possible alternative

to the other two solutions. This synthesis gas could probably fully replace natural gas.

Opportunities to increase energy efficiency and reduce CO_2 emissions include various technologies. The implementation of TES systems would result in lower natural gas consumption. A identified technology, which could fulfill the requirements is a PBTES system. This would allow dissipated energy to be temporarily stored and retrieved at a later time. As a consequence, the additional thermal oil heater could eventually be replaced by a TES system. Additional WHR from the exhaust gas is a possibility to generate energy for other applications. Different opportunities which can be used for this purpose are heat pumps or the production of hot water.

Based on the created overview of the different technologies and possibilities to reduce CO_2 emissions, further decisions can be made by the industrial company. The next step would be that more detailed studies need to be conducted to enable further steps in the direction to implementation. After that, a decision for one or a combination of several technologies would be possible.

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