PHOSGENE PRODUCTION FROM CARBON MONOXIDE SEPARATED FROM STEEL INDUSTRY FLUE GAS AND CHLORINE

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Authors	
Bart de Jong	S2745313
Anne-Jan Kleiweg	s2722399
Chiem van Miltenburg	S2757990
Sari Wempe	S2760398

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Supervisors Dr. Ir. J. Winkelman (RUG) Ir. W. Leusman (Tebodin/Bilfinger) K. Zuur (RUG) b.c.a.de.jong@student.rug.nl a.kleiweg@student.rug.nl c.j.m.van.miltenburg@student.rug.nl s.f.wempe@student.rug.nl

Contents

Executive sun	nmary	6
1. Phosgene f	rom CO and Cl ₂	7
1.1 Intr	oduction	7
1.1.1	Phosgene	7
1.1.2	Process safety	7
1.1.3	Handling leakage of phosgene	7
1.2 Che	micals	8
1.2.1	Feed composition	9
2. Feed clean	up	9
2.1 Introdu	iction	9
2.2 Sulfur c	lioxide removal1	0
2.2.1 The	e dry process1	0
2.2.2 The	e semi-dry process1	1
2.2.3 The	e wet process1	1
2.3 Carbon	dioxide removal1	1
2.3.1 CO	2 PSA 1	1
2.3.2 Am	nine gas treating1	2
2.3.3.	Physical Solvents1	3
2.3.4 Me	embrane separation1	4
2.3.5 Co	nclusion1	4
2.4 Water i	removal1	5
2.4.1 Co	ndensation1	5
2.4.2 Wa	ater adsorption1	5
2.5 Carbon	monoxide removal	6
2.5.1 Pre	essure swing adsorption1	6
2.5.2 Liq	uid absorption1	7
2.6 Hydrog	en and Methane removal1	8
2.6.1 Cry	vogenic system1	8
2.7 Nitroge	n removal1	9
2.7.1 Cry	vogenic system1	9
2.7.2 Me	embrane separation1	9
2.8 Final Cl	ean-up route1	9
2.9 Waste	gases2	0
2.9.1 Co	mposition of the clean-up flare2	0

2.9.2 Energy output	20
2.9.3 Flammability	21
2.10 Purge	22
3. Phosgene synthesis and purification	22
3.1 Reaction	22
3.2 Reactor choice	24
3.2.1 The reactor	24
3.2.2 The catalyst	25
3.3 phosgene purification	26
3.3.1 Amine gas treating	26
3.3.2 Dehydration of product stream	26
3.3.3 Phosgene distillation	27
4. The model	27
4.1 Process description	27
4.2 Section model description	28
4.2.1 Section 1 the SO $_2$ scrubber	28
4.2.2 Section 2 the CO ₂ and H ₂ S absorber	30
4.2.3 Section 3 the pressure swing adsorber	30
4.2.4 Section 4 to 6 the production and purification	32
4.2.5 Section 7 the destruction	37
4.3 Pump design	38
4.4 Heat Exchanger Design	38
4.4.1 Design Method	38
4.4.2 Specifications	38
4.4.3 Results	40
4.4.4 Discussion	40
4.5 P&ID's	40
4.5.1 Nomenclature	40
4.6 HAZOP	41
5. Mass and Heat balances	43
 5. Mass and Heat balances 5.1 General remarks 	43 43
 5. Mass and Heat balances 5.1 General remarks 5.2 Section 1 	43 43 43
 5. Mass and Heat balances 5.1 General remarks	43 43 43 43
 5. Mass and Heat balances	43 43 43 43 44 44

	5.6 Section 7	. 44
6.	Economic Analysis	. 44
	6.1 Comparison to global yearly production	. 45
7.	Discussion and Conclusion	. 46
8.	References	. 48
9.	Appendix	. 55
	A. PFD's	. 55
	A.1 Section 1	. 55
	A.2 Section 2	. 56
	A.3 Section 3	. 56
	A.4 Section 4-7	. 57
	B. Section 1	. 58
	B.1 P&ID	. 58
	B.2 Mass Balance	. 59
	B.3 Heat Balance	. 60
	B.4 Code Specifications	. 60
	C. Section 2	. 61
	C.1 P&ID	. 61
	C.2 Mass Balance	. 62
	C.3 Heat Balance	. 63
	C.4 Code Specifications	. 63
	D. Section 3	. 65
	D.1 P&ID	. 65
	D.2 Mass Balance	. 66
	D.3 Heat Balance	. 67
	D.4 Code Specifications	. 67
	E. Section 4	. 70
	E.1 P&ID	. 70
	E.2 Mass Balance	. 72
	E.3 Heat Balance	. 73
	E.4. Code Specifications	. 74
	F. Section 5	. 76
	F.1 P&ID	. 76
	F.2 Mass Balance	. 78
	F.3 Heat Balance	. 79

F.4 Code Specifications	80
G. Section 6	82
G.1 P&ID	82
G.2 Mass Balance	83
G.3 Heat Balance	84
G.4 Code Specifications	84
H. Section 7	86
H.1 P&ID	86
H.2 Mass Balance	87
H.3 Heat Balance	88
H.4 Code Specifications	89
I. Stream specifications	91
I.1 Section 1-3	91
I.2 Section 4-7	92
J. HAZOP	95
J.1 HAZOP table	95
J.2 P&ID's after HAZOP	102
K. Economic Analysis	108
K.1 Executive summary	108
K.2 Project summary	110
K.3 Equipment cost	114
L. Pumps	117
L.1 Pump selection chart	117
L.2 Impeller curve	118
M. SO ₂ scrubber sizing calculations	119

Executive summary

In this project, phosgene was produced from the flue gases of the steel industry. The flue gas from the steel industry contained 30 w% carbon monoxide which was purified out of the stream in the following steps.

First the SO₂ was removed in a wet limestone scrubbing process. This process had a removal efficiency of 99.99%. Secondly the flue gas was subjected to a MEA absorber to remove the CO₂ and H₂S from the stream. This process had a removal efficiency of roughly 100% for CO₂ and 100% for H₂S. Afterwards the now wet flue gas was dried in a desiccation process. 1 ppm of water was left after this process. In the last purification step the flue gas was subjected to a pressure swing adsorber. 364.1 ton/h CO was obtained, with a purity of 99.91 w% based on literature and calculations.

After purification the CO was mixed in excess with Cl₂ and reacted in a tube and shell reactor, using activated carbon as a catalyst. The stream was split in five, because of its size. All Cl₂ converted, 1235.8 ton/h of phosgene was created, with a purity of 98.79 w%. To remove a small amount of CO₂ the product stream was subjected to MEA absorption, removed all CO₂. This was done to deliver the product as pure as possible, so no issues occur during the subsequent polymer synthesis, for which phosgene is used. To remove the leftover MEA and water in the product stream, it was dried using glycerol. All water and MEA was removed, some phosgene was lost in this process as well. In the final step the phosgene was further purified in five distillation towers in parallel. The product had a purity of 99.99 w% and 1156 ton/h. This results in a yield of 93.6%. Purge streams were destroyed using steam to form HCl and KOH to neutralize the HCl.

Mass- and heat balances over the different sections were created, where section 1 is the SO₂ scrubber, section 2 is the CO_2/H_2S removal, section 3 is the desiccating tower and PSA, section 4 the reactor and CO_2 removal, section 5 the dehydration, section 6 the distillation and section 7 the destruction of purged phosgene.

Economic analysis was performed which turned out to be profitable with 7 billion euros per year. However this is dependent on the phosgene price, phosgene free routes emerging, market size and logistical limitations from the OPCW.

Process flow diagrams and piping and instrumentation diagrams were created and HAZOP was performed over the P&ID, expanding the P&IDs.

1. Phosgene from CO and Cl₂

1.1 Introduction

One possibility to reduce climate forcing emissions is recycling carbon emissions from industry into products. In this way less fossil resources are needed in production systems. [1] In the steel industry, lots of combustion gases are emitted while not only having an energetic value, but also a contribution to global warming.

Therefore, it is explored how carbon containing gases can be used in the synthesis of other chemicals. In this specific assignment, phosgene is synthesized from chlorine and carbon monoxide, carbon monoxide is delivered from a feed of exhaust gases, meaning that the gas needs to be cleaned up. The potential of this flue gas is nowadays vanished because these gasses are solely used for energy regeneration or otherwise flared. [1]

From a flue gas stream of 10.8 Mton/year with a carbon monoxide content of 30%, 3,240,000 ton carbon monoxide per year is obtained. This corresponds, assuming an operating factory of 8000 hours/year, and an overall efficiency of the gas cleanup process of 85% with 364.1 ton carbon monoxide/ h.

After the reaction and subsequent purification a yield of 93.6% of phosgene, with a purity of 99.99 w% was obtained. This results in a production of 1156 ton/h of phosgene in all five factories combined.

1.1.1 Phosgene

Phosgene is a toxic colorless gas (at room temperature) which was used in the first world war as a chemical weapon. The gas can be recognized by the odor of freshly mown hay. If one is to be exposed to the gas, hydrolysis takes place, resulting in the formation of hydrochloric acid and carbon monoxide. This leads to choking, blurred vision, burning sensation in the throat and eyes etc. and eventually, if exposed to large quantities, to death. [2] The odor detection threshold for phosgene is 0.4 ppm, which is four times the threshold limit value (0.2 mg/m³). [3] Today, phosgene is used in the production of polyurethanes. In these plants, special care has to be taken when handling this gas because of the high risks. Phosgene can be synthesized from carbon monoxide, CO, and chlorine, Cl₂, in the presence of a catalyst. A possible catalyst is activated carbon.

1.1.2 Process safety

The main target of this process is to find a way to safely produce phosgene gas. Because of the toxicity of phosgene, extensive safety measures have to be taken into consideration when designing the plant. For this reason, it is important that the plant is equipped with a safety absorption system, which ensures absorption of any released phosgene and destruction by circulation with a caustic solution containing ammonia. Also, the reaction is strongly exothermic (enthalpy of formation = -107.6 kJ/mol), making it inevitable to cool the reactor. The reaction is performed at a temperature range of 50-150°C, because at temperatures above 200°C phosgene reverts to carbon monoxide and chlorine, which are both toxic/fatal if inhaled. [4] [5] It is assumed that the gas is fed to the process in the ratio 15% H₂, 35% N₂, 30% CO, 14% CO₂, 5% CH₄, such that carbon monoxide doesn't have to be synthesized on site. [3] Since Cl₂ is delivered, and not synthesized on site, no extra action is needed for this gas.

1.1.3 Handling leakage of phosgene

First of all, care has to be taken to prevent moisture of entering the phosgene gas container. This leads to the formation of hydrochloric acid and carbon dioxide, which results in possible corrosion of the

container. In the case that leakage does occur, the leaked phosgene needs to be neutralized, which is possible with alkali or alkali solutions (a solution of strong base solids dissolved in water). The reaction of phosgene with an ammonia solution is particularly effective being that this forms urea. [6] Urea, also known as carbamide, is an odorless, non-toxic, colorless solid which is highly soluble is water, when dissolved in water it is neither acidic nor alkaline. [7]

1.2 Chemicals

Table 1. Chemical properties of chemicals used in the synthesis of phosgene [8]

Substance	Chemical	Molar	Density at 0	m.p.	b.p. [°C]	Solubility in water
	Formula	mass	°C, 1 atm	[°C]		(at 20°C, g/kg
		[g/mol]	[kg/m3]			water) ¹
Phosgene	COCl ₂	98.9	4.25 (15 °C,	-118	8.3	Insoluble, reacts
			gas)			
			1.43*10 ³ (0			
			°C, liquid)			
Carbon	CO	28.0	1.25	-205	-192	0.27
monoxide						
Chlorine	Cl ₂	70.9	3.21	-101	-34.0	7.1
Hydrogen	H ₂	2.02	8.99*10 ⁻³	-259	-253	1.60*10 ⁻³
Nitrogen	N ₂	28.0	1.25	-210	-196	1.90*10 ⁻²
Carbon	CO ₂	44.0	1.98	-56.6	-78.5	1.75
dioxide					(sublim	
					ation)	
Methane	CH ₄	16.0	0.717	-183	-164	2.40*10 ⁻²
Hydrogen	H ₂ S	34.1	1.45 (15°C)	-85	-60.4	7.00
sulfide [9]						
Sulfur	SO ₂	64.1	2.76 (15C)	-72	-10.02	225
dioxide						
MEA [10]	C ₂ H ₇ NO	61.1	1.02*10 ³	10	70	miscible
Glycerol	$C_3H_8O_3$	92.1	1.26*10 ³	20	182	miscible
[11]						
Carbon	CCl ₄	154	1.59*10 ³	-23	76	0.81
tetrachlori						
de [12]						
Hydrochlo	HCI	36.5	1.30*10 ³	-114	-85	720
ric acid						
[13]						
Potassium	КОН	56.1	2.04*10 ³	361	>1000	1.12*10 ³
Hydroxide						
[14]						
Potassium	KCI	74.6	1.98*10 ³	770	>1000	360
Chloride						
[15]						

Methanol	CH₃OH	32.04	792	-98	64.7	miscible
[10]						
Water	H ₂ O	18.0	1000	0	100	na
Limestone	CaCO₃	100	2700-2950	1.34	decomp	insoluble
[17]				*10 ³	osition	
Gypsum	CaSO ₄ .2H ₂ O	17	2320	100-	na	2
[18]				150		

1.2.1 Feed composition

In Table 2 the composition of the flue gas can be found.

Table 2 Flue gas composition

Component	Mass Fraction	Component Mass Flow [ton/h]
N ₂	0.35	472.5
СО	0.30	405.0
H2	0.15	202.5
CO ₂	0.14	189.0
CH ₄	0.05	67.5
SO ₂	0.002	2.7
H ₂ S	0.008	10.8
Total	1	1350

2. Feed cleanup

2.1 Introduction

Several clean-up routes and processes were considered, specifically, 3 clean-up routes were considered. The first route is based on first removing all components but carbon monoxide from the flue gas, ending up with pure carbon monoxide. The second route starts with the separation of carbon monoxide, after which the other compounds are separated in order to be able to dispose them. The last route considered is a compromise of the two other routes, meaning that first some compounds are removed from the flue gas, in order to decrease the flow and the corrosive behavior, after which the carbon monoxide gets separated from the remaining compounds.

Within these routes, several different removal processes were considered. For example; for the removal of carbon dioxide multiple processes are available; amine gas treating, the Selexol process and the Rectisol process. All considered routes and clean-up processes are shown in Figure 1. All clean-up methods for the varying 'impurities' are discussed in the following sections.



Figure 1. All possible clean-up routes and processes considered in the flue gas clean-up [19]

Figure 2. Gas separation

2.2 Sulfur dioxide removal

For the removal of SO_2 there are many processes available, of which the most commercially used ones can be divided in three different processes: Dry, semi-dry and wet processes [20]. All known desulfurization processes are performed at $50^{\circ}C$. [21]

2.2.1 The dry process

The dry process, where the SO_2 is bound to activated Calcium compounds, has an efficiency of 65% to 80%, and is a function of the Ca to SO_2 ratio. This ratio is typically in the 2 to 5 range, consequently this makes the solid handling troublesome. [20] The dry process produces a large volume of waste, which

does not have many uses due to its properties, i.e., permeability, soluble products, etc. [22] However, since no water is used in this process, the gas stream does not have to be dried even further afterwards.

2.2.2 The semi-dry process

The semi-dry process has an efficiency of up to 92% of SO_x collection. For this process the lime is made into a slurry which is sprayed in the reactor. Subsequently, the dry dust is collected using bag filters or electrostatic precipitators. The semi-dry process needs a lower calcium to SO_x ratio than the dry process, which makes them preferred because of the easier solid handling. However, compared to the dry process the pump power required is higher. [20]

2.2.3 The wet process

The wet process can be done with multiple absorbents: lime, caustic, double alkali, ammonia and sea water based systems. When lime(stone) is used, the following reaction occurs: [23]

Limestone: CaCO ₃ (s) + SO ₂ (g) \rightarrow CaSO ₃ (s) + CO ₂ (g)	Reaction equation 1.
Lime: Ca(OH) ₂ (s) + SO ₂ (g) \rightarrow CaSO ₃ (s) + H ₂ O(I)	Reaction equation 2.

Normally the lime based system is used, which is one of the most economically available. [20] In this system the gasses enter the SO2 absorber at the bottom and travel upwards. The alkaline slurry/solution is sprayed (atomized) counter-current in stages in the reactor. In the bottom of the tank the scrubbing liquor is collected, which is kept at a constant pH of 7 to 7.5, and recirculated. A part of this scrubbing liquor is removed to remove the salts created in the process (CaSO₄, CaCO₃, Na₂SO₃ and Na₂SO₄ can all occur, based on the process being a lime or a caustic process). Clean gases are removed at the top of the reactor after passing through a mist eliminator. It is possible to blow oxidation air into to the scrubbing liquor in the case of the cheaper lime system, this turns the calcium sulphite into gypsum according to the following reaction: [23]

 $CaSO_{3}(s) + \frac{1}{2}O_{2}(g) + 2H_{2}O(I) \rightarrow CaSO_{4} \cdot 2(H_{2}O)(s).$ Reaction equation 3.

After bleeding the tank, the slurry is then dewatered and the gypsum is removed as wet cake. It is also possible to treat the slurry in a caustic system, but this is expensive. [20] Because salts are used in this process, there is a chance that scale forms in the pipes and sprayers, which affects the atomization and reduces the scrubbing efficiency. Scale on the return pipes reduces flow rate and has a negative effect on thermals. It is possible to add additives to reduce the scaling effect such as chelating agents and phosphates. This is only evident at higher pH levels. In order to prevent scaling, pH control is necessary, as indicated earlier. [23]

It is possible to use a magnesium enhanced lime based process by adding 3 to 8 w% of MgO to the slurry. Because of the better solubility of MgO salts compared to the CaCO₃ and Ca (OH)₂, the slurry becomes more alkaline. This in turn gives a higher SO₂ removal efficiency so that less solvent is needed, which means less pumping power and a smaller absorbing tower. An efficiency of 99.9% of the sorbent is achieved which removes 98% of the SO₂ from the gas. Gypsum with a 98% purity is produced in the magnesium enhanced lime process. [24]

2.3 Carbon dioxide removal

2.3.1 CO2 PSA

In section 2.4 the process of PSA for carbon monoxide is described. By changing the packing of the column of a pressure swing adsorber, the adsorbed compound can also be changed. For example, also

 CO_2 can be adsorbed on an adsorber in a PSA process. Zeolites are a good option for a packing in a CO_2 -PSA process. Zeolites exhibit good CO_2 adsorption capacity and selectivity at low pressures and moderate temperatures. [25] Another possibility would be using activated carbon as a packing. The selection of the adsorbent depends on the process conditions.

2.3.2 Amine gas treating

Alkanol amines are known absorbents for acidic gases (CO_2 , H_2S). The principal reactions that occur when aqueous solutions of a primary amine, such as monoethanolamine, are used to absorb CO_2 and H_2S are shown in Figure 3.

Ionization of water:

$\mathbf{H}_{2}\mathbf{O} = \mathbf{H}^{+} + \mathbf{O}\mathbf{H}^{-}$	(2-1)
Ionization of dissolved H ₂ S:	
$\mathbf{H}_2 \mathbf{S} = \mathbf{H}^+ + \mathbf{H} \mathbf{S}^-$	(2-2)
Hydrolysis and ionization of dissolved CO ₂ :	
$CO_2 + H_2O = HCO_3 + H^+$	(2-3)
Protonation of alkanolamine:	
$RNH_2 + H^+ = RNH_3^+$	(2-4)
Carbamate formation:	
$RNH_2 + CO_2 = RNHCOO^- + H^+$	(2-5)

Figure 3 principal reactions in amine gas treating

After absorption in a packed-bed column, the H_2S and CO_2 rich solution is stripped, which is done by the application of heat. [26]

2.3.2.1 Advantages

2.3.2.1.1 Alkanolamines in general

Amine gas treating is one the most widely applied technology for CO₂ capture. It has been commercially in use for decades. Of all alkanol amines, monoethanolamines is chosen for the process.

2.3.2.1.2 MEA

Monoethanolamine is preferred as solvent for gas streams that contain relatively low concentrations of H_2S and CO_2 . This solvent is preferred when a gas stream needs to be treated at low pressures and when maximum exclusion of H_2S and CO_2 is vital. Due to the low molecular weight of MEA, a MEA solution has a high capacity at STP conditions. Also, due to the high alkalinity of the solution, and the relative ease at which it can be regenerated from contaminated solutions are advantageous [26] Other advantages of MEA over other alkanolamines, is the fact that it is the cheapest of all [27] and that it is not reactive towards carbon monoxide, unlike diethanolamine. [28]

2.3.2.2 Disadvantages

2.3.2.2.1 Alkanolamines in general

The major disadvantages for the use of alkanolamines as absorbent are: a high energy consumption during regeneration of the absorbent in the stripper and large equipment sizes. [29] The high energy

consumption can be partially reduced by placing a heat exchanger, which re-uses the heat from the stripper to pre-heat the stream entering the stripper.

Another important disadvantage is the formation of heat stable amine salts (HSAS), which accumulate in the amine solution. HSAS are formed by reaction of MEA with acidic contaminants. They become more corrosive with time. HSAS also reduce the absorbing ability and efficiency of the amine solution by reducing the amount of pure amine. [30]

In order to control HSAS accumulation no more than 20 w% MEA solution is used. Also, the amine solution is cleaned continuously by purging and making up the amine solution in the acid gas removal. Finally, the material of construction is chosen to be SS 304 to minimize corrosion effects.

2.3.2.2.2 MEA

For MEA specifically, the most important disadvantage is the fact that it is more corrosive than secondary or tertiary amines. However, this effect is of more important matter when the flue gas contains a lot of acid gas. This should not cause troubles in this process, since CO_2 and H_2S are not present in large concentrations.

Direct corrosion by MEA is also prevented by a maximum of 20 w% MEA in water and using SS 304 as material of construction. [30]

2.3.3. Physical Solvents

Physical solvents are nonreactive organic solvents that are able to physically dissolve acid gases. Unlike amine gas treating, the absorption occurs according to Henry's Law, meaning they depend on temperature and pressure. As a consequence, the acid gas can be stripped by reducing the pressure or application of heat. [31] The most common physical solvents are Rectisol, Fluor Solvent and Selexol.

2.3.3.1 Selexol process

Since 1969, Selexol has been used to remove CO_2 and H_2S from natural gas. The process uses di-methyl ether polyethylene glycol $[CH_3(CH_2CH_2O)_nCH_3]$ with n between 2 and 9. [32] Its basic flow scheme is therefore simple: an absorption stage is followed by flash vessels at decreasing pressures. [26] The process has several advantages. To start with, Selexol solvent has high affinity with water so the sweet gas comes dry out of the absorber; the initial plant and operating cost are low and solvent regeneration requires no heat from the reboiler.

It also has several disadvantages. The high circulation rate results in high pump power requirements; the high viscosity, thus reduced mass transfer rates, tray efficiencies and increased packing or tray requirements [33]. The last disadvantage is that the process is most efficient at elevated operating pressures

2.3.3.2 Fluor Solvent

Because the feed is primarily sour due to CO_2 , the Fluor solvent process is an attractive option. [31] The solvent consists of propylene carbonate ($C_4H_6O_3$), which is a polar solvent with a high affinity for CO_2 .

The usage of a Fluor solvent has several advantages. It has a high CO_2 solubility; no make-up water is needed; the operation is simple; the gas output is dry. However, also this solvent has several disadvantages. The solvent circulation for the Fluor solvent is high; the Fluor solvent is very expensive; Fluor solvent slowly reacts irreversibly with water and carbon dioxide at temperatures around 90°C and is therefore unsuitable for the feed clean-up [34]

The high circulation rate and high cost make the Fluor solvent too expensive to be applied in the feed clean-up.

2.3.3.3 Rectisol process

The Rectisol process uses methanol which is chilled because of its high vapor pressure. The process usually is operated at a temperature between -73 and -34 °C. Its advantages include: high CO₂ and H₂S carrying capacity at operating pressure; low viscosity at operating pressure, thus high mass transfer rates; very sharp separations, resulting in H₂S concentrations of 0.1 ppm and CO₂ concentrations of just a few ppm in treated gas and lastly favorable for cryogenic downstream processes due to its low operation temperature. [35] However there are a few disadvantages such as: very complex flow schemes; need for low level refrigeration which is energy costly; high plant costs and more equipment needed than for other physical solvents.

Cryogenic distillation was considered as a purification step in the feed clean-up. Because cryogenics are operated at very low temperatures (lower than -73 °C), Rectisol was a serious option for the removal of acid gas. When it was decided cryogenic distillation is not suitable for the process, the low temperature of the Rectisol process made it too energy intensive to be applied in the feed clean-up.

2.3.4 Membrane separation

The difference in interactions of gas and vapor species with polymeric materials are used to accomplish gas separations and purifications with membrane devices. In a membrane gas separator, the gas is fed to one side of the membrane, where a part of the gas stream will diffuse to the low pressure side and a part will stay at the high pressure side. [36] Membranes are developed to have permeability for specific compounds. However, an efficiency of 100 % cannot be obtained with this technique, since the separation is not based on an absolute barrier to one compound. [37]

Figure 4. Photo from transport processes and separation process principles [36]

Low cost, high performance CO_2 separation membranes have been developed. For example, cardo polyamide membranes were found to have good CO2 separation performances, demonstrating the ability to separate CO_2 from exhaust steel gas at steel works at a cost comparable to that of the conventional amine solution method. [38]

2.3.5 Conclusion

Two feasible processes were researched: Amine gas treating and gas sweetening with several different physical solvents. Amine gas treating was chosen in the feed clean-up, because it has been widely applied in industry for several decades. In addition, physical solvents turned out to be either too

expensive, too energy costly or too complex. PSA is not needed when amine gas treating is used, because amine gas treating removes both CO_2 and H_2S .

The advantages of using MEA as CO₂ and H₂S absorbent outweigh its disadvantages. Most of its disadvantages are prevented by selecting correct material of construction, recycling heat streams, using a correct ratio of MEA/water and continuous purge and make up of amine solution. Therefore it is applied in the clean-up of the phosgene production process.

2.4 Water removal

2.4.1 Condensation

Water in the flue gas has to be removed in order to prevent unwanted side reactions and to decrease the flowrate. Water removal can be achieved by flue gas condensation, since a condensable vapor can be recovered from a mixture with other gases that have much lower dew points by partial condensation. A condenser can be used to remove water from the gas. Any type of heat exchanger can be used as condenser, but the conventional shell and tube exchangers are most commonly used. The next step in the removal is the exclusion of condensed liquid in the gas flow. This exclusion is ensured by using a vapor-liquid settling drum. [39] By changing the pressure, the solubility of water vapor in the gas changes and water condense out of the vapor. This water is then removed in a gas/liquid separator. [40] In order to condense water from the gas mixture, the gas mixture has to be brought to the dew point. The dew point of water in gas depends on the temperature and pressure. While condensing water from the gas, also latent heat can be recovered. Depending on the temperature of the flue gas. This is why normally exhaust gasses are dried in industrial processes, to recover energy. [41]

2.4.2 Water adsorption

Another way to dry a gas mixture is by an adsorption or absorption process. Commercial adsorbents, which exhibit ultra-porosity, have been used for the selective separation of gases. For the separation of water from a gas mixture activated alumina can be used. [42]

Activated alumina is a pure form of aluminum oxide, completely free of water. The product is supplied in small spheres of 3–6 mm in diameter and is an inexpensive- and efficient material for drying gases, especially process air. Assuming there is enough sweep gas, the activated alumina can be regenerated at a fairly low temperature to elute water. The regeneration gas must supply a driving force to remove water which was condensed in the pores and adsorbed on the high surface area of the activated alumina. Activated alumina has a lower heat of wetting than for example a molecular sieve. The heat of wetting is defined as the heat evolved when an insoluble solid is wetted by a liquid (like water). [43] Therefore, activated alumina has an advantage since the regeneration requires less energy. [42]

This process requires at least two desiccation towers in order to regenerate the packing of one tower while the other is operating. Regeneration is needed since retained liquid water may cause breakage or fracturing of the activated alumina spheres. A gradual decline in adsorption capacity of the activated alumina is typical in process air dryers, but this condition plateaus after a while. The decline is caused by a loss of surface area and micro pore volume by repeated wetting and heating of the adsorbent. Given good conditions for air and inert sweep gases, the operating life of the activated alumina should be around 10 years. The dual-activated tower unit generally operates on an 8 h time cycle, but this of course depends on the amount of water to be absorbed and the amount of alumina. One tower in operation, whereas the other(s) get regenerated with heat. [42] The capacity of activated alumina is based partly on experience. A rule of thumb is that the dynamic desiccant capacity is one third of the static capacity, which is explained in section 4.2.3. [42]

2.5 Carbon monoxide removal

2.5.1 Pressure swing adsorption

Pressure swing adsorption (PSA) works by the principles of reversible adsorption. A gas flow is adsorbed on a packing under high pressure. This gas can be regenerated by reducing the pressure. This also regenerates the bed. The adsorbents are porous solids, preferably with a high contact area. Components that are not adsorbed on the adsorbent can pass through the column faster than the compounds that show high affinity with the adsorbent. In order to obtain the separation, the feed must be stopped before the high affinity compound breaks through the column. Since the adsorption equilibrium is specific for the operating conditions (temperature, pressure and composition), it is possible to regenerate the adsorbent by changing one of these parameters. In the case of PSA, the pressure is swung between the high pressure for the adsorption stage and low pressure for the regeneration. The PSA process is associated with low energy consumption and is preferred to other processes if the concentration of the components to be removed is important. [44] A PSA set-up consists of 2 or more columns that work alternatingly. All columns undergo cycles consisting of four stages:

- 1. Feed
- 2. Blow
- 3. Purge
- 4. Press

In the feed step the gas is fed to the column under high pressure. The adsorbent will adsorb a certain compound from the gas feed while the other compounds will run through.

In the blow step, the pressure is released resulting in a release of the adsorbed gas. In the third step, the purge, this release of gas is promoted by blowing an enriched gas through the column. Since the pressure is low at this point, the adsorption of compounds from this gas is not substantial.

In the last stage, the press step, the pressure is increased again and the column can be used for a new cycle. [44]

Pressure swing adsorption processes are isothermal, which means that the temperature stays constant. Rapid cycling gives efficient use of the adsorbent and leads to smaller vessel sizes and lower capital cost. [45]

2.5.1.1 PSA in the process of purifying CO

In 1989 the first commercial CO-PSA plant was built. The adsorbent used in this process consists of an activated alumina carrier with appropriate pore size distribution and uses an impregnated carbon and copper compound as the active chemisorption species. [46] These CO-separation plants consist of a pretreatment section and a PSA section. In the pretreatment section water and sulfuric compounds are removed. Subsequently, the pretreated gas is fed to the PSA section, which includes four adsorption towers containing 80 liters of adsorbent each, for this specific plant. The adsorption is at higher pressure than atmospheric pressure and the recovery is at around atmospheric pressure. In a commercial plant a feed gas with a CO% of 58-78% was purified to 99% with a yield of more than 90% at an adsorption pressure of 30 bar. The flow rate of the product gas was 2000 Nm³/h.

One factor which is of great importance in order to achieve high purity CO gas, is high selectivity of the catalyst. A higher operating temperature leads to higher selectivity of CO/CO2 for a copper adsorbent.

[47] As mentioned earlier, an activated aluminum career with impregnated carbon and copper compound is used in commercial CO-PSA processes. This adsorbent adsorbs strongly the CO with a reversible chemical reaction on the pi-pi interactions. The recovery of this adsorbent is done by blowing enriched gas through the column at the purge step. Part of the product CO flow is used as enriched gas for the purge step.

The efficiency of the purge step can be improved by using variable purge gas concentration method (VCPM). In this method the concentration of CO of the gas stream is varied. In the beginning of the purge step, the purge gas does not need a CO concentration of 99% since about 50% is sufficient. The CO concentration of the gas during the purge step is increased over time. [47] In other words the enriched gas in the purge step does not have to be pure CO gas during the whole step. In the first part of the step a lower CO content/ a less enriched gas is sufficient as well.

2.5.2 Liquid absorption

A possible liquid absorption process is the COSORB process. This process involves selective reversible complexation of CO to an activating agent, which is in this case CuCl₄AI (copper(I)-tetrachloroaluminate(III)) in an aromatic solution (benzene or toluene). The complex forms through reaction 4. [48]

 $\mathsf{CO} + \mathsf{CuCl}_4\mathsf{Al}.aromatic \Leftrightarrow \mathsf{CO}.\mathsf{CuCl}_4\mathsf{Al} + aromatic. \qquad \qquad \mathsf{Reaction equation } 4.$

Unfortunately NO_x, H₂O, NH₃, H₂S and SO₂ are poisonous to this complex, which means that they have to be removed before the reaction. The cryogenic separations of N₂ and CO is hard because of the small difference in boiling points of N₂ and CO, with COSORB this is not an issue, which makes COSORB favorable over cryogenic separation. In a typical process the yield of CO is 99% with a 99% purity. [48] [49] However the downside of this process, the degeneration of the complex, means that the process is seldom used. In Figure 5 a process schematic is shown. [48]

Figure 5. COSORB process schematic

The reaction can also be described as in equation 5. This reaction is mass transfer controlled, meaning that for equipment design the reaction is instant with regard to mass transfer. [50]:

$CO + CuAlCl_4.tol(2) \leftrightarrow CuAlCl_4.tol.CO + tol.$	Reaction equation 5.
with k(eq) = $\frac{[CuAlCl4.tol.CO][tol]}{[CO][CuAlCl4.tol(2)]} = 3.4 \times 10^{3}$	at 300K

Costello improved on this process with their COpure process, which has extensive pre-treatment to remove undesirable components, indirect cooling and heating and more. They do not specify these claims on their website. [51]

Figure 6 the COpure process

Stripping is usually performed in a stripping column where the absorbed solute is removed from the solvent by using a countercurrent vapor of the solvent. [52] The stripping process in the COSORB process can be described as follows. The carbon monoxide rich-solvent originating from the absorber, gets heated against hot lean solvent from the bottom of the stripper. This solvent flows to the top of the column. The heat of the kettle reboiler connected to the stripper provides stripping of the solvent in order to recover the carbon monoxide. Typically, a purity of 99% is achieved. The regenerated lean solvent exits at the bottom of the stripper and provides heat to the stripper feed. [49]

2.6 Hydrogen and Methane removal

Hydrogen and methane are both entrained in the flue gas. These gases both have a calorific value, which means that these gases can be used as energy supply when separated from the flue gas. A possible exclusion method is cryogenic distillation.

2.6.1 Cryogenic system

The cryogenic distillation process is a separation process based on liquefaction. The field of cryogenics generally involves systems that operate at temperatures below -150° C (123 K). [53] Multiple cryogenic processes are available; Hampson -, Linde -, Claude -, Heylandt - and Cascade process. Only the Cascade process was considered since this system focuses on the condensation of a series of liquids of progressively lower boiling points under pressure at a temperature produced by the evaporation of the next higher boiling point. [54] Therefore, methane and hydrogen can separately be excluded from the gaseous stream. In order to obtain methane as a liquid, the feed needs to be cooled down to a temperature of \pm -170°C, because the boiling point of methane is -161.5°C. However, the boiling point of carbon dioxide is -87°C [55] and the boiling point of water is 100°C. Since the temperature has to be

reduced below the point where H_2O and CO_2 start to condense or freeze out, these components must be removed prior to lowering the temperature. [56] After cooling down to \pm -170°C, methane is obtained as a liquid and can be separated from the gas feed. This separation is followed by a further decrease in the temperature of the feed to \pm -200°C, which results in the liquefaction of carbon monoxide (boiling point is -191.5°C) and nitrogen (boiling point is -195.8°C). However, hydrogen is still in the gas phase at this temperature, meaning that gaseous hydrogen can be separated from the liquid feed. The major drawbacks of this method are possible freezing of carbon dioxide and water and the energy consumption. Cooling the entire flue gas stream to a temperature of \pm -200°C consumes an enormous amount of energy, which is not economic feasible.

2.7 Nitrogen removal

Since N_2 is an inert gas, it does not react. In the case that the nitrogen is left in the flue gas feed, the reaction will be a lot less efficient, since 35% of the feed consists of nitrogen, meaning that every piece of equipment needs to compensate for this large 'useless' flow. Known processes used for the separation of nitrogen from gas feeds can be classified as cryogenic (low-temperature) processes, adsorption processes, and membrane separation.

2.7.1 Cryogenic system

The cryogenic process was already discussed in section 2.6.1. However, now the focus is on the separation of nitrogen instead of hydrogen and methane. As described earlier, the cryogenic process is the separation based on liquefaction. The problem with this process is the presence of carbon monoxide in the feed. The boiling point of carbon monoxide is -191.5°C, whereas the boiling point of nitrogen is -196°C, making it hard to separate these components. Another reason for the exclusion of this process, is the amount of energy it costs to cool the feed to a temperature of \pm -196°C. The feed is delivered at ambient temperature and pressure (e.g. 25°C, 1 atm), meaning that the feed needs to be cooled \pm -220°C.

2.7.2 Membrane separation

Membrane separation is a separation technology which is already explained in section 2.3.4. An efficiency of 100 % cannot be obtained with this technique, since the separation is not based on an absolute barrier to one compound. [37] However, membranes with an efficiency of 95-99% are already available. For example, the 7200 HP Nitrogen Membrane from the company Generon can achieve this efficiency. [57]

2.8 Final Clean-up route

In order to obtain (almost pure) carbon monoxide, it was found that PSA is a good option to separate carbon monoxide from a gas mixture. The first target of the clean-up was to reduce the corrosive and toxic properties of the flue gas. Since sulfuric compounds exhibit these properties, it was decided to first remove these compounds. The technology chosen for desulfurization is a wet process, in this case a limestone based process (this process was described in section 2.2.3). This process only removes SO₂. The chemical which was chosen to be removed secondly was the other sulfuric compound, i.e. H₂S. An amine process showed to be beneficial for the removal of H₂S as well as CO₂ (this is described in section 2.3.1). First of all, CO2 can be stored underground, leading to less emission of greenhouse gases to the environment. Secondly, this leads to a huge decrease in the total flow, which is especially economically beneficial to the sizing of the rest of the equipment, meaning the desiccating towers and the PSA. During the amine- and the limestone process, water gets entrained in the gas flow. It is of great importance that no water enters the reactor, since water will react with chlorine to form hydrochloric acid, which is very corrosive. Next to this, the PSA which will be used is only 99% selective to carbon

monoxide, meaning that 1% of the 'impurities' will remain in the gas flow. Therefore, the next step in the clean-up is water removal, the technique chosen for this is drying with desiccating towers (this is described in section 2.5.2). The final step chosen was the separation of carbon monoxide from the other gases by means of PSA. This technique delivers a 99+% pure carbon monoxide stream and a mixture of other gases, which can be burned (see calculation on Wobbe index and flammability in section 3.3.3).

2.9 Waste gases

2.9.1 Composition of the clean-up flare

A mixture of CH_4 , H_2 , N_2 , and some traces of NO_x and CO is left after the PSA. From the percentages given for the gaseous waste feed, the composition of the flare gas can be recalculated. As an example, the recalculated percentage of CH_4 is shown:

 $Recalculated \ percentage \ CH4 = \frac{Original \ percentage \ CH4 * 100\%}{Total \ percentage \ original} = \frac{5\% * 100\%}{(35\% + 15\% + 5\%)} = 9\%$

The recalculated percentages of the other components in the flare are shown in Table 4.

Component	Mass Fraction
N ₂	0.35
СО	0.30
H ₂	0.15
CO ₂	0.14
CH ₄	0.05
SO ₂	0.002
H ₂ S	0.008
Total	1

Table 3 given composition flue gas feed

Table 4 Recalculated composition of the flare

Component	Mass fraction
N ₂	0.64
H ₂	0.27
CH ₄	0.09
Total	1

2.9.2 Energy output

The Wobbe index is a measure the amount of energy that can be obtained. The Wobbe index (W) [J/m3] is defined by calorific value divided by the square root of the relative density of the gas. The relative density is the density of the gas divided by the density of air at the same temperature and pressure (1 atm, 273.15K), these conditions are called Standard Temperature and Pressure (STP). [58] The lower heating value (LHV) and the higher heating value (HHV) [59], i.e. the net calorific value and the gross calorific value, of each component is used in order to obtain the lower Wobbe index and the Higher Wobbe index, where the calorific value of nitrogen equals zero.

	N2	H2	CH4	Air
Density [kg/m3]	1.2506	0.0899	0.7170	1.293
Relative density (Q)	0.9672	0.0695	0.5545	1
Sqrt relative density	0.9835	0.2637	0.7447	1
LHV (H) [MJ/m3]	0	10.8	35.8	na
HHV (H) [MJ/m3]	0	12.7	39.8	na
Lower Wobbe index (W) [MJ/Nm3]	0	40.96	48.08	na
Upper Wobbe index (W) [MJ/Nm3]	0	48.16	53.45	na

Table 5 Data components present in the flare at STP conditions

The calculated Wobbe indices for methane and hydrogen comply with values for these indices found in literature. [60]

Table 6 Wobbe indices found in literature

	H ₂	CH ₄
Upper Wobbe Index (W) [MJ/Nm3]	48.2654	53.3189
Lower Wobbe Index (W) [MJ/Nm3]	40.6706	47.9472

gas requires 4.017*1.5 + 12.05*0.5= 12 mol of oxygen.

From the calculated Wobbe index of each component and the mass fractions of each component in the flare the total Wobbe index can be calculated. The calculation of the total upper Wobbe index is shown below:

$$W_{total} = x_{N2} * W_{N2} + x_{H2} * W_{H2} + x_{CH4} * W_{CH4}$$
$$= 0.64 * 0 + 0.27 * 48.16 + 0.09 * 53.45$$
$$= 0.1799 MJ/Nm^{3}$$

reaction equation 10.

Resulting in a total upper Wobbe index of 0.1799 MJ/Nm³ and a lower Wobbe index of 0.1554 MJ/Nm³.

2.9.3 Flammability

 $H_2 + 0.5 O_2 \rightarrow H_2O$

In order for the gas to be flammable, the concentration must be above the lower flammability level n

	•		-						•	
(LFL or LEL).	The LEL for	hydrogen	is 4.0%	and the	LEL fo	r methane	is 5.0%.	[61] Th	e combi	ustion
reactions for	hydrogen ar	nd methane	e are sho	own belo	w.					

$CH_4 + 1.5 O_2 \rightarrow CO_2 + H_2O$	reaction equation 11.
Generally, 44.6 mol of any gas are present in one Nm ³ at 273.15 flare gas consists of 27% hydrogen and 0% CH. Thus, one m ³	iK (from ideal gas law). The recalculated
12.05 mol H_2 . From the combustion reactions can be deducte	ed that the combustion of one m ³ flare

Commonly, air consists of 21 mole% oxygen, 78% nitrogen and 1% others. [62] Meaning that in one Nm³ of air, (0.21*44.6=) 9.73 mol O₂ is present. Since, 12 mol of oxygen is needed for the combustion of one m³ flare gas and 9.73 mol oxygen is present in 1 Nm³ normal air, (12/9.73=) 1.24 Nm³ normal air is needed to combust 1 Nm³ of flare gas. Resulting in a total combustion volume of 2.24 Nm³. The data needed to calculate the molar concentration, as well as the calculated concentration can be found in Table 7.

	Amount present in 1.24 m ³ of air [mol]	Amount present in 1 m ³ flare gas [mol]	Amount present in total combustion volume (2.24m ³) [mol]	Molar concentration combustion mixture [mol/Nm ³]
CH_4	na	4.017	4.017	(4.017/2.24=) 1.79
H ₂	na	12.05	12.05	5.38
N ₂	(0.78*44.6*1.24=) 43.14	(0.64*44.6=) 28.5	(43.14+28.5=) 71.64	31.98
O ₂	(0.21*44.6*1.24=) 11.61	na	11.61	5.18
extra	(0.01*44.6*1.24=) 0.58	na	0.58	0.26
total				44.6

Table 7 Data and molar concentrations of the flare components in 1 Nm3 air

Regarding the results, it can be concluded that the molar concentration of methane isn't above the LEL. However, the molar concentration of hydrogen is above the LEL of hydrogen. Therefore the flare gas mixture, mixed with 1.24 Nm³ of air, results in combustion.

From the Wobbe index it can be seen that the combustion of 1 Nm^3 of flare gas, yields an energy production between of 0.1554 MJ/Nm^3 and 0.1799 MJ/Nm^3 .

2.10 Purge

Some units in the synthesis/ purification route need a purge. This purge contains, among others, phosgene. As mentioned earlier, phosgene is a highly toxic gas and therefore the phosgene needs to be destroyed. This can be done by hydrolysis. [63]. Hydrolysis is performed with phosgene and steam, resulting in HCl and CO₂. The obtained HCl can be reacted with a KOH solution in order to form a KCl solution.

3. Phosgene synthesis and purification

3.1 Reaction

Phosgene can be produced from carbon monoxide and chlorine in several ways. One way is catalysis by UV light. [64] Another method is a reaction which is catalyzed with active carbon. [3] Since the synthesis with active carbon is mostly used in industry and easier compared to a process using UV, it was chosen to use the carbon catalyzed reaction. Active carbon is the definition for carbon particles with a high surface area compared to volume. The reaction consists of a two-step Eley-Rideal type mechanism. [65] An Eley-Rideal reaction is a reaction which is performed on the surface of a solid. Part of the reaction mechanism is the adsorption of one of the reactants on a surface. In this case, the chlorine is adsorbed on the active carbon. After this adsorbance, the other reactant reacts directly from the gas phase with the adsorbed reactant. In our process the gaseous carbon monoxide reacts with the adsorbed chlorine. [66] This is schematically shown in Figure 7.

Figure 7. Eley Rideal reaction, taken from Weinberg, W. (1996). Eley-Rideal surface chemistry

Gupta, N et al have investigated the active carbon catalyzed synthesis of phosgene using C60 fullerene as a model catalyst. [65] In this model, it can be seen that chlorine is adsorbed on the carbon surface, creating an anion radical on a chlorine atom (Figure 8). This reacts with the carbon monoxide resulting in a radical on the carbon. After this a chlorine atom will react with the carbon radical resulting in the formation of the product. This mechanism can be found in Figure 9.

Figure 8. Chlorine (green) adsorbed on a C60 particle taken from Gupta, N.

Figure 9. Bent carbon surface moieties as active sites on carbon catalysts for phosgene synthesis

When a catalyst, such as active carbon, is specified in a process, the reactor design should guarantee maintenance of catalytic activity and that the catalyst can be recovered for regeneration, re-use or safe disposal. Two types of catalysts are available, namely heterogeneous- and homogeneous catalysts. Active carbon is an example of a heterogeneous catalyst. The benefit of heterogeneous catalysts is that they are easier to recover and re-use. This recovering might be needed due to catalyst deactivation. This deactivation can be caused by poisoning, amalgamation, coking, leaching and plugging, making the catalyst inaccessible for the reactants. Strategies to tackle this, are temperature ramping, where the temperature of the reactor is increased over time as the activity drops over time, and use of excess catalyst. [45] In both cases, it might be needed to substitute or clean the catalyst after a certain period of time.

The feed to the reactor consists mostly of chlorine and carbon monoxide. Since the gas feed of carbon monoxide is not completely pure, the reactions of the other gases with chlorine and carbon monoxide should be considered. The amount of these other gases is almost negligibly small, however, when present, the following side reactions might occur:

$H_2 + CI_2 \rightarrow 2HCI$	reaction equation 6
$2 \text{ CO+ } 2 \text{ Cl}_2 \rightarrow \text{CCl}_4 + \text{CO}_2$	reaction equation 7
$CO + H_2 \rightarrow C + H_2O$	reaction equation 8
$CH_4 + 4Cl_2 \rightarrow CCl_4 + HCl$	reaction equation 9

This means that in the purification step of the product it could be necessary to remove these sideproducts.

3.2 Reactor choice

3.2.1 The reactor

For the production of phosgene a reactor with a parallel catalyst tubes aligned in the longitudinal direction, is used. The ends of the pipes are fixed with a tube plate and a cap. The reaction gases are passed through the hollow catalyst tubes. Baffles are in place with ends opposite to each other. A heat transfer liquid is passed around the intermediate spaces between the catalyst tubes, in the latitudinal direction, around the baffles. Each catalyst tube can be looked at like a single PFR.

Heat transfer medium enters and exits at (11) in Figure 10, reaction mixture enters and exits at top or bottom.

There will be a pressure drop over the reaction, because of the many small pipes, a compressor before the reactor is probably required. [67]

Figure 10 tube and shell reactor

The reaction conditions in the reactor are as following (for this patented example):

- reaction temperature: 40-50°C
- catalyst particle size: 3-5 mm
- tube diameter size: 50-70 mm
- pressure: 1-3 bar (super atmospheric conditions are used so that the phosgene can be condensed by using cooling water)

Reactor materials (for this patented example):

- The number of catalyst tubes is preferably in the range from 100 to 10000, in particular from 1000 to 3500.
- the catalyst tubes, and preferably the entire reactor, are made from corrosion resistant material (1.4462, 1.4571 or 1.4541 stainless steel)
- Each catalyst tube preferably has a wall thickness in the range from 2.0 to 4.0 mm, in particular from 2.5 to 3.0 mm
- Each catalyst tube has an internal tube diameter in the range from 20 to 90 mm, preferably in the range from 30 to 35 mm
- The catalyst tubes preferably have a length in the range from 1.5 to 6.0 m, in particular in the range from 2.0 to 3.5 m.
- The tubes are in a triangular pitch with ratio between directly adjacent tubes/external tube diameter between 1.15 and 1.4, preferably between 1.2 and 1.3.
- The internal diameter of the reactor is, if it is a cylindrical apparatus, from 0.5 to 6.0 m, preferably from 1.0 to 3.0 m.

3.2.2 The catalyst

Cabot is a manufacturer of many different forms and sizes of activated carbon, powdered, granular and extruded, with the brand name Norit. [68] In chapter 4.2.3.1.1 the design choices for our catalyst are given in Table 11.

3.3 phosgene purification

As hot spots are inevitable when dealing with such an exothermic reaction, carbon dioxide and carbon tetrachloride are formed in the reactor. Phosgene is used in the synthesis of MDI, which in turn is used to create poly urethanes. The creating of polymers is a sensitive process where impurities can have a negative effect on the molecular weight of the polymers. Therefore phosgene must undergo some purification steps after its formation in the reactor.

3.3.1 Amine gas treating

The first step in the purification of phosgene is the removal of CO_2 from the product stream. This is once again conducted by amine gas treating. The process is identical to the amine gas treating in 2.5.2 described earlier.

3.3.2 Dehydration of product stream

Because amine gas treating is a wet process, water is entrained in the product stream. Water reacts with phosgene, producing hydrochloric acid and CO_2 . At 25°C, the reaction rate of water and phosgene is negligible at 6 sec⁻¹. When the temperature rises to 35°C however, the pseudo first-order reaction rate constant increases to 22 sec⁻¹, which is only four times faster. [69] It is therefore important to remove water from the product stream.

A normal flasher is not able to separate phosgene and water properly. Figure 11 is obtained from Aspen, this shows that water and phosgene cannot be separated, because the ratio between water and phosgene remains roughly constant throughout the analysis. Therefore, another method should be used for the drying process of phosgene.

Therefore, it was decided to use glycerol to dehydrate the product stream. This process is similar to the amine gas treating except glycerol dehydration is based on physical absorption instead of chemical absorption.

The product stream enters the absorption tower at the bottom, with liquid glycerol entering at the top. The streams flow counter current, dissolving water in the glycol, and a dehydrated product stream leaving the top of the tower. The glycerol is then thermally regenerated in the stripper.

There are several advantages to using glycerol: glycerol has low vapor pressure [70], which reduces vapor losses, especially at the high operational temperatures. Besides that, it is non-corrosive and non-toxic.

Glycerol dehydration has disadvantages as well: since glycerol has a high viscosity [70] (1.5 Pa s⁻¹ at 20°C), pumps have to deliver a high duty to pump the liquid around. In addition, it has a high boiling point (290°C). [70] Hence, the reboiler duty in the stripper is large. However, the high boiling point of glycerol makes a sharp separation between water and glycerol achievable.

3.3.3 Phosgene distillation

After glycerol dehydration, the phosgene still contains several impurities including nitrogen, methane and carbon monoxide. The stream is fed to a distillation tower, where phosgene is separated from these impurities. Due to the maximum capacity of distillation towers, five towers are placed in parallel.

Since phosgene has a boiling point of only 8°C, while the other gaseous impurities have a much lower boiling point, satisfactory separation is realized in the towers.

4. The model

4.1 Process description

The first step in the process is the clean-up of the flue gas, in order to obtain pure carbon monoxide. Since the gas feed originates from the steel industry, it contains hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane and sulfur compounds. The weight percentages are specified. The clean-up starts with a wet process using a lime slurry in order to separate the sulfur dioxide. Hereafter, the carbon monoxide and hydrogen sulfide are separated by washing with an amine solution. After which the gas is fed to a desiccating tower in order to exclude possible entrained water. Finally, carbon monoxide is separated from the gas feed by Pressure Swing Absorbance (PSA). A gas mixture of nitrogen, methane and hydrogen is removed, and flared. The cleaned gas, which now only contains carbon monoxide, is fed to the reactor together with chlorine. Chlorine is obtained from an external source. Special care has to be taken in the process to prevent hydrolysis, i.e. reaction with water, this results in the formation of hydrochloric acid. This can be avoided by minimizing the hydrogen content of the gas feed stream.

The purified carbon monoxide stream and chlorine are fed to a reactor, which contains a catalyst. The carbon monoxide is added in excess to ensure full conversion of chlorine. This will prevent emission of chlorine gases. The catalyst in this reaction is activated carbon. Besides the main reaction, also some side reactions can occur. Hydrogen and chlorine might react to hydrochloric acid and carbon monoxide and chlorine might react to the carcinogenic carbon tetrachloride, see reaction equation 6 and 7. [71]

 $H_2 + CI_2 \rightarrow 2HCI$

Reaction equation 6.

 $CO + Cl_2 \rightarrow CCl_4 + CO_2$

Reaction equation 7.

The carbon dioxide, which is possibly formed, is removed using an ethanolamine (MEA) scrubber. The MEA is regenerated in a stripper. During the CO₂ absorption, unwanted water gets entrained in the gas mixture. This water is absorbed by glycerol in the next absorber. Also this glycerol is regenerated by stripping glycerol from phosgene. In the final purification step the dry phosgene is further purified by distillation in five different towers in parallel. All phosgene containing purges are fed to a second reactor where the phosgene is hydrolyzed with steam. This results in the formation of hydrochloric acid and water. This yields, upon condensation, an aqueous and a gaseous stream. The aqueous stream contains an aquatic HCl solution and the gaseous stream consists of gaseous HCl and trace carbon monoxide and carbon dioxide. These streams are fed to a third reactor where the HCl is reacted with an aqueous KOH solution in order to form aqueous KCl and gaseous CO₂ and CO. The gaseous stream is disposed, possibly underground, and the aqueous stream can be disposed in the sea or used as a fertilizer.

4.2 Section model description

Section 1 is the SO₂-scrubber and was calculated using excel. Section 2 was modeled in Aspen, in this section H₂S and CO₂ are removed from the flue gas. Section 3 was calculated using excel. Section 4-7 consists of three main steps modeled in aspen; the production of phosgene, the purification and the destruction of leftover phosgene. In the end, a yield of 93.96% of phosgene, with a purity of 99.99 w% was obtained. The yield is based on the amount of phosgene coming out of the distiller divided by the amount of phosgene produced in the reactor. The reactor sizing for section four on the tube and shell side, was calculated in excel. All PFDs and P&IDs of the sections are in the appendix. The PFD are in appendix A. The P&ID for section 1 to 7 are in appendix B.1 to H.1 respectively.

4.2.1 Section 1 the SO₂ scrubber

For the SO₂ removal, a model was created in excel to describe the different flow in the wet limestone scrubber. A few assumptions were made for this process:

- The reactor is twenty meters in height because of the high gas flow
- The gas flow is divided by five at the start of calculations, this means that there are actually five scrubbers in parallel
- The falling velocity of the droplet is 9 m/s
- The process is mass transfer controlled where the mass transfer is from the gas phase to the water droplet, the mass transfer in the droplet to the limestone is neglected
- The mass transfer coefficient is 0.01 m/s
- The change in volumetric flowrate is neglected; the water droplet consists of 10 w% limestone and 90 w% water
- The gas behaves as a plug flow reactor
- The diameter of the limestone particles exiting the crusher is 0.044 mm. [72]

First, the mass transfer for one droplet of limestone slurry was calculated using $J_A = k_g * C_{AG}$, where k_g is the mass transfer coefficient, C_{AG} is the concentration of Sulfur dioxide in the gas phase and J_A is the flux in mol/(s*m²). Using this formula and the assumption that the gas stream behaves as a plug flow reactor the concentration of the Sulfur dioxide leaving the reactor could be calculated using Equation 1.

$$[SO_2]_{out} = [SO_2]_{in} * \exp(\frac{-k_g * A_{droplet} * H * n_{droplets}}{\phi_v/_5})$$

Equation 1

In excel, a list of increasing droplets was created for calculation of flow rates. The amount of droplets used for further calculations was $1.30*10^8$, because this number of droplets was close to the efficiency $([SO_2]_{out}/[SO_2]_{in})$ found in literature, 98%. However this number is applicable when a small amount of MgO is added to the slurry, which was not modelled because of the limits of the model. [24] This number of droplets also had a round number of nozzles. The efficiency calculated in our model is 99.99%. Using the volume of the droplet, the falling velocity and the number of droplets, the flow rate of slurry exiting the nozzles was calculated. With the nozzle flow rate found in literature, the number of nozzles was calculated to be 7, with the MaxiPass nozzle which can spray up to 0.28 m³/s. This nozzle was also capable of handling dirty and lumpy liquids, which is perfect for our slurry. [73] The amount of water and limestone pumped around was also calculated using the weight percentages and the number of droplets per second, these amounts were $6.73*10^6$ kg/h and $7.47*10^5$ kg/h respectively.

In the model it is assumed that all Sulfur dioxide is turned into gypsum and that the dewatered wet gypsum cake removed contains 25 w% water. This produces a total of 1.45 ton/h of gypsum which has a value of \pounds 18.61. This also requires a total of 134.9 kg/h of oxygen to be added to oxidize the CaSO₃ to CaSO₄ in order to create the gypsum, which we add at 1.5 bars to make sure no back up occurs in the oxygen blower. The total amount of limestone and water to be added to the process are 843.6 kg/h and 787.3 kg/h respectively. The total amount of carbon dioxide released in the scrubber is 371.0 kg/h.

To make sure that no entrainment of droplets occurred, even though there is a demister in the top of the reactor, the gas velocity had to be lower than the droplet velocity. If the velocity of the gas would be higher than the velocity of the droplet, the drag force of the gas on the droplet would be higher than its gravitational force, causing entrainment. A gas velocity of 8.55 m/s was assumed. Using this number and the flow rate a tower diameter of 5.37 m was calculated.

For the pressure drop over the column the mass flow rate was assumed to be an average of the inlet and outlet, to calculate the density using the constant gas flow rate. The Bernoulli equation was used. The pressure drop is only 75 mbar, however due to the size of the gas stream there is still a lot of compressing power required to make sure it returns to 1 bar.

The tank collecting and mixing the slurry and where the oxidization to gypsum occurs (T1101) was assumed to be roughly 30 m³, with a height of 3 m and a diameter of 3.5 m. This is to ensure enough space is available for all the slurry pumped up every second, and all the oxygen and extra limestone slurry added. The tank mixing the water and the limestone particles into a slurry was taken to be 3 m³. The demister was taken to be 15cm in thickness.

Column height (m)	column diameter (m)	flow rate slurry pumped to nozzle	nozzle flow rate (m ³ /h)	number of nozzles	gas flow rate (m³/h)
20	5.37	7067.06	1008	7	6.97*10 ⁵
limestone added (kg/h)	water added (kg/h)	pressure drop slurry (bar)	pressure drop gas (bar)	Oxygen flowrate (m ³ /h)	Residence time (s)
843.6	787.3	2.07	7.5*10 ⁻⁴	94.4	2.22

Table 8 dimensions, flow rates and pressure drops for a single scrubber system

4.2.2 Section 2 the CO_2 and H_2S absorber

First an equilibrium based RadFrac was made, to model absorption tower C1201. The RadFrac was tuned to achieve maximum CO_2 and H_2S absorption in the MEA solution. The number of stages was set to 8, with the MEA solution entering above stage 1 and the flue gas at stage 8. No condenser or reboiler was used in the tower. The pressure of the top stage was set to 5.5 bar.

Secondly, stripper C1202 was modeled as an equilibrium based RadFrac. The number of stages was set to 10, with a partial-vapor condenser and a kettle reboiler. The molar reflux ratio was set to 60, the molar boil up ratio was set to 0.3. These setting were used to achieve maximum concentration of CO_2 and H_2S in the sour gas stream leaving at stage 1.

After that, stream 1221 was attached to heat exchanger E1201. Stream 1224 was then led to the purge section, which is required in Aspen to close a recycle loop. The splitter was set to 30 w% purge, otherwise running Aspen resulted in a mass balance error.

Stream 1224 was continued to P1201, which was set to a discharge pressure of 5.5 bar. Stream 1224 was then attached to E1204, which was set to an outlet temperature of 20°C.

Mixer B2 was modeled to mix amine make-up stream 1203 with 1204. The amine make-up stream was initially set to 900 ton/h. The stream leaving the mixer, 1205 was attached to C1201, closing the recycle loop.

E1201 was set to a hot side temperature leaving the exchanger of 100 °C, to reduce reboiler power required in C1201 while reducing cooling power of E1204.

4.2.2.1 Design Spec

As soon as the loop was closed, it was obvious that the amine make-up stream was too large. Design spec MAKE-UP was introduced to reduce the amount of amine make-up and reduce the purge stream. Stream 1203 was to be varied, resulting in a mass flow equality of: 1203+1202 = 1215+PURGE+1206

After the design spec was introduced, the splitter was set to a split fraction of 0.04. The amine makeup stream 1203 was successfully reduced to 88127 kg/h.

Consequently, design spec MAKE-UP was deactivated. All streams were reconciled, resulting in the current Aspen model.

4.2.3 Section 3 the pressure swing adsorber

The pressure swing adsorber could not be modeled in aspen plus. Therefore, the calculations on this piece of equipment were done in excel and some assumptions were made. In high purity CO gas separation by pressure swing adsorption by F. Kasuya and T. Tsuji a pilot PSA plant and the first commercial plant are described. [46] In these plants carbon monoxide is extracted from a flue gas. The commercial plant in this article was able to produce a 99%+ pure outflow of carbon monoxide with a yield of more than 90%. These numbers are also used for the calculations on the PSA section. In these calculations, it is assumed that the 1% impurities consist of the other gases present in the gas feed and are distributed by their concentration. This means that, before the PSA the gas mixture consists, besides carbon monoxide, of hydrogen, methane and nitrogen, and therefore these three are considered as impurities in the gas feed. Since nitrogen is present in the highest quantity before the PSA, it is also considered to be the main component of the 1% impurities.

In the pilot plant described in the mentioned article, it is stated that 4 adsorption columns of each 80 liters adsorbent are needed for a gas feed of 15 Nm^3/h . This corresponds to $4.7*10^{-2} Nm^3/h$ for every liter adsorbent.

СО	H ₂	CH ₄	N ₂	total
405000 kg	202500 kg/h	67500 kg/h	472500 kg /h	
14464 kmol/h	101250 kmol/h	4208 kmol/h	16870 kmol/h	136798 kmol/h

Table 9 Conversion of the mass flow to the molar flow of the components considered by PSA

The total molar flow (136798 kmol/h) corresponds (assuming Vm of 24.5l/mol) to a volumetric flow of $3.35*10^6$ Nm³/h. This means that $7.15*10^7$. Liters of adsorbent is needed. This corresponds to $7.15*10^4$ m³ of adsorbent. This amount should be divided over multiple columns and multiple plants. When columns are considered which have an adsorbent with 40% void fraction and have assumed dimensions of 5 by 20 meters, a column can hold 157 m³ of adsorbent. This means that 455 columns are needed for this process. This number should be even, in the model 456 columns are simulated.

Before the PSA, the gas is dried using desiccating towers. These are filled with activated alumina. The activated alumina has a dynamic drying capacity of up to 15. [42] The dynamic drying capacity is the amount water absorbed on a bed, divided by the mass of the bed. [74] Since the desiccating towers have to remove 149.7 ton/h of water, it can be calculated that 9980 kg activated alumina is needed/ hour. Since in normal drying processes one cycle takes about 8/hours, this means that 79840 kg alumina is needed for a cycle. Since normally one tower is generated while another tower is in process, two times this amount is needed in the process. This corresponds with a total of 159680 kg activated alumina.

The activated alumina has a particle density of around 800 kg/m³. [75] This means that $200m^3$ of activated alumina is needed. When a packing of 40% is assumed together with towers of 2*8 m, every tower will hold 10 m³. This means that 20 towers are needed for the desiccating part.

The desiccating towers have to be heated to 57°C in order to remove water. Since there are 20 towers from which 50% is being dried constantly, this means that 10 towers have to be heated. This heating has to be only 7 degrees. Therefore, this energy together with the heat of wetting is ignored.

The pressure drops are calculated using the Ergun equation, Equation 2. This resulted in a pressure drop of 2.6 bar over the desiccating towers. For this, an average particle diameter of 25 μ m was assumed, based on the vending information provided by Sigma-Aldrich. [76] For the viscosity of air, a value of $1.96*10^{-5}$ Pa.s was assumed, which is the viscosity of air at 57.5°C and 5.5 bars. The dimensions for the columns are used as they are described in the above section. The gas superficial velocity is determined by the gas flow [m³/h] divided by the area of the columns [m²] and is determined to be 0.12 m/s.

The PSA section has a pressure drop of 3.6 bar, with the assumed particle size of 2 mm. [77] The viscosity of the gas mixture entering this section, was taken to be $1.96*10^{-5}$ Pa.s. The superficial velocity was calculated to be 0.104 m/s. The density was calculated to be 1.019 kg/m³.

$$\Delta p = \frac{150 \,\mu\,L}{D_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} v_s + \frac{1.75 \,L\,\rho}{D_p} \frac{(1-\varepsilon)}{\varepsilon^3} {v_s}^2$$

Equation 2 Ergun equation

Where ε = the void fraction of catalyst

D_p = the spherical diameter of the catalyst,

 v_s = the superficial velocity of the gas if no catalyst was present in the tubes

 μ = the viscosity, in our case the viscosity of air was assumed

L = length of the packing in the pipe, the entire length of the pipe was used for packing,

 ρ = density of the gas mixture

4.2.3.1 Notes on heat balance

The inlet pressure is 5.5 bar before compressor K1301. The desired pressure of the outlet of the desiccating towers is 3 bar. From the Ergun equation, it was calculated that the pressure drop over the desiccating towers (C1301 and C1302) equals 2.6 bar. Therefore, the compressor (K1301) needs to compensate 0.1 bar. This compressor was modeled in Aspen in order to determine the required energy.

The compressor in the PSA section (K1302) needs to be able to achieve two different pressures, i.e. the pressure in the feed step should be 30 bar and the pressure in the blow step should be 0.1 bar. In the blow step, the feed is plugged. This means that the outlet pressure has to be reduced from 30 to 0.1 bar. In the feed step, the compressor has to compensate for the pressure drop over the adsorption towers (C1304 and C1305). From the Ergun equation, it was calculated that this pressure drop equals 3.6 bar.

For the heat balance, the power of the compressor (K1302) was based on the pressure drop it needs to deliver in the feed step. Since most of the operating time, the outlet pressure of PSA will be 30 bar. It is assumed that the outlet pressure of the compressor is adjustable. The outlet temperature of the compressor (K1302) equals 418°C, meaning that the heat exchanger has to reduce the temperature to 25° C, i.e. Δ T= 393° C, and the pressure is reduced to 3 bar in order to be fed to section 4.

4.2.4 Section 4 to 6 the production and purification

In section 4 phosgene is produced and the CO₂ is removed. In this section, MEA is also regenerated.

4.2.4.1 The production

The three streams, which were put into a mixer, were defined. One containing only chlorine, one containing only carbon monoxide, which was in small excess (500 kmol/h) to the chlorine, and one containing the impurities which were left over from the previous flue gas clean-up. After mixing these streams, 80% was split off to other plants, because of the high quantity of flue gas coming from the steel mills.

The mixture was added to a stoichiometric reactor model. In this reactor a conversion of 0.05% was defined for a reaction between chlorine and carbon monoxide to simulate the trace amount of carbon tetrachloride formed at the hot spots in the physical reactor. The reaction equation which shows the formation of carbon tetrachloride can be seen below (eq. 7). The carbon dioxide formed in this reaction is dealt with in the purification process, the tetra could not be removed. This reactor was operated at 40°C and 3 bar.

$2\text{CO} + 2\text{Cl}_2 \rightarrow \text{CCl}_4 + \text{CO}_2$

reaction equation 7

After the stoichiometric carbon tetrachloride reactor, the mixture was put into an equilibrium reactor for the phosgene production. Research found that the reactions equilibrated at 99.99% conversion of chlorine [78] (hence the excess of carbon monoxide described earlier). This means that the use of an equilibrium reactor is allowed. The equilibrium reactor operates at 40°C and 3 bars and converts all chlorine left after the stoichiometric reactor, to phosgene. No kinetic data was available so no multi tubular reactor could be modeled in aspen.

The streams leaving the reactors consisted of the following amounts: 98.78 w% phosgene, 0.038 w% carbon tetrachloride, 1.11 w% carbon monoxide, 0.01 w% carbon dioxide and the rest consisted of the nitrogen and methane impurities which could not be removed from the flue gas.

4.2.4.1.1 phosgene reactor design, tube side

Figure 12 the tube and shell reactor [67]

In reactor R1401, the formation of phosgene from carbon monoxide and chloride takes place: $CO + Cl_2 \rightarrow COCl_2$. Since this reaction is highly exothermic a patented tube and shell reactor is used. Carbon monoxide and chloride flow through the tubes that are filled with an active carbon catalyst. A solution of 50 w% ethylene glycol in water [79], acting as coolant, flows through the shell. It is of importance to properly cool the reactor to prevent the formation of hot spots. The unwanted formation of carbon tetrachloride CCl_4 occurs in hot spots. The reaction takes place at the tube side at 40°C. The gas produced can be corrosive, therefore the tubes are made of stainless steel 316. The ends of the tubes are fixed with a tube plate and cap.

On the shell side the cooling liquid flows. Baffles are placed on opposite ends of each other and a cooling liquid is passed through to keep the reactor at 40°C. The heat released in our reactor is 75 MW as calculated in aspen. N.B. as also described in the aspen modeling chapter, the gas flow into the reactor is only a fifth of the total flow rate. N.B. as also explained in the aspen chapter, the aspen reactor is modeled as two different reactors.

The reactor was modeled in excel with the dimensions given in

Table 11, with numbers chosen according to the patent while calculating reasonable pressure drops. [67] For the calculations the extend Ergun equation was used given in Equation 2. [80]

The viscosity of air was assumed because aspen cannot calculate a mixture of components. Since two gas molecules react into one, the volumetric flow rate halves. As a consequence, the gas velocity halves which affects the Ergun equation. For simplicity purposes two pressure drops were calculated: for the gas velocity at the start of the reactor and for the gas velocity at the end of the reactor. The gas velocity in the reactor was assumed to be the average of these two, thus the average of these pressured drops was taken as the overall pressure drop over the reactor. The results are depicted in Table 10.

Table 10 pressure drop calculations in the reactor

	Start reactor	End reactor
flow rate (m ³ /h)	41565.53	21564.05
superficial velocity gas (m/s)	2.21	1.15
density (kg/m ³)	6,02	11,60
viscosity (Pas) (air)	1.92*10 ⁻⁵ (at 3 bars)	1.92*10 ⁻⁵ (at 1 bar)
dP (pa)	3.08*10 ⁵	1.60*10 ⁵
Average pressure drop (Pa)	2.34	*10 ⁵

The tubes are configured in a triangular pitch which is 1.25 times the outside tube diameter. The amount of 1500 is justified by the size of the gas stream and because of the low pressure drop it has as a consequence, which is necessary because at high pressures side products such as carbon tetrachloride can be created. A total of 7.82 m³ of activated carbon is necessary for the pipes, which can have a variety of densities, this number is already considering the void fraction of 40%.

internal tube diameter (m)	3.57*10 ⁻³ (OD 1.5")
number of tubes	1500
total tube cross sectional area (m ²)	5.77
tube length (m)	2.50
Tube wall thickness (m)	2.41*10 ⁻³
pitch (mm)	47.6
packing void fraction	0.40
heat transfer area (m ²)	420
D _p catalyst (m)	0.004
Pressure drop (bars)	2.34

Table 11 reactor dimensions tube side

4.2.4.1.2 phosgene reactor design, shell side

Using the required heat flow, a simple cooler was modelled in Aspen. The coolant cannot reach a temperature higher than 40°C in the reactor. By performing a sensitivity analysis, the required utility stream consisting of 50w% ethylene glycol solution in water was identified to be $1.84*10^{6}$ kg/h, at 0°C. See Figure 13.

FIGURE 13 SENSITIVITY ANALYSIS FOR 50W% GLYCOL FLOW RATE

The bundle diameter was calculated using Equation 3. The shell clearance was set to 96 mm.

$$D_b = d_o (\frac{N_t}{K_1})^{1/n_1}$$

Equation 3 bundle diameter

Where Nt = number of tubes

D_b = bundle diameter, mm

d_o = tube outside diameter, mm

TABLE 12 BUNDLE, SHELL AND BAFFLE DIMENSIONS

Bundle	Bundle diameter	Shell	Shell inside	Number	Baffle
diameter	(m)	clearance	diameter	of	spacing
(mm)		(mm)	(mm)	baffles	(mm)
1987	1.987	96	2083	4	415

The shell clearance was chosen to be 96 mm, to obtain a standard sized shell diameter of 2083 mm (82") and a reasonable pressure drop. The method of design is very similar to the heat exchanger design in section 4.4.

Table 13 pressure drops over R1401

R1401	Shell side
Exchanger pressure drop (bar)	0.97
Nozzle pressure drop (bar)	0.12
Total pressure drop (bar)	1.10

The pressure drops over R1401 are reasonable. The shell side is filled with a liquid coolant, which means the allowable pressure drop is 3.5 bar. The pressure drop of 1.10 bar is thus well below the maximum. [45]

4.2.4.2 The purification

The gas stream leaving the reactor went through three purification steps: a carbon dioxide removal step using ethanolamine (MEA) in water, a water removal step using glycerol, and a dry phosgene distillation to remove the remaining impurities. All RadFracs in the simulation have tray spacing of 600 mm because of the high volumetric flow. The trays were also modeled as bubble cap trays. For the maximum jetflood and downcommer/tray size, 80% was assumed.

4.2.4.2.1 the CO₂ absorption using MEA

In this process, a rate based RadFrac was used to simulate the absorption process. This RadFrac, with no reboiler nor condenser, was put on method: amines. The amines property method uses the Kent-Eisenberg correlation for K-values and enthalpy. It is designed for systems containing water, an ethanolamine, hydrogen sulfide and/or carbon dioxide present in gas sweetening processes, which is applicable for our process. [81] This RadFrac had two inlets: The CO₂ rich gas stream from the reactor and a MEA in water stream. The MEA had a mass fraction of 20 w%, this ratio was determined by trial and error. The streams, which were both kept at 4 bars using compressors and pumps and 59°C and 25°C for the gas and MEA streams respectively, were put counter current through the RadFrac. Subsequently, the CO₂ lean phosgene gas stream, which now contained some water, was transported to the water removal purification step.

The CO₂ rich MEA stream was fed to a stripper, i.e. another RadFrac using rate based method, which used the NTRL-RK method. The method was switched for simulation purposes; the NTRL-RK method for the stripper behaved as expected i.e. all the CO₂ was stripped from the MEA. This was not achieved using the AMINES method. In this stripper, all the CO₂ and phosgene, which also dissolved in the previous column, was removed. All MEA was recycled using a purge, a fresh supply of MEA and water, and a design spec. This stripper operated at an inlet of 37°C and had gas and liquid outlets of 140°C and 147°C respectively. 15 mol/h of phosgene was lost in this entire absorption and desorption process. Below a table of RadFrac dimension are given in Table 14. This makes the CO₂ absorber 9 m and the stripper 12 m high.

column	pressure drop [bar]	trays	diameter [m]	molar boil up ratio	molar reflux ratio	downcommer width [m]	clearance [m]	weir [m]
CO ₂ absorber	0.11	15	3.6	0	0	0.2	0.2	0.2
CO ₂ stripper	0.17	20	0.9	0.8	0	0.05	0.15	0.15

Table 14 RadFrac dimension for CO₂ absorber and stripper

4.2.4.2.2 the water removal using glycerol

The phosgene stream containing water and a small amount of MEA was pumped to a water absorber. Before going into the compressor it first had to pass a heater, because the stream leaving the CO₂ absorber was below its dew point. The absorber was modeled as a rate based RadFrac of dimensions shown in Table 15. With 15 trays, it has a height of 9 m. A reboiler was modeled as a flasher set to 200°C to ensure that most phosgene went to the dry phosgene gas stream coming from the top of the column. A normal reboiler could have been possible as well, however this allowed us to model another tray in the tray rating and therefore a more accurate pressure drop. The RadFrac has two entering stream, the wet phosgene stream in the bottom and a pure glycerol stream entering in the top. Running the stream counter current allowed us to remove all the water, however a small amount of
114 kmol/h of phosgene was lost and purged in the destruction step. A loop of this lost phosgene back to the absorber showed to be too hard because of the large amount of glycerol still in the stream after the glycerol stripper. The liquid outlet of the absorber contained 0.7 w% water and 9 w% phosgene, the rest consisted of glycerol.

The glycerol stripper was again modeled as a rate based RadFrac, with its dimensions shown in Table 15. With 30 trays, it is the largest column in the process and has a height of 18 meters. Because of the stream entering at already 200°C and the high boiling point of glycerol the reboiler runs quite hot with a glycerol recycle stream coming out of the bottom of 324°C. In the loop a small amount is purged to make sure no accumulation happens and the gas stream leaving the stripper is destroyed in a later step.

column	pressure drop [bar]	trays	diameter [m]	molar boil up ratio	molar reflux ratio	downcommer width [m]	clearance [m]	weir [m]
Water absorber	0.25	15	3.7	flasher at 200°C	0	0.45	0.15	0.15
glycerol stripper	0.43	30	5	3	10	1.5	0.15	0.15

Table 15 RadFrac dimensions for water absorber and glycerol stripper

4.2.4.2.3 the distiller

The almost pure dry phosgene gas leaving the water absorber was compressed to 4 bars and subsequently cooled to 10°C, slightly below the boiling point of phosgene. It was decided that the stream had to be divided by five different distiller in parallel, represent as manipulator blocks before and after the distiller. The rate based RadFrac, with a flasher put on 2°C as a condenser and a normal reboiler has dimensions shown in Table 16. With 29 trays, it has a height of 17.4 m. The gas stream leaving the top of the reactor contains, after multiplying by five, still a negligible amount of carbon monoxide (3.8% compared to the inflow at the start of the reaction) and is therefore not recycled. Especially considering there is an even larger flow of carbon monoxide available from the flue gas, which was divided by five in the beginning. In the end a yield of 93.96% of phosgene, with a purity of 99.99 w% was obtained.

Table 16 RadFrac dimension for the distillers

column	pressure drop [bar]	trays	diameter [m]	molar boil up ratio	molar reflux ratio	downcommer width [m]	clearance [m]	weir [m]
distiller	0.36	29	1.4	1	flasher at 3°C	0.4	0.15	0.15

4.2.5 Section 7 the destruction

Three leftover streams were combined (1704) using a mixer. The three leftover streams were the one coming out of the top of the carbon dioxide stripper (1422), the one coming out of the glycerol stripper (1529) and the one coming out of the distiller (1625). This stream's composition and magnitude were copied into a different aspen simulation.

In an equilibrium reactor the phosgene and trace amount of carbon tetrachloride were reacted with steam to create HCl and CO_2 . Subsequently, this gas mixture was cooled in a flasher set on 20°C to

condense most of the water. Finally, the gases were reacted with KOH in water (16 w% KOH) to create a neutral mixture of KCl. The liquid outlet will be returned to the ocean, the gas outlet will be burned or released. No phosgene or carbon tetrachloride was present after the destruction.

4.3 Pump design

The pump chosen to be designed using pump curves was the pump transporting the MEA/water solution to the CO_2 -absorber in section 4, P1402. In this pump a total of 11922.63 kg/h or 11.95 m³/h has to be increased from 1 bar to 4 bars.

The process starts by calculating the pressure head given in Equation 4. Where p_g is the pressure difference in Pa, ρ is the density of the flow in kg/m³ and g is the gravitational acceleration, 9.81 m/s. Filling in the numbers gives a total head of 30,64m.

$$\psi = \frac{p_g}{\rho * g}$$

Equation 4 pressure head

Based on appendix L.1 pump CPKN – 32-160 was chosen, with has a rotational speed of 2900 rpm. Using appendix L.2 an impeller of 169 mm was chosen which resulted in a NPSH_R of 0.9m and a required power input of 2.15 kW. Using Aspen an efficiency of 55% was measured.

4.4 Heat Exchanger Design

4.4.1 Design Method

Heat exchanger E1401 is used to cool the lean amine stream coming from stripper C1402. E1401 was modelled in Aspen to calculate the pressure drop and design specifications. The first step was to identify the duty that is delivered by the heat exchanger in the process. Next, a simple heater with that duty (1055 kW) was built in Aspen. A cooler with a duty of -1055 kW was used to identify the utility stream that absorbs the heat. A 50/50 w% water/ethylene glycol stream at -15 °C was used. Subsequently, a heat exchanger model was built, using "Shortcut" method with an estimated overall heat transfer coefficient of 800 W/m².K. The specification was set to a duty of 1055 kW. Aspen estimated the heat exchange area to be 29.92 m².

Layout & tube size, number of tubes, bundle & shell diameter and baffle spacing were designed to match the required heat exchange area. An excel model was built to easily see how each parameter influences the exchange area.

4.4.2 Specifications

4.4.2.1 TEMA type

E1401 is chosen to be a shell and tube exchanger. Shell and tube exchangers commonly used, since they provide large surface area, allow many different materials of construction, are easily cleaned and are commercially available in lots of variations.

This heat exchanger is a TEMA type F- two shell pass to maximize heat exchange area while keeping pressure drops reasonable. For the ease of cleaning, a split ring floating head exchanger is chosen.

4.4.2.2 Coolant

As coolant, a 50w% aqueous ethylene glycol solution is used. At -15 °C, it is recommended to use ethylene glycol over propylene glycol. Propylene glycol is more viscous at these conditions thus will require more power to be pumped. [79]

4.4.2.3 Corrosion by heat stable amine salts

H₂S absorbed in the MEA solution reacts with the carbon steel surface. This forms a passive iron sulfide layer which protects the material of construction from corrosion. [30]

A problem is the formation of heat stable amine salts (HSAS), which accumulate in the amine solution. HSAS are formed by reaction of MEA with acidic contaminants. They become more corrosive with time. HSAS also reduce the absorbing ability and efficiency of the amine solution by reducing the amount of pure amine.

In order to control HSAS accumulation no more than 20 w% MEA solution is used. Also, the amine solution is cleaned continuously by purging and making up the amine solution in the acid gas removal. Finally, the material of construction is chosen to be SS 304 to minimize corrosion effects. [30]

4.4.2.1 Geometry

The geometry of the heat exchanger was calculated using the method from Towler and Sinnott. [45]

Tube length, outside diameter and inside diameter were set to general values. A triangular pitch is chosen for a higher heat-transfer rate, with a tube pitch of 1.25 times the outside diameter of the tubes.

TEMA shell type	Number of shell passes	Number of tube passes	Tube length [m]	Outside diameter [mm]	Inside diameter [mm]	Triangular pitch [mm]
F	2	2	5	19.05	14.83	23.8125

Table 17 layout and tube size

Subsequently, the required number of tubes and the resulting tube side velocity were calculated.

Table 18 number of tubes

Area of one tube [m ²]	Number of tubes	Tubes per pass	Tube cross- sectional area [m ²]	Area per pass [m ²]	Tube side velocity [m/s]
0.299	105	50.1	1.73E-04	8.65E-03	0.293

Finally, the bundle and shell diameter were calculated using Equation 3.

Constants K_1 and n_1 are given in

Table 20.

The number of baffles was set to 4, the minimum for 2 passes. Baffle spacing was chosen to be $D_b/5$.

Table 19 bundle, shell and baffle dimensions

Bundle	Bundle	Shell	Shell inside	Number of	Baffle spacing
diameter	diameter [m]	clearance	diameter	baffles	[mm]
[mm]		[mm]	[mm]		
306	0.306	56	362	4	72.5

Table 20 K1 and n1

Triangular pitch, pt=1.25d ₀						
No. Passes	1	2	4	6	8	
K ₁	0.319	0.249	0.175	0.0743	0.0365	
n ₁	2.142	2.207	2.285	2.499	2.675	

The nozzle diameters were chosen to be 30 mm each to prevent a high pressure drop over the nozzles.

Table 21 nozzle dimensions

Nozzle	Shell side	Tube side
Inlet diameter [mm]	30	30
Outlet diameter [mm]	30	30

4.4.3 Results

Table 22 pressure drops over E1401

E1401	Shell side	Tube side
Exchanger pressure drop [mbar]	0.34	12.3
Nozzle pressure drop [mbar]	85.7	123.2
Total pressure drop [mbar]	86.1	135.5

Table 22 shows the pressure drops Aspen calculated over the shell side, tube side and the nozzles. The pressure drops are reasonable. They are far below the general maximum allowable pressure drops of 3.5 bar. The velocity at the tube side is low, as it preferably is between 1 and 2 m/s. [45]

4.4.4 Discussion

Most of the geometry was based on Towler's method. However, the number of baffles and nozzle diameter were arbitrarily chosen to keep a reasonable pressure drop.

The velocity at the tube side is too low, as it should be between 1-2 m/s. Currently, the velocity is not high enough to prevent suspended solids settling. Higher velocities reduce fouling. Fouling was not taken into account, while it may have significant influence on heat transfer and equipment lifetime.

4.5 P&ID's

4.5.1 Nomenclature

In the P&ID's the standard nomenclature is used. The abbreviations of various equipment is shown in

Table 23. The code of every piece of equipment consists of a letter and four numbers and every stream only of the four numbers, i.e. 1111. The first number represents the plant number, the second number represents the section number and the last two numbers represents the ordinal number of a stream or equipment. For example, if PV3502 needs replacement, then an engineer should be send to the second valve of section 5 in plant 3. Next to this, identical parallel equipment is also coded. This is done by the addition of a letter to the code. For example, PV3502B means that this valve has, at least, one duplicate.

Table 23. Equipment coding abbreviation list

Α	General
С	Column
Е	Heat exchanger/Condenser
Κ	Compressor
М	Mixer
Р	Pump
R	Reactor
Т	Tank
PV	Pneumatic Valve
V	Vessel
	Stream

Furthermore, in the P&ID's varying controllers are used. These abbreviations are listed in Table 24.

xAH/xAL	Alarm High/Alarm Low
CIC	Concentration Indicator Controller
CIS	Concentration Indicator Switch
comp	Computer
FIC	Flow Indicator Controller
FIS	Flow Indicator Switch
FSH	Flow Switch High
GD	Gas Detector
HPSD	High Pressure Shutdown
LIC	Level Indicator Controller
MIC	Moisture Indicator Controller
pHIC	pH Indicator Controller
pHIS	pH Indicator Switch
PIC	Pressure Indicator Controller
PIS	Pressure Indicator Switch
TIC	Temperature Indicator Controller
TIS	Temperature Indicator Switch
TSL	To Save Location

Table 24. Controllers coding abbreviation list

4.6 HAZOP

The P&IDs after HAZOP can be found in Appendix J.2. In order to identify hazards and operability problems of the process, a HAZOP study was done, this can be found in Appendix J.1. Over every type of equipment one HAZOP is performed. The results of this study can be found in the appendix. These types of equipment are: reactor, compressor, distillation column, absorption column, stripper, tank, heat exchanger, scrubber and a condenser. Of every type of equipment, the most dangerous or important one is chosen in order to be as complete as possible.

When the reactor was analyzed, the danger of the chlorine and phosgene present in the reactor, was heavily taken into account. Both these chemicals ae toxic and very corrosive. Corrosion is one of the dangers that is analyzed extensively in this HAZOP. Because of this, several gas detectors are present in order to prevent harmful situations, due to leaking pipes and flanges.

During the analysis of the compressor, corrosion and wear are two threats that are possible to the equipment, which can cause leakage of dangerous chlorine vapor for this specific compressor. This problem was counteracted by installing a second compressor in parallel. Also smaller problems such as higher environmental temperature and too much flow coming into the compressor caused us to install a secondary compressor. Finally a back-up power supply was added to the HAZOP for possible power outages.

For the HAZOP of the distillation column again corrosion and wear were an issue, gas detectors to detect the dangerous phosgene were added to the process. Another problem was drying up of stages. Due to a change in the flow in the column and the insufficient reboil and boil up ratio for this specific flow, stages could dry up. A pressure and level indicating switch were added to the P&ID. Lastly too much pressure in the column could cause leakage. It was assumed that there is a safe location, high pressure shut down is possible and a flow indicating switch was installed.

Again for the CO_2 absorption column, C1401, drying up of stages is a possible threat. This can be caused by the MEA flow into the column being lower than needed for its corresponding CO_2 flow into the column. To tackle this problem an extra pump was installed in parallel, controlled by a FIS. Alternatively the MEA flow into the column can also be higher than expected, which can be caused by a too high recycle stream. This problem was addressed by installing a shut off valve to stream 1412. Again the pressure in the column can be too high causing equipment failure, a HPSD/TSL was installed as a safety measure.

For the CO₂ from MEA stripper, the boil up ratio can be too high or too low, which can be caused by a deviation in the heating liquid temperature. Not counteracting this problem can cause a loss of MEA or insufficient stripping, respectively. To counteract the too high boil up ratio, a TIS was installed on the hot liquid inflow for the reboiler. To counteract the too low boil up ratio, a TIS controlling a shut off valve on the phosgene inflow to the CO₂ absorber. This allows us to restrip the MEA of its remaining CO₂. Again a too high pressure can occur, with again a HPSD/TSL. In the case that the pressure gets too low, which caused the CO₂ to not be properly stripped, a TIS connected to the reboilers heating liquid flow was installed.

For the glycerol tank the level can be either too high or too low. In the case that it is too high, caused by the high inflow of the glycerol recycle, which can result in an overflow of the tank. In order to tackle this problem a level indicating switch controlling a shut off valve on the fresh glycerol supply was installed. A too low level can only occur when the tank is empty, which causes no water to be absorbed. Too much glycerol was purged or too little glycerol was supplied. Again a level indicating switch connected to the fresh glycerol supply was installed.

The heat exchanger chosen for HAZOP is the heat exchanger which is used to cool down the glycerol coming out of the striper. The temperature of the glycerol leaving the heat exchanger can still be too high, which can be caused by a higher temperature in the inflow of glycerol or insufficient cooling. To address this problem which cannot be addressed by the already existing TIC, a TIS was installed to close the inflow into the heat exchanger. The composition of the cooling water can give an indication on possible tears in the heat exchanger. Therefor a glycerol detector on the cooling stream giving an alarm when glycerol is in the cooling medium, was installed. Lastly the pressure can deviate from normal conditions, caused by the change in inflow temperature for the glycerol.

The SO_2 scrubber might encounter too much pressure in the tower, due to gas trapped in the tower. This can be caused by stuck particles in the demister in the top of the tower. To counteract possible leakages a PIS controlling a shut off valve controlling the gas flow in, was installed. Also a pressure alarm high was added to the column. In the collection tank of the slurry the pH can be too low or too high, which has consequences for the removal of the SO_2 from the flue gas. For a too low pH the gas flow is switched off and limestone is added till the pH is at the desired level. For a too high pH the gas flow keeps flowing and less limestone is added. pH indicating alarms are installed in the scrubber.

For the condenser in the phosgene destruction section, the gas flow in can be too high, caused by a sudden increase in phosgene which has to be destroyed. Due to this HCl might be insufficiently condensated. The cooling water in the condenser is already regulated to counteract this problem. The reactor is also designed to destroy gaseous HCl. The composition of the coolant can deviate when HCl gets into the coolant, indicating failure of the tubes inside the condenser. Therefor a pH indicating alarm is installed in the outflowing cooling water. Lastly the flow of HCl into the condenser can be too lower, which causes a waste of energy. All risks for the condenser are accepted.

5. Mass and Heat balances

5.1 General remarks

Some compressor in the process are installed to make sure that the pressure drop over equipment is correctly compensated for. All these compressors probably deliver a pressure increase in the order of 0-1 bar. To take the energy into account for these pumps an assumption has to be made. When an arbitrary compressor in section 4-7 is programmed in aspen it gives an indication of the amount of work needed for such a pump. Since the pressure in the reactor section is everywhere around 3 bar, a model is made increasing the pressure of the gas stream from 3 to 3.1-4 bar. The results can be found in Table 25. The compressor efficiency was obtained from Aspen, the efficiency was 0.72.

Pressure increase [bar]	0.1	0.3	0.5	0.7	1
Work required [kW]	858	2517	4105	5630	7811

Table 25. Compressor power versus pressure increase

In order to make an assumption about the work required an assumption about the pressure needed is necessary. But in the case this pressure is around 0.1 bar (from 5.5 bar to 5.6 bar, to account for the pressure drop of 2.6 bar in the desiccating tower) the work needed is only 858 kW. The energy input in the heat exchangers in the reaction section require an energy input up to 20 MW and the reboilers need up to 57 MW. Since the amount of work needed for a compressor is not in the same order of magnitude as these values, the energy input in compressors that are only needed for making up for small changes can and will be ignored.

Sometimes a lowering in pressure is needed. This can be done using a turbine. However also a thermal expansion valve can be used for this. A thermal expansion valve cannot regenerate energy from this expansion and therefore some energy loss is inevitable.

The mass- and energy balances of all the sections can be found in Appendix B-H.

5.2 Section 1

Section one could not be modeled in Aspen. Therefore, the magnitude of the in- and outflow of this section was calculated by hand. An efficiency of 99.88% was calculated, this calculation can be found

in Appendix M. It was also calculated that seven spray nozzles per plant provided this efficiency. The required pump energies were obtained from Aspen.

5.3 Section 2

Section two could be modeled in Aspen, making it possible to obtain the magnitude of the mass– and energy flows. The input for this section was taken from the output from section 1, however, the model was based on a flow that was not divided over 5 plants but over 4.48 due to a human error. It was assumed that this makes no difference for the process.

5.4 Section 3

Section three could not be modelled in Aspen. Therefore, also this section was calculated by hand. Since the section consists of two parts, namely the water-desiccating and the pressure swing adsorber (PSA), two calculations were made. The desiccating part of the section was divided over five plants, whereas the pressure swing adsorber section consists of 228 plants. This difference in the amount of plants needed is caused by the maximum allowable dimension of the towers. The flow entering the desiccating towers contained water, which could be removed down to 1 ppm. [42] The PSA has an efficiency of 90% and a selectivity of 99%. This results in 1% of impurities in the gas outflow. These impurities are defined as the other gases present in the gas feed. Since the water content after the desiccating towers is 1 ppm, it will be around 10 ppb after the PSA. Therefore, the presence of water after section 3 is neglected. The other gases still present in the carbon monoxide flow were of non-negligible magnitude.

5.5 Section 4-6

These sections were modeled in Aspen, making it possible to obtain the magnitude of the mass– and energy flows. The flow in these sections was divided by five in order to be able to use reasonable sized equipment. The pumps, compressors and heat exchangers with a high utility were modeled in Aspen. Section four generates a substantial amount of heat, due to the exothermic reaction. This heat can possible be used in the other energy-demanding sections. However, these utility streams were not linked, because this is out of the scope of this assignment. In sections the flow gets distributed again over five distillation columns, labeled A to E. This means that a total of 25 distillation columns are used in the entire process. The purge of section six can partially be used as recycle stream to section four, this was also not modeled.

5.6 Section 7

Section seven could also be modeled in Aspen, this section contains all purge stream from sections 4-6. The magnitude of the mass- and heat flows could be obtained from Aspen.

6. Economic Analysis

To make an estimation of the cost of this project Aspen's economic analysis tool was used. Though most equipment was possible to be added to the list, some things were not. Only one heat exchanger was added to the economic analysis because only one heat exchanger was modeled. Valves and pipes were also excluded from this project, because it went beyond the scope. Reboilers and condensers were again not modeled in aspen or in another way, so these were also not added to the economic analysis for chlorine, MEA, water, coolant, steam, glycerol and KOH were also not added to the economic analysis due to the limitations of the programs.

However, most equipment is modeled with the correct quantities, such as pumps with known head, compressors with known pressure changes, all the columns, the reactors, sometimes with assumed dimensions, tanks with assumed dimensions, and packings for the PSA, desiccating towers and reactor.

Since the analyzer has the option to choose materials a consideration was also made on this account. For example, all equipment that had to deal with corrosive chemicals such as the phosgene, were made out of stainless steel 316 for its improved abilities against corrosion. [82] [83] The first CO₂ absorber was made from SS304.

For every heat exchanger, reboiler and condenser not added to the analyzer $\leq 30,000$ in equipment cost and $\leq 132,000$ in direct cost was added, resulting in 343 total missing parts. For every pump and turbine not added to the analyzer $\leq 150,000$ in equipment cost and $\leq 300,000$ in direct cost was added, resulting in resulting in 65 missing parts. The total equipment cost added is $\leq 10,440,065$ and the total direct cost added is $\leq 64,776,000$. Where direct cost is the total cost of manpower, piping, civil, paint, etc. combined with the equipment cost. An installation factor of 3 was used for these pieces of equipment, because it is about an average of the different factor for the different types of equipment

The reported value for chlorine in June 2010, in Germany, was 346 USD/metric ton [84], or in EUR when using the conversion rate in June 2010, ≤ 260.15 /metric ton. The reported value for steam in June 2010, in Germany, was ≤ 33.29 per metric ton. [85] The reported value for potassium hydroxide is ≤ 707.97 / metric ton. [86] The reported value for limestone is ≤ 172.29 / metric ton. [87] The reported value for phosgene is 1 USD/kg, which is ≤ 0.88 /kg phosgene.

For calculation purposes, a factorial installation factor proposed by Hand was used to multiply with the equipment cost. This obtained the installed cost for the equipment. [88] Using the data mentioned above, the material cost mentioned in appendix K.3. and assuming an operability time of 10 years with 8000 hours per year, Table 26 was created. From this data it is visible that the factory has a profit of roughly 5 billion annually.

material	cost/year	cost/hour	cost/kg phosgene
chlorine	€ 1,844,567,560.00	€ 230,570.95	€ 0.19941
КОН	€ 515,685,348.00	€ 64,460.67	€ 0.05575
Steam	€ 18,695,664.00	€ 2,336.96	€ 0.00202
limestone	€ 5,816,510.40	€ 727.06	€ 0.00063
installed equipment cost	€ 532,788,144.50	€ 66,598.52	€ 0.05760
total expenses	€ 2,917,553,226.90	€ 364,694.15	€ 0.32
phosgene sales	€ 8,140,000,000.00	€ 1,017,500.00	€ 0.88
total	€ 5,222,446,773.10	€ 652,805.85	€ 0.56

Table 26 expenses and incoming funds for the phosgene factory

6.1 Comparison to global yearly production

Annually, the factory produces 1156 ton/h which equals 9240000 ton/annum = 9.24 Mton/year phosgene. The global production worldwide in the year 2015 was 8.5 Mtons/year. [89]

The yearly production of this plant is higher than the global production in 2015. As a consequence, the supply of phosgene more than doubles. It is predicted that the market will grow 35% in 2015-2021. However, the enormous increase in supply would lead to a big decrease in market price. As a result,

the phosgene production would lose its margin. The profit would decrease, possibly leading to losses making the plant economically impossible.

7. Discussion and Conclusion

From an environmental point of view, the recycling of carbon monoxide is a goal that should be encouraged. It was found that the conversion of carbon monoxide to phosgene is a process that can be done with a high conversion factor for the carbon monoxide and with very pure results. The CO_2 removed in the flue gas purification step is removed in a high quantity and purity. Therefore, it is possible to store this CO_2 underground or sell it to other parts of industry.

However, phosgene is a highly toxic chemical with many dangers surrounding its production and uses. Many phosgene free routes to producing chemicals which used to require phosgene, have been found. [40] [90] [91] [92]There is also the fact that phosgene is on the OPCW list on schedule 3, meaning that it can only be produced in a factory where it also has to be used as a reagent. [93] Therefore one might argue that the high CO content in flue gas from the steel industry can better be used for the synthesis of less dangerous chemicals.

For the process design, it was decided to create the SO_2 scrubber, the CO_2 absorber and the production and purification process five times. This was done by splitting the gas stream into five. It could have been possible to only split certain parts into multiple pieces of equipment in parallel, in order to save pumps and compressors.

Because a lot of purification methods for the gas flow were considered, it was possible to design an efficient and effective CO purification route. Since the corrosive sulfides are removed at first, it was possible to use cheaper steel in the following sections.

By a smart order in gas purification techniques it was possible to obtain a gas mixture consisting of mainly N_2 , H_2 , CO, and CH_4 . This means that this gas mixture can be burned and that therefore the emission of the greenhouse gas CH_4 is avoided.

From a flue gas stream of 10.8 Mton/year with a carbon monoxide content of 30%, 3,240,000 ton carbon monoxide per year is obtained. This corresponds, assuming an operating factory of 8000 hours/year, and an overall efficiency of the gas cleanup process of 85% with 364.1 ton carbon monoxide/ h. After the reaction and subsequent purification a yield of 93.96% of phosgene, with a purity of 99.99 w% was obtained. This resulted in a production of 231.3 ton/h of phosgene per factory, a total of 1156 ton/h.

 SO_2 particles in the feed were effectively removed using the limestone scrubber. Almost all the SO_2 was converted into gypsum by oxidation after the absorption. This gypsum is beneficial to the construction industry. 7.3 ton/h of gypsum was created.

During the CO₂ and H₂S removal, which conveniently could be done in a single step, MEA was used in combination with a stripper and a recycle loop to ensure as little MEA as possible was wasted. The molar reflux ratio of 60 is not realistic, especially with the large mass flow that are dealt with. Almost all CO₂ was removed, the remained was removed in the PSA step. All H₂S was removed. The CO₂ and H₂S left the stripper with only water as an extra impurity. This means that it can be disposed of in a way that is not harmful to the environment, for example underground.

Although a lot of desiccating towers and a lot of pressure swing absorbers were required, it did the job. The large quantity was simply due to the amount of flue gas coming from the steel mill. Afterwards

the size of the stream is reduced by a huge amount because of the removal of the large amount of nitrogen. Although the nitrogen does not matter for the reaction, it does however mean that larger equipment and duties are needed.

The tube and shell reactor itself, requires a large amount of pipes. It could have been possible to create multiple reactors in parallel, although this one only required a shell of 2 meters in diameter. The reactor performed with a reasonable pressure drop. Proper cooling should keep the CCl₄ formation to a minimum.

During the reaction, trace amount of carbon dioxide was formed, which had to be removed from the gas stream, due to of the applications of phosgene in the formation of poly urethanes. The CO₂ could prove hazardous for the purity of those processes. Removing the CO₂ was again completed using MEA, however, this meant that afterwards the product gas stream had to be dried from the water and small amounts of MEA. This was done using glycerol as an absorbent, which was subsequently stripped and recycled. The glycerol did however prove to be hard to strip, because of its high boiling point. This meant that the reboiler of the stripper needs a high amount of heat. The distillation step for the dry phosgene coming from the glycerol absorber was done in five parallel distillation towers because of the large quantity of phosgene. This proved to be successful.

In the destruction process of the waste gasses a large amount of phosgene was present, because it had dissolved in the MEA and glycerol, or because it could not be removed during distillation. The phosgene was reacted with steam to form HCl, which was subsequently destroyed using potassium hydroxide. This simple process was a good solution to get rid of the dangerous phosgene. However the use of steam should be noted, since steam is expensive to create due to the energy required. Nevertheless, not much steam was required, which still made the process viable. All phosgene and carbon tetrachloride was destroyed and no KOH was left.

The profits gained during this process should be noted, a small 56 euro cents per kilogram of phosgene produced. However, fluctuation in the market, especially with phosgene free routes emerging, this process could quickly go from profitable to non-profitable. Furthermore, the economic analysis was incomplete because no piping and buildings were analyzed, but added with the factor described. A more complete analysis would be preferable, but this is beyond the scope of this project.

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9. Appendix

A. PFD's A.1 Section 1



A.2 Section 2



A.3 Section 3



A.4 Section 4-7



B. Section 1





The flue gas (1112) is fed to the column (C1101) to react counter currently with a limestone slurry (1109). The slurry falling down in the column is collected in T1101, where oxygen is added (1113) to form gypsum which is bled off (1105) and dewatered (gypsum 1107, water 1106). The oxygen supply is controlled by a PIC connected to a blower (K1101). The water is recycled and added to the water supply (1103). The supply of limestone is controlled by the amount of gypsum removed from the process (1107) using a FIC. It is assumed that the tank (T1101) is oversized.

B.2 Mass Balance



Total Mass	Balance (5	plants)					
Section 1	Streams	Phase	Temperature [°C]	Pressure [bar]	Mass flow [ton/h]	Main component(s)	Comments
Ingoing	1112	g	50	1	1350	N ₂ , CO ₂ , CO	Inflow flue gas
	1103	1	50	1	3.94	H ₂ O	
	1101	s	50	1	4.22	Limestone	
	1114	g	50	1	0.67	O ₂	Oxidation agent
Outgoing	1107	g/l	50	1	9.7	Gypsum	
	1115	g	50	1	1349	N ₂ , CO ₂ , CO	Outflow flue gas
Production	= In - Out				0		

B.3 Heat Balance

Total Heat Balance (5 plants)	Equipment	Heat exchanger	Pump	Compressor	
	Code	E1101	P1101	K1102	K1101
	Delivered Energy [kW]	-40050	×	×	×
	Required Energy [kW]	×	240.0	11515	10
Ingoing Stream	Code	1115	1108	1114	1110
	Temperature [C]	60	50	50	25
	Pressure [bar]	1	3.07	0.925	1
	Enthalpy [kW]	-1.60E+07	-1.60E+07	-9.77E+05	-4.50E-02
Outgoing Stream	Code	1201	1109	1113	1201
	Temperature [C]	25	50	60	75
	Pressure [bar]	1	1	1	1.5
	Enthalpy [kW]	-1.01E+06	-1.60E+07	-9.65E+05	8.61

B.4 Code Specifications

PID Part(s)	stream name/ equipment	code
SO2 scrubber	Conveyor belt	A1101
	Limestone	1101
	Wet ball mill	A1102
	Crushed limestone	1102
	Valve Water	PV1101
	Water	1103
	Mixer	M1101
	Mixed	1104
	Valve mixed	PV1102
	Scrubbing liquor tank	T1101
	Turbine	K1101
	Gypsum bleed	1105
	Dewaterer	A1103
	Water recycle	1106
	Wet gypsum cake	1107
	Limestone slurry	1108

Pump	P1101
Pumped limestone slurry	1109
Sulfide scrubber	C1101
Mist eliminator	A1104
Sprayers	A1105
Gas in	1112
gas out	1110
turbine	K1102
SO2 free gas	1201
SO2 absorbed	1112
Compressed oxygen	1113
oxygen	1114
heat out	1115
cold	1116
hot	1117
Heat exchanger	E1101
shut off valve gas in	PV1103
shut off valve gas in	PV1104
shut off valve limestone	PV1105
HeatX cooling liquid valve	PV1106

C. Section 2

C.1 P&ID



The SO₂ free flue gas (1201) enters the column (C1201), where it is mixed with an MEA solution (1203). The CO₂ and H₂S free flue gas leaves the column at the top (1206) and the CO₂ and H₂S rich MEA solution leaves at the bottom (1207) and is fed to the stripper (C1202). The CO₂ and H₂S leave at the top (1215) and the lean MEA solution leaves at the bottom (1221) and gets recycled to the absorber (C1201). Stream 1221 is used to preheat

stream 1207. The pressure is reduced using a pressure relief valve (P1202). The temperature of the reboiler is controlled using a PIC. The condenser is controlled using a TIC.

C.2 Mass Balance



Total Mass	s Balance (5 plants)					
Section 2	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)	Comments
Ingoing	1202	g	25	5.5	1349	N ₂ , CO ₂ , CO	Inflow flue gas
	1203	I	20	5.5	394	MEA+H ₂ O	MEA solution
Outgoing	1215	g	95.4	1.9	259	CO ₂ +H ₂ S	Disposed sour gas, to CCS
	1222	g	56	1.9	327	MEA+H ₂ O	Purge does not contribute to mass flow, because the purge is very small
	1206	g	20	5.5	1157	N ₂ , CO ₂ , CO	Outflow flue gas

C.3 Heat Balance

Total Heat Balance (5 plants)	Equipment	Heat exchanger					dund		Compressor
	Code	E1201	E1202	E1203	E1204	E1205	P1201	P1202	K1201
	Delivered Energy [kW]	×	×	-9.65E+05	-2.37E+05	-229765	×	-786.9	×
	Required Energy [kW]	6.07E+05	1.26E+06	×	×	×	946.1	×	1.15E+05
Ingoing Stream	Code	1207	1211	1210	1223	1202	1224	1208	1201
	Temperature [C]	31	na	na	56	500	56	100	25
	Pressure [bar]	5.5	па	na	1.9	20	2	5.5	1
	Enthalpy [kW]	-3.04E+07	na	na	-2.94E+07	-6.89E+05	×	-2.98E+07	-1.00E+06
Outgoing Stream	Code	1208	1221	1215	1224	1227	1204	1209	1202
	Temperature [C]	100	122	95	20	25	56	100	273
	Pressure [bar]	5.5	1.9	1.9	1.9	20	9	2	9
	Enthalpy [kW]	-2.98E+07	-2.88E+07	-6.81E+05	па	-1.00E+06	×	-2.99E+07	-6.89E+05

C.4 Code Specifications

Part(s)	Stream name/equipment	Code
wet amine	flue gas in	1201

compressor	K1201
compressed gas	1202
absorber	C1201
mea make up	1203
mea valve	PV1201
mea recycle pumped	1204
mea pump	P1201
mea total	1205
sweet gas	1206
sour gas	1207
 heat exchanger	E1201
 heated gas	1208
 pressure relief	P1202
decompressed gas	1209
stripper	C1202
 sour gasses out	1210
mea to reboiler	1211
reboiler	E1202
mea back to stripper	1212
hot	1213
 valve hot	PV1202
 cold	1214
CO2 + H2S out	1215
 gas to condenser	1216
 heat exchanger	E1203
 cold	1217
 valve cold	PV1203
 hot	1218
 to reflux drum	1219
 reflux drum	V1201
 back to column	1220
 MEA + H2O	1221
 purge	1222
 recycle hot	1223
 recycle cold	1224
 cold	1225
 valve cold	PV1204
 hot	1226
 heat exchanger	F1204
 Valve condenser	D\/1205
	F V 1205
 valve pulge	F1205
 Heat exchanger after compressor	E1205
Compressed stream after heat exchanger	1227

Cold	1228
hot	1229
Valve cold	PV1207

D. Section 3 D.1 P&ID



The wet flue gas enters in column C1301, This means that PV1302 is closed and PV1301/PV1309 are open, the water gets adsorbed on the alumina packing of the column, The gas is fed to the PSA section after this desiccating step. While column C1301 is operating, C1302 is dried. This is done by blowing an enriched gas 1339, through the column. PV1303 is closed and PV1304 is open so that this gas leaves at 1327.

The dry gas enters column C1304, in this column, PV1311 is open, the CO is adsorbed on the packing while the other gasses break through this column and leave the system in stream 1317. Meanwhile, the CO that was absorbed before in the other column C1305, is obtained by lowering the pressure in this column and opening PV1318. The CO is transported via 1335 to C1306 where it is collected. Part of this gas is used to clean the column. This is done by opening PV1313. When this process is finished, PV1313 and PV1318 close, and PV1312 is opened in order to start a new cycle while CO is desorbed from C1304 in the same way as described for C1305.

D.2 Mass Balance



Total Mas	s Balance					
Section 3	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)
Ingoing	1206	g	20	5.5	1297	Inflow flue gas
Outgoing	1326+1327	g	25	1	932.7	Rest gas
	1322	g	25	1	364.5	Outflow flue gas, i.e. pure CO

D.3 Heat Balance

Total Heat Balance	Equipment	Heat Exchanger		Compressor	
	Code	E1301	E1302	K1301	K1302
	Delivered Energy [kW]	na	-83433.2	×	×
	Required Energy [kW]	×	×	2326.5	448550
Ingoing stream	Code	1302	1321	1206	1335
	Temperature [C]	22	418	20	22
	Pressure [bar]	5.6	30	5.5	33.6
	Enthalpy [kW]	na	-3.89E+05	-5.50E+05	-399630
Outgoing	Code	1328	1334	1302	1321
stream	Temperature [C]	22	25	22	418
	Pressure [bar]	5.6	3	5.6	30
	Enthalpy [kW]	и	-4.45E+05	-5.47E+05	-3.89E+05

D.4 Code Specifications

Part(s)	Stream name/equipment	Code
Water desiccating	feed gas	1206
	Turbine	K1301
	compressed gas	1302
	valve in left	PV1301
	valve out left	PV1302
	valve in right	PV1303

	valve out right	PV1304
	Gas between valves	1303
	gas in column left	1304
	gas in column right	1305
	column left	C1301
	column right	C1302
	dry gas left	1306
	dry gas right	1307
	valve blow left	PV1305
	valve blow right	PV1306
	valve left	PV1307
	valve right	PV1308
	Gas to PSA section	1310
	cold	1329
	hot	1330
	Cooled gas	1328
	valve cold	PV1321
	heat exchanger	E1301
PSA	Valve left 1 up	PV1309
	valve left 2 up	PV1310
	valve left 1 down	PV1311
	valve right 1 up	PV1312
	valve right 2 up	PV1313
	valve right 1 down	PV1314
	gas column in left	1311
	gas column in right	1312
	column left	C1304
	column right	C1305
		1313
	gas out right	1214
	gas out right	1314 DV/1315
		PV1315
		PV1316
		PV1317
	valve product right	PV1318
	valve drying towers right	PV1319
	valve rest gas right	PV1320
	gas product left	1315
	gas drying left	1316
	gas rest left	1317
	gas product right	1318
	gas drying right	1319
	gas drying combined	1339
	gas rest right	1320

vacuum pomp	K1302
gas holder	C1306
product	1322
recycle gas	1323
gas for cleaning left column	1324
gas for cleaning right column	1325
gas for cleaning column combined	1337
gas for cleaning column left	1338
rest gas end (1317 or 1320)	1326
wet gas rest	1327
Heat exchanger	E1302
hot gas compressed	1321
cold in	1332
hot out	1333
valve	PV1322
cold gas to gas holder	1334
Gas product combined (1318+1315)	1335




The Cl₂ (1404) and the CO (1322) are mixed (1406) before entering the reactor (R1401) at 3 bar. The product stream (1410) is fed to the absorber (C1401) at 4 bar. The CO₂ lean stream continues to the next section (1427). The CO₂ rich stream is stripped in C1402. MEA is recycled back to the absorber (1420). The recycled amount is controlled by an FIC on PV1404. Both C1401 and C1402 are connected to a HPSD (High Pressure ShutDown), which is a safety measurement. When the pressure gets too high, due to less phosgene production, the HPSD will send a signal to compressors K1401 and K1402. These compressors will be shut down, resulting in a shutdown of the entire factory. PV1405 is attached to be able to deal with too high pressures in K1403.

E.2 Mass Balance



Total Mass	s Balance (1 p	olant)				
Section 4	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)
Ingoing	1322	g	25	3	72.9	СО
	1404	g	25	3	177.3	Cl ₂
	1411	I	25	1	5.62	MEA, H ₂ O
	1628	g	3	3	0.00	CO, COCl ₂ , N ₂
Outgoing	1427	g	37.2	3	251.1	COCl ₂
	1421	I	25	3.279	2.10	MEA + H2O
	1422	g	139.6	3.1	2.67	COCl ₂

E.3 Heat Balance

Total Heat Balance (5	Equipment	Compress or			pump				Heat exchanger		Reactor
plants)	Code	K1401	K1402	K1403	P1403	P1401	P1402	P1404	E1401	E1402	R1401
	Delivered Energy [kW]	вп	ра	×	na	na	×	na	-5.27E+03	×	-3.77E+05
	Required Energy [kW]	na	na	3.65E+03	na	па	11.1	na	×	1.36E+04	×
Ingoing	Stream Code	1402	1404	1410	1430	1407	1412	1432	1418	1416	1406
	Temperature [C]	25	25	40	38.9	па	25	па	146	na	24
	Pressure [bar]	£	m	0.66	3.1	na	1	na	3.27	na	ñ
	Enthalpy [kW]	-3.99E+05	-8.13E+02	-7.74E+05	-1.76E+05	па	-1.96E+05	na	-1.15E+05	na	-4.00E+05
Outgoing Stream	Stream Code	1403	1405	1426	1431	1408	1413	1414	1419	1418	1410
	Temperature [C]	25	25	59	38.9	па	26	na	25	146	40
	Pressure [bar]	3	3	4	3.1	na	4	na	3.27	3.27	0.66
	Enthalpy [kW]	-3.99E+05	-8.13E+02	-7.70E+05	-1.76E+05	na	-1.96E+05	na	-1.20E+05	-1.15E+05	-7.74E+05

E.4. Code Specifications

Part(s)	stream name/	code
roactor 1	equipment	1222
Teucior 1	CO(g)	1522 DV1401
		1020
	CO recycle	1628
	CO combined	1402
	Compressor CO	K1401
		1403
		1404
	Compressor CI2	K1402
	Compressed CI2	1405
		1406
	Reactor 1	R1401
	Coolant	1407
	Pump Coolant	P1401
	Pumped Coolant	1408
	Heated Coolant	1409
	COCI2 g	1410
	Chlorine tank	T1401
	shut off valve flow	PV1411
	valve chlorine	PV1412
	shut off valve	PV1415
CO2 Absorber	MEA + H2O (I)	1411
	Valve MEA	PV1404
	MEA recycle	1420
	MEA combined	1412
	Pump MEA	P1402
	Pumped MEA	1413
	CO2 Absorber	C1401
	COCl2 g	1410
	MEA + CO2 (I)	1430
	COCl2 + H2O (g)	1427
	COCl2 to save location	1435
	Valve TSL	PV1405
	shut off valve pump	PV1417
	shut off valve column	PV1417
MEA stripper	MEA + CO2 (I)	1430
Scripper	Pump MEA	P1403
	Pumped MEA	1431
	Stripper	C1402
	Cold	1432

Pump Cold	P1404
Pumped Cold	1414
Valve Cold	PV1406
Heat exchanger	E1401
Hot	1415
MEA from stripper to reboiler	1416
MEA back to stripper	1417
valve reboiler	PV 1418
MEA from reboiler to HeatX	1418
MEA	1419
MEA recycle	1420
MEA valve	PV1407
MEA purge	1421
CO2 purge/purge 1	1422
CO2 TSL	PV1408
TSL	1423
Hot	1424
Valve Hot	PV1409
Cold	1425
Kettle reboiler	E1402
shut off valve heating	PV1419
shut off valve on 1410	PV1420







As mentioned earlier (in 4.2.4.2.2) the product stream (1427) going into the compressor first had to pass a heater, because the stream leaving the CO₂ absorber (C1401) was below its dew point. The product stream enters the H₂O absorber (C1501) at the bottom (1507) where it reacts counter currently with glycerol (1505). The dry product stream leaves the absorber in 1512. The glycerol containing water is stripped in C1502. The pressure is measured at V1501 to account for the amount of gas in the drum. PV1507 reacts accordingly. Pump P1504 is controlled via a computer which is connected to two signals, a LIC on the kettle reboiler (E1503) and a PIC on 1515. The recycled glycerol is collected in a tank (T1501), the liquid level is this controlled by a LIC connected to a fresh supply of glycerol (1501). If the level gets too high the supply is stopped.

F.2 Mass Balance



Total Mas	s Balance	(1 plant)				
Section 5	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)
Ingoing	1427	g	37.2	3	251.1	COCl ₂
	1501	1	25	4	13.05	Glycerol
Outgoing	1503	1	25	4	8.15	Glycerol
	1512	g	79.3	3	238.7	COCl ₂
	1529	g	263	2	17.22	COCl ₂ , H ₂ O

F.3 Heat Balance

Equipment	Compressor	Pump				Heat exchanger				
Code	K1501	P1501	P1502	P1503	P1504	E1501	E1502	E1503	E1504	E1505
Delivered Energy [kW]	×	па	na	na	×	×	-1.11E+05	×	-2.24E+05	×
Required Energy [kW]	3.95E+03	na	вп	na	3.15E+01	6.04E+04	×	2.87E+05	×	4.39E+03
Stream Code	1428	1501	1504	1510	1521	1508	1515	1519	1524	1427
Temperatur e [C]	57.2	25	25	200	324.3	93.4	324.3	па	na	37.2
Pressure [bar]	3	4	4	3.24	2.4	3.24	4	na	na	3
Enthalpy [kW]	-7.86E+05	-1.31E+05	-1.07E+06	-1.07E+06	-9.15E+05	-1.26E+06	-9.15E+05	na	na	-7.91E+05
Stream Code	1507	1502	1505	1511	1515	1510	1518	1521	1529	1428
Temperatur e [C]	76.6	25	25	200	324.3	200	25	324.3	263	57.2
Pressure [bar]	4	4	4	3.24	4	3.24	4	2.4	2	3
Enthalpy [kW]	-7.82E+05	-1.31E+05	-1.07E+06	-1.07E+06	-9.15E+05	-1.07E+06	-1.03E+06	-9.15E+05	-8.84E+04	-7.86E+05

otal leat alance 5 Plants	ngoing tream	utgoing tream	
	l ⊢ o	× O	

F.4 Code Specifications

Part(s)	stream name/ equipment	code
H ₂ O absorber	Glycerol (I)	1501
	Pump Glycerol	P1501
	Pumped Glycerol	1502
	Tank Glycerol	T1501
	Glycerol Purge	1503
	Valve glycerol purge	PV1501
	Glycerol out tank	1504
	Pump Glycerol 2	P1502
	Pumped glycerol 2	1505
	Absorber	C1501
	Valve COCl2	PV 1502
	COCl2 + H2O (g) before HeatX	1427
	Heat exchanger	E1505
	Hot water in HeatX	1530
	diaphragm valve on hot water inlet	PV1510
	Cooled water out	1531
	COCl2 + H2O (g) after HeatX	1428
	Shut off valve tank in	PV1510
	shut off valve heat exchanger	PV1509
	Compressor COCI2	K1501
	Compressed COCI2	1507
	Glycerol Water to reboiler	1508
	Glycerol from reboiler to stripper	1509
	Reboiler	E1501
	Glycerol out	1510
	Pump glycerol	P1503
	Glycerol (I)	1511
	COCI2 dry	1512
	Hot	1513
	Valve Hot	PV1503
	Cold	1514
	Glycerol recycle	
	Pump glycerol recycle	P1504
	Pumped Glycerol	1515
	Cooler	E1502
	Cold	1516
	Valve cold	PV/150/
	Hot	1517
	Πυι	121/

	Cool glycerol	1518
Stripper Glycerol	Glycerol	1511
	Absorber	C1502
	Glycerol to reboiler	1519
	glycerol back to stripper	1520
	reboiler	E1503
	Glycerol recycle	1521
	Hot	1522
	Valve Hot	PV 1505
	Cold	1523
	COCl2 (g)	1524
	Cooler	E1504
	Valve controlling amount of coolant	PV1508
	Cold	1525
	Hot	1526
	Cooled COCI2	1527
	Reflux drum	V1501
	Out liquid	1528
	Valve	PV 1506
	Purge out	1529
	Valve purge	PV1507

G. Section 6 G.1 P&ID



The dry product stream (1512) goes through a compressor (k1601) to overcome the pressure drop and a cooler (E1601) into the distillation tower (C1601A), which is controlled by a PIC. Stream 1606 is split into five different streams controlled by FICs which all enter their own distillation tower (C1601A/B/C/D/E). On the liquid side of the column 1617 the product is collected. 1625 is purged.

At the start of the P&ID a HPSD is installed connected to a valve (PV1601) which is connected to a safe location.

G.2 Mass Balance



Total Mass	Balance (1	plant)				
Section 6	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)
Ingoing	1512	g	79.3	3	238.7	COCl ₂
Outgoing	1625A-E	g	3	3	7.48	CO, COCl ₂
	1628	g	3	3	0	CO, COCl ₂ , N ₂
	1629	g	43.3	3.36	231	COCl ₂

G.3 Heat Balance

eat (5	Equipment	Compressor	Heat Exchanger		
	Code	K1601	E1601	E1602A/B/ C/D/E	E1603A/B/ C/D/E
	Delivered Energy [kW]	×	-9.70E+04	×	-6.15E+04
	Required Energy [kW]	3.96E+03	×	7.32E+04	×
-	Stream Code	1602	1603	1615	1620
	Temperature [C]	2.97	6.99.3	na	u
Ч	ressure [bar]	3	4	na	na
E	nthalpy [kW]	-7.31E+05	-7.27E+05	na	na
	Stream Code	1603	1606	1617	1624
	Temperature [C]	99.3	10	43.3	8
_	^p ressure [bar]	4	4	3.36	3
-	Enthalpy [kW]	-7.27E+05	-8.24E+05	-7.82E+05	-3.00E+04

G.4 Code Specifications

Part(s)	stream name/ equipment	code
Distillation column	COCl2 dry	1512
	COCI 2 TSL	1601
	TSL valve	PV1601
	COCl2 before compressor	1602
	Compressor	K1601
	Compressed COCI2	1603
	Heat exchanger	E1601
	Cold	1604
	Valve cold	PV 1602
	Hot	1605
	Hot COCl2	1606
	Hot COCl2 A	1607
	Hot COCl2 B,C,D,E	1608
	Hot COCl2 B	1609
	Hot COCl2 C,D,E	1610
	Hot COCl2 C	1611

Hot COCl2 D,E	1612
Hot COCl2 D	1613
Hot COCl2 E	1614
Valve B	PV 1603
Valve C	PV 1604
Valve D	PV 1605
Valve E	PV 1606
Column A	C1601
COCl2 to reboiler	1615
COCl2 back to stripper	1616
COCl2 Product	1617
Reboiler	E1602
Hot	1618
Valve Hot	PV 1607
Cold	1619
COCI 2 (g)	1620
Heat exchanger	E1603
Cold	1621
Valve cold	PV 1607
Hot	1622
Cold COCl2	1623
Reflux drum	V1601
Imp + trace COCl2	1624
Purge	1625
CO recycle A	1626
Reflux COCl2	1627
COCl2 recycle to Reactor 1	1628
Valve Reflux	PV1608
Valve Recycle	PV1609
Shut off valve	PV1610
shut off valve LIS	PV1611
shut off valve PIS	PV1612

H. Section 7 H.1 P&ID



All purges (1422, 1529, and 1625) are connected to a vessel (V1701) and collected. The compressor (K1701) is controlled by two FICs connected to a computer. Under pressure it is mixed with steam in R1701 to destroy the phosgene. The reactor again has a HPSD. After the reactor the stream is condensed in E1701 and subsequently reacted with KOH (1715) in a reactor (R1702). The flow of KOH is controlled by a pump connected to the gas a liquid stream leaving the condenser (1713 and 1714). After the reactor the waste is disposed (1721 and 1732).

H.2 Mass Balance



Total Mass	s Balance (1	plant)				
Section 7	Streams	Phase	Temperature [°C]	Pressure [bar]	Total mass flow [ton/h]	Main component(s)
Ingoing	1422	1	139.6	3.1	2.67	H2O, MEA
	1529	g	263	2	17.2	COCl ₂ , H ₂ O
	1625A-E	g	3	3	7.48	CO, COCl ₂
	1701	g	100	1	3.60	H ₂ O
	1715	I	25	1	32.2	KOH, H₂O
Outgoing	1721	g	25	1	9.04	CO ₂
	1723	1	25	1	54.3	CO ₂ , H ₂ O, KCl

H.3 Heat Balance

Equipment	Compressor		dmnd			Reactor			Condenser	
Code	K1701	K1703	P1701	P1702	P1703	R1701	R1702		E1701	
Delivered Energy [kW]	na	па	па	na	na	-1.88E+03	-7.13E+03		-1.52E+04	
Required Energy [kW]	па	па	ра	na	na	×	×		×	
Stream Code	1701	1720	1705	1715	1722	1707	1717	1714	1710	
Temperature [C]	100	25	227	25	25	227	20	20	179.6	
Pressure [bar]	1	1	2	1	1	2	1	1	1	
Enthalpy [kW]	-6.65E+04	-5.66E+03	-1.66E+04	-2.13E+05	-3.31E+05	-8.31E+04	-2.99E+05	-1.37E+04	-8.50E+04	
Stream Code	1702	1721	1706	1716	1723	1710	1720	1722	1713	1714
Temperature [C]	100	25	227	25	25	179.6	25	25	20	20
Pressure [bar]	1	1	2	1	1	1	1	1	1	1
Enthalpy [kW]	-6.65E+04	-5.66E+03	-1.66E+04	-2.13E+05	-3.31E+05	-8.50E+04	-5.66E+03	-3.31E+05	-8.65E+04	-1.37E+04

Total Heat Balanc e (5 plants)	lngoin g Stream	Outgoi ng Stream
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H.4 Code Specifications

	Specifications	
Part(s)	stream name/ equipment	code
Reactor 2	Steam	1701
	Compressor steam	K1701
	Compressed steam	1702
	Purge 1	1422
	Purge 2	1529
	Purge 3	1625
	Purge 1+2	1703
	Purge 1+2+3	1704
	Vessel	V1701
	Purge out vessel	1705
	Pump	P1701
	Pumped purge	1706
	Steam +Purge in	1707
	Reactor 2	R1701
	Cold	1708
	Valve cold	PV1701
	Hot	1709
	HCI	1710
	HCl to save location	1711
	Valve TSL	PV 1702
	shut off valve vessel	PV 1705
	TSL valve	PV1706
	shut off valve gas detector	PV1707
Condenser	HCI	1710
	Cold water	1711
	Valve	PV 1703
	Heated water	E1712
	Condenser	1701
	HCI (I)	1713
	HCl (g)	1714
Reactor 3	HCI (g)	1714
	HCl (aq)	1713
	КОН	1715
	Pump	P1702
	Pumped KOH	1716
	HCI + KOH	1717
	Reactor 3	R1702
	Cold	1718
	Valve	PV1704

Hot	1719
Gas	1720
Compressor	K1702
Burn	1721
Liquid	1722
Pump	P1703
Sea	1723

I. Stream specifications

I.1 Section 1-3

Based on the total mass flow (1350 ton/h)

	1322	25	1	364	364.1	0	8.7E-02	2.96E-02	0	0.210	0	0	0	0	0	U
	1326+1327	25	1	793	40.9	0	202.4	67.4	9.8	472.288	3.178E-03	0	4.8E-04	0	0	0
3	1206	25	5.5	1157	405.0	0	202.5	67.5	9.8	472.5	3.178E-03	0	4.3E-02	0	0	0
	1206	20	5.5	1157	405.0	0	202.5	67.5	9.8	472.5	0	0	4.3E-02	0	0	0
	1222	56	1.9	327	0	0	0	0	248.4	0	0	0	78.4	0	0	0
	1215	95.4	1.9	259	0	190.9	0	0	57.06	0	0	10.8	4.3E-01	0	0	0
	1203	20	5.5	394	0	0	0	0	315.3	0	0	0	78.8	0	0	0
2	1202	25	5.5	1349	405.0	190.9	202.5	67.5	0.0	472.5	3.178E-03	10.80	0	0	0	0
	1115	50	1	1349	405.0	190.9	202.5	67.5	0	472.5	3.178E-03	10.80	0	0	0	0
	1107	50	1	9.68	0	0	0	0	2.42	0	0	0	0	0	0	7.257

Section	1			
Streams	1112	1101	1103	1114
Temperature [°C]	50	50	50	50
Pressure [bar]	1	T	1	1
Total mass flow [ton/h]	1350	4.22	3.94	0.67
CO mass flow [ton/h]	405.0	0	0	0
CO ₂ mass flow [ton/h]	189.0	0	0	0
H ₂ mass flow [ton/h]	202.5	0	0	0
CH4 mass flow [ton/h]	67.5	0	0	0
H₂O mass flow [ton/h]	0	0	3.94	0
N2 mass flow [ton/h]	472.5	0	0	0
SO ₂ mass flow [ton/h]	2.700	0	0	0
H₂S mass flow [ton/h]	10.80	0	0	0
MEA mass flow [ton/h]	0	0	0	0
Limestone mass flow [ton/h]	0	4.22	0	0
O2 mass flow [ton/h]	0	0	0	0.67
Gypsum hydrate [ton/h]	0	0	0	0

I.2 Section 4-7

Based on one of the five plants.

1701	1715	1721	1723
100	25	25	25
1	1	1	1
3.603	32.248	9.042	54.262
0	0	2.75	5.24E-02
0	0	0	0
0	0	6.07	1.07
0	0	1.74E-02	0
0	0	0	0
0	0	5.33E-02	5.91E-03
0	0	0	0
3.603	14.04	1.13E-01	23.98
0	0	4.14E-02	5.90E-05
0	0	0	0
0	0	0	0
0	0	0	9.74E-02
0	0	0	4.9
0	0	0	0
0	18.21	0	2.33E-03
0	0	0	24.16

5					9				7		
1427	1501	1503	1512	1529	1512	1625A-E	1628	1629	1422	1529	1625A-E
63	25	25	79.3	263	79.3	3	3	43.3	139.6	263	3
3	4	4	3	2	3	3	3	3.36	3.1	2	3
251.06	13.054	8.151	238.74	17.217	238.74	7.483	0.000	231.26	2.673	17.217	7.483
2.80	0	0	2.80	0	2.80	2.80	0	0	0	0	2.80
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	2.75E-02	0	0
1.70E-02	0	0	1.74E-02	0	1.74E-02	1.74E-02	0	0	0	0	1.74E-02
247.2	0	0	235.812	11.353	235.812	4.564	0	231.25	1.47E-03	11.353	4.564
5.92E-02	0	0	5.92E-02	0	5.92E-02	5.92E-02	0	0	0	0	5.92E-02
9.61E-02	0	0	1.03E-02	8.58E-02	1.03E-02	0	0	1.03E-02	0	8.58E-02	0
0.867	0	0	0	0.867	0	0	0	0	2.558	0.867	0
4.20E-02	0	0	4.20E-02	0	4.20E-02	4.20E-02	0	0	0	0	4.20E-02
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0.0107	0	0	0	1.07E-02	0	0	0	0	8.67E-02	1.07E-02	0
0	13.054	8.151	2.83E-03	4.9	2.83E-03	0	0	2.83E-03	0	4.9	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0

Section	4						
Streams	1322	1404	1411	1628	1427	1421	1422
Temperature [°C]	25	25	25	3	37.2	25	139.6
Pressure [bar]	3	3	1	3	3	3.3	3.1
Total mass flow [ton/h]	72.89	177.3	5.623	0.000	251.06	2.10	2.673
CO mass flow [ton/h]	72.820	0	0	0	2.8	0	0
Cl ₂ mass flow [ton/h]	0	177.26	0	0	0	0	0
CO ₂ mass flow [ton/h]	0	0	0	0	0	0	2.75E-02
H ₂ mass flow [ton/h]	1.7E-02	0	0	0	1.70E-02	0	0
COCl ₂ mass flow [ton/h]	0	0	0	0	247.2	0	1.47E-03
CH4 mass flow [ton/h]	0.01	0	0	0	5.92E-02	0	0
CCl4 mass flow [ton/h]	0	0	0	0	9.61E-02	0	0
H ₂ O mass flow [ton/h]	0	0	4.49809	0	0.867	1.073	2.558
N ₂ mass flow [ton/h]	0.042	0	0	0	4.20E-02	0	0
SO ₂ mass flow [ton/h]	0	0	0	0	0	0	0
H ₂ S mass flow [ton/h]	0	0	0	0	0	0	0
MEA mass flow [ton/h]	0	0	1.12	0	1.07E-02	1.03E+00	8.67E-02
Glycerol mass flow [ton/h]	0	0	0	0	0	0	0
HCl mass flow [ton/h]	0	0	0	0	0	0	0
KOH mass flow [ton/h]	0	0	0	0	0	0	0
KCl mass flow [ton/h]	0	0	0	0	0	0	0

J. HAZOP

J.1 HAZOP table

No.	Element	Guide	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
R1401	composition	Word other than	corrosion; vibration	Leakage of tube side	Phosgene in cooling fluid; corrosion of P1401;	replacing tubes periodically; gas detector in cooling water with an alarm controlling shut off valve on 1406	Assume tubes are replaced correctly	install gas detector controlling shut off valve
R1401	temperature	High	reactor temperature increases, choked flow,	too little coolant, or coolant too hot	1. hot spots; tetra formation; 2. over reactor design temperature; reactor meltdown	TIC in reactor controlling valve feed; TIS high in reactor controlling shut off valve; P1401 A/B	Assume temperature cooling water is representative for temperature in reactor	install TIS high on 1409 controlling shut off valve on 1406; install P1401 B
R1401	composition	other than	corrosion in tube side flange	phosgene leakage of tube side flanges	production loss; phosgene in environment	phosgene detector controlling ammonia curtain	Assume gas detector detects phosgene before harmful ppm is reached;	install phosgene detector controlling ammonia curtain

R1401	composition	different	less active catalyst	catalyst is corroded, degraded or physically transported	production loss; corrosion of equipment downstream due to chlorine; damage due to carbon particles	replacing tubes periodically; composition meter on 1410 controlling shut off valve 1406	Assume tubes can be replaced practically;	replacing tubes periodically; install composition meter
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
K1402	pressure	low	corrosion; wear;	Leakage; pump malfunction; corrosion	toxic chlorine vapor emission	PIS with PAL controlling shut off valve on 1404 and 1322; K1402 A/B	Assume that two compressors parallel never fail at same time	Install K1402B and PIS
K1402	temperature	high	Compressor rotates too fast; high environmental temperature	No sufficient heat exchange to environment	compressor gets overheated; compressor gets above design temperature	TIS on pump activating compressor 1402B;	Assume temperature drops after activating second compressor	compressor parallel
K1402	flow	high	The pressure increase over the compressor is reduced	Compressor cannot handle the flow rate, flow stalls	Compressor tears, toxic chlorine emitted	Install FIS activating compressor 1402B	Assume two compressors parallel can provide sufficient gas flow	compressor parallel
K1402	power	none	power shutdown	power outage	Compressor stops; no chlorine to reactor	back-up power supply	assume back up power supply can immediately be activated	immediately switch to back-up power supply

V1701	pressure	high	Increased inflow of purge streams	More purge than anticipated	phosgene leakage, explosion	Overdesign; installing ammonia curtain; Install PIS controlling TSL and controlling shut off valve at 1704	Assume that a save location is available	install PIS, ammonia curtain and create safe location
V1701	Composition	other than	leakage of vessel	corrosion	toxic phosgene purges are released	gas detector activating ammonia curtain and controlling shut off valve at 1704	Assume gas detector detects phosgene at a ppm lower than harmful	install gas detector and ammonia curtain
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
P1702	flow	low	decreased flow after pump	oversaturated KOH solution, solid KOH gets stuck in pump	HCl not fully neutralized, leaving acidic water in waste stream	guarantee that the KOH solution is definitely not saturated	assume sieve filters out all solid particles, assume the extra water guarantees the solution never gets saturated	Extra supply of water, installing a sieve
P1702	flow	low	leakage of pump	corrosion due to the basicity of the solution	HCl not fully neutralized, leaving acidic water in waste stream	Install P1702AB and flow detector activating P1702B	Assume pump 1702B can deliver enough flow	Install pump 1702B and composition detector
P1702	temperature	high	pump cannot be cooled sufficiently	pump works too fast, high environmental temperature	Temperature can get above design temperature	TIS activating pump 1702B	Assume 2 pumps in parallel will not breakdown at same time	Install TIS and pump 1702B
C1601	flow in column	low	composition inflow different	wrong reflux/boil up ratio;	Drying up of stages; separation of components fails.	PIS on reboiler; LIS on condenser	Assume low flow in column is not caused by low flow in	Install PIS and LIS

C1601	Composition	other than	leakage of column	corrosion of column	leakage of toxic phosgene	safety box; gas detector activating ammonia curtain	Assume gas detector detects phosgene at a lower ppm than harmful	install safety box; gas detector and ammonia curtain
C1601	pressure	high	too high inflow	compressor is over performing	Column gets above design pressure/ temperature; possible leakage	TSL; HPSD; FIS controlling shut off valve on 1606	Assume there is a safe location	install TSL, HPSD and FIS
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
C1401	mea flow in	low	desired flow is higher than normal	underperforming pump	drying up of stages; CO2 is not sufficiently absorbed; CO2 in product	FIS controlling pump 1402B	Assume extra pump con provide enough flow	Install FIS; and P1402B
C1401	mea flow in	high	too much mea/water enters absorber	too much recycled; too much added after recycle	phosgene too wet and too much absorbed in MEA; loss of product	FIS controlling shut off valve on 1412		install FIS for MEA inflow and recycle
C1401	pressure	high	too high gas inflow	too little phosgene produced in reactor therefore more CO and chlorine gasses occupying a larger volume	leakage of toxic gasses (phosgene, chlorine)	install HPSD/TSL	Assume there is a safe location available	install HPSD, TSL and create safe location

C1401	composition	other than	tears	corrosion	leakage of toxic phosgene	put column inside; gas detector controlling shut off valve on 1426	assume that gas detector can detect phosgene at lower ppm than harmful	put column inside; install gas detector
C1401	pressure	low	less gas supplied	not enough inflow before reactor	MEA and energy wasted			accept risk
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
C1402	temperature reboiler	low	boil up ratio too low	deviation in heating liquid for reboiler	CO2 not properly stripped; accumulation of CO2 in mea loop	TIS to shut off valve on 1410	Assume deviation in temperature of heating liquid is not caused by malfunctioning heat exchanger	Install TIS
C1402	temperature reboiler	high	boil up ratio too high	deviation in heating liquid for reboiler	loss of MEA	TIS on column controlling shut off valve on heating liquid flow	Assume technicians know actions required when pressure deviates	pressure too high: decrease hot water stream
C1402	pressure	high	more CO2 dissolved in mea in stream 1430 than expected	more CO2 produced in reactor; deviation in heating liquid for reboiler	possible leakage; loss of MEA	HPSD/TSL	Assume there is a safe location available	create safe location install HPSD

C1402	pressure	low	boil up ratio too low	deviation in heating liquid for reboiler	CO2 not properly stripped	TIS on column controlling shut off valve on heating liquid flow	Assume deviation in temperature of heating liquid is not caused by malfunctioning heat exchanger	Install TIS
T1501	level	high	more glycerol in tank than normal	too much glycerol in inflow/recycle	overflowing of tank	LIS on tank controlling shut off valve on stream 1501	assume high level is caused by to high inflow instead too low outflow	install LIS
T1501	level	No	tank is empty	too much glycerol purged/too little glycerol supplied	no water absorption	LIS on tank controlling pump	Assume there is always a glycerol stock present	Always have glycerol to add to tank; install LIS
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
E1502	temperature	high	outlet temperature is too high	hotter inflow; insufficient coolant	glycerol vapor in tank	TIS controlling shut off valve on 1515	Assume that high temperature is not caused by a malfunctioning heat exchanger	Install TIS
E1502	composition	other than	tears	high temperature gradient	glycerol in coolant and coolant in glycerol	glycerol detector on cooling stream giving alarm when glycerol is in cooling medium	Assume that glycerol detector detects glycerol before danger becomes severe	when alarm is activated the plant has to be shut down in order to safely replace to heat exchanger
E1502	pressure	different	pressure drop	viscosity of	choked flow;	viscosity indicator	Assume viscosity	after heat

C1101	pressure	high	too much gas in tower	gas trapped in tower	possible leakage, pressure above design pressure	PIS to shut off valve on gas stream in; PAH indicating demister needs to be cleaned	Assume operator knows what causes gas trapping and how to fix this	install PIS and pressure alarm
C1101	рН	low	not enough limestone	supply failure	no SO2 absorption in tower	pH switch controlling shut off valve on gas inflow	assume more limestone will be provided	install pH controller
C1101	рН	high	too much limestone	supply too high	too much solid in tower: scaling occurs	pHIS on limestone supply	assume a pHIS can control the supply of a solid	pH indicator
E1701	flow	high	Gas flow in condenser too high	more phosgene destroyed in previous reactor	insufficient condensation of HCI		more HCl will result on more cooling water so system will regulate this	accept risk
No.	Element	Guide Word	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required
No. E1701	Element composition	Guide Word other than	Deviation Failure of tubes inside condenser.	Possible causes corrosion; vibration	Consequences HCl in coolant	pHIA	Comments when an alarm is encountered, the plant has to be shut down in order to safely replace the condenser	Actions required

J.2 P&ID's after HAZOP

Section 1



PIS to C1101 connected to PV1103 in case of too high pressure. pHIS controlled to T1101 in case of too high or low pH in the tank. pHIS connected to PV1104 and PV1105.



T1401 contains chlorine which is fed to the reactor. This tank is added to prevent clocking. 1401 contains a shut off valve PV1411 so the flow can be stopped. A flow alarm high and low are installed. The compressor, K1402 is equipped with a pressure indicating switch. The mixed feed, 1406 is fed to the reactor, a safety box is installed. This contains a gas detector and a pressure indicating switch to detect leakage and are connected to shut off valve PV1415. A

composition indicating switch is placed on 1410 in order to deal with failure of the reactor. A temperature indicating switch is placed on the cooling liquid, activating an extra pump for the cooling liquid. A gas detector is placed on 1409 to detect leakage of the tubes. A shut of valve on the MEA make up stream is installed and controlled with a flow indicator switch on 1413 and a level indicator switch on C1401. The level of the liquid in reboiler E1402 is controlled with a level indicator controller on PV1418. A Tis is installed on stream 1425 controlling the inlet stream 1410 of C1401. A temperature indicating switch is placed on cooling stream 1424 when a shutdown is needed.



PV1510 was added controlled by a LIS on P1501 and T1501, this is to ensure no overflowing occurs in the tank. If temperature problems arise PV1509 was added controlled by a TIS, to shut down the system. A CD was added to 1517 to detect leakages in E1502.

Section 6



A second compressor in parallel was added for K1601 controlled by a FIS. Another FIS was added to shut down the flow into the distillation column using PV1610. A LIS as well as a PIS is added to E1602 to control PV1612 to shut down the boil up in stream 1616. A Gas detector is connected in the area around the distillation column to detect any phosgene leakages.




PV1707 is controlled by a PIS and a GD connected to the construction around V1701 to detect any phosgene leakage. A TSL is also connected via PV1706. pH indicator is connected to 1712 to detect any shell side leakage of HCl in E1701. P1702 has another pump added in parallel and is controlled by a TIS in case of overheating and a FIS in case of too high flow in 1716.

K. Economic Analysis

K.1 Executive summary

EXECUTIVE SUMMARY		
PROJECT NAME:	phosgene factory	
CAPACITY:	ERR	
PLANT LOCATION:	Rotterdam	
BRIEF DESCRIPTION:	phosgene production and purification	
SCHEDULE:		
Start Date for Engineering	1-jan-14	
Duration of EPC Phase	200,00	Weeks
Completion Date for Construction	Thursday, November 02, 2017	
Length of Start-up Period	20,00	Weeks
INVESTMENT:		
Currency Conversion Pate	-	
	1,00	OPEAN
		EURO
Total Project Capital Cost	3.225.288.986,34	EUR
Total Operating Cost	494.542.605,60	EUR/Year
Total Raw Materials Cost	0,00	EUR/Year
Total Utilities Cost	308.239.820,00	EUR/Year
Total Product Sales	0,00	EUR/Year
Desired Rate of Return	20,00	Percent/'
		Year
P.O. Period	0,00	Year
PROJECT INFORMATION:		
Simulator Type	- No Simulator	
Version		
Report File		
Report Nate		
Economic Analysis Type	IDE	

Version	34.0.0	
System Cost Base Date	1Q 14	
Project Directory		
Analysis Date	Thu Jun 14 12:53:04 2018	
Country Base	EU	
Project Type	Grass roots/Clear field	
Design code	ASME	
Prepared By		
NOTES:		
	-	

K.2 Project summary

PROJSUM.ICS (Project Summary)		
ITEM	UNITS	VALUE
PROJECT INFORMATION		
Project Name		phosgene factory
Project Description		phosgene production and purification
Analysis Date and Time		Thu Jun 14 12:53:04 2018
Simulator Type		No Simulator
Simulator Version		
Simulator Report File		
Simulator Report Date		
Economic Analysis Type		IPE
Version		34.0.0
Project Directory		
Scenario Name		phosgene production and purification
Scenario Description		phosgene factory
CAPITAL COST EVALUATION BASIS		
Date		14-jun-18
Country		EU
Units of Measure		METRIC
Currency (Cost) Symbol		EUROPEAN EURO
Currency Conversion Rate	EUR/EUROPEAN EURO	1,00
System Cost Base Date		1Q 14
Project Type		Grass roots/Clear field
Design code		ASME
Prepared By		
Plant Location		Rotterdam
Capacity		ERR
Time Difference Between System Cost Base Date and Start Date for Engineering	Days	-88,00
User Currency Name		EURO
User Currency Description		EUROPEAN EURO
User Currency Symbol		EUR
TIME PERIOD		
Period Description		Year
Operating Hours per Period	Hours/period	8.000,00
Number of Weeks per Period	Weeks/period	52,00
Number of Periods for Analysis	Period	20,00
SCHEDULE		
Start Date for Engineering		1-jan-14
Duration of EPC Phase	Weeks	200,00
Length of Start-up Period	Weeks	20,00
Duration of Construction Phase	Weeks	96,00

Completion Date for Construction		Thursday, November 02, 2017
CAPITAL COSTS PARAMETERS		
Working Capital Percentage	Percent/period	5,00
OPERATING COSTS PARAMETERS		
Operating Supplies (lump-sum)	Cost/period	0,00
Laboratory Charges (lump-sum)	Cost/period	0,00
User Entered Operating Charges (as percentage)	Percent/period	25,00
Operating Charges (Percent of Operating Labor	Percent/period	25,00
Costs)		
Plant Overhead (Percent of Operating Labor and	Percent/period	50,00
Maintenance Costs)	Descent for start	
G and A Expenses (Percent of Subtotal Operating	Percent/period	8,00
GENERAL INVESTMENT PARAMETERS		
Tax Rate	Percent/period	40.00
Interest Rate	Percent/period	20.00
Economic Life of Project	Period	10.00
Salvage Value (Fraction of Initial Capital Cost)	Percent	20,00
Depreciation Method		Straight Line
ESCALATION		
Project Capital Escalation	Percent/period	5,00
Products Escalation	Percent/period	5,00
Raw Material Escalation	Percent/period	3,50
Operating and Maintenance Labor Escalation	Percent/period	3,00
Utilities Escalation	Percent/period	3,00
PROJECT RESULTS SUMMARY		
Total Project Capital Cost	Cost	3.225.288.986,34
Total Raw Materials Cost	Cost/period	0,00
Total Products Sales	Cost/period	0,00
Total Operating Labor and Maintenance Cost	Cost/period	99.440.000,00
Total Utilities Cost	Cost/period	308.239.820,00
Total Operating Cost	Cost/period	494.542.605,60
Operating Labor Cost	Cost/period	2.040.000,00
Maintenance Cost	Cost/period	97.400.000,00
Operating Charges	Cost/period	510.000,00
Plant Overhead	Cost/period	49.720.000,00
Subtotal Operating Cost	Cost/period	457.909.820,00
G and A Cost		36.632.785,60
PROJECT CAPITAL SUMMARY		Total Cost
Purchased Equipment	Cost	1.837.012.224,00
Equipment Setting	Cost	15.395.213,00
Piping	Cost	259.624.240,00
Civil	Cost	61.493.220,00
Steel	Cost	25.975.316,00

Instrumentation	Cost	103.878.936,00
Electrical	Cost	42.222.144,00
Insulation	Cost	26.093.838,00
Paint	Cost	11.693.151,00
Other	Cost	239.385.616,00
Subcontracts	Cost	0,00
G and A Overheads	Cost	77.548.872,00
Contract Fee	Cost	66.417.064,00
Escalation	Cost	16,00
Contingencies	Cost	498.013.184,00
Total Project Cost	Cost	3.264.753.034,00
Adjusted Total Project Cost	Cost	3.225.288.986,34
ENGINEERING SUMMARY		Cost
Basic Engineering		5.586.300,00
Detail Engineering		23.813.200,00
Material Procurement		2.816.800,00
Home Office		5.594.600,00
Total Design, Eng, Procurement Cost		37.810.900,00
RAW MATERIALS COSTS AND PRODUCTS SALES		
Raw Materials Cost per Hour	Cost/Hour	0,00
Total Raw Materials Cost	Cost/Period	0,00
Products Sales per Hour	Cost/Hour	0,00
Total Products Sales	Cost/Period	0,00
Main Product Name		
Main Product Rate		0,00
Main Product Unit Cost	ERR	0,00
Main Product Production Basis		
Main Product Rate per Period	ERR	0,00
Main Product Sales	EUR/Year	0,00
By-product Sales	EUR/Year	0,00
OPERATING LABOR AND MAINTENANCE COSTS		
Operating Labor		
Operators per Shift		11,00
Unit Cost	Cost/Operator/H	20,00
Total Operating Labor Cost	Cost/period	1.760.000,00
Maintenance		
Cost/8000 Hours		97.400.000,00
Total Maintenance Cost	Cost/period	97.400.000,00
Supervision		
Supervisors per Shift		1,00
Unit Cost	Cost/Supervisor/ H	35,00
Total Supervision Cost	Cost/period	280.000,00
UTILITIES COSTS		

Electricity		
Rate	KW	497.161,00
Unit Cost	Cost/KWH	0,08
Total Electricity Cost	Cost/period	308.239.820,00
Potable Water		
Rate		
Unit Cost	Cost/M3	0,00
Total Potable Water Cost	Cost/period	0,00
Fuel		
Rate		
Unit Cost	Cost/MEGAWH	26,81
Total Fuel Cost	Cost/period	0,00
Instrument Air		
Rate		
Unit Cost	Cost/M3	0,00
Total Instrument Air Cost	Cost/period	0,00
Subtotal Cost	Cost/period	308.239.820,00

K.3 Equipment cost

EQUIPICS								
Equipment								
Area Name	Component Name	Component	Total Direct Cost	Equipment Cost	Equipment	Installed	factor	installed cost
		Туре			Weight	Weight		
			(EUR)	(EUR)	KG	KG		
Main Area	MEA/CO ₂ absorber	DTW TRAYED	€ 6.765.600,00	€ 3.671.500,00	1,79E+05	3,08E+05	4	€ 14.686.000,00
Main Area	MEA/CO ₂ stripper	DTW TRAYED	€ 1.645.900,00	€ 943.500,00	3,10E+04	5,71E+04	4	€ 3.774.000,00
Main Area	H ₂ O absorber	DTW TRAYED	€ 6.919.800,00	€ 3.806.500,00	1,88E+05	3,20E+05	4	€ 15.226.000,00
Main Area	glycerol stripper	DTW TRAYED	€ 11.715.300,00	€ 9.391.500,00	5,35E+05	7,05E+05	4	€ 37.566.000,00
Main Area	distiller	DTW TRAYED	€ 3.411.300,00	€ 2.083.000,00	7,55E+04	1,21E+05	4	€ 8.332.000,00
Main Area	amine pump	DCP CENTRIF	€ 443.600,00	€ 72.000,00	1,30E+03	1,20E+04	4	€ 288.000,00
Main Area	glycerol pump	DCP CENTRIF	€ 1.168.200,00	€ 106.000,00	3,00E+03	5,06E+04	4	€ 424.000,00
Main Area	preCO ₂ abscompressor	DGC CENTRIF	€ 23.142.000,00	€ 16.828.000,00	1,30E+05	3,31E+05	2,5	€ 42.070.000,00
Main Area	preH ₂ O abscompressor	DGC CENTRIF	€ 24.079.900,00	€ 16.955.000,00	1,33E+05	3,57E+05	2,5	€ 42.387.500,00
Main Area	Predistiller compressor	DGC CENTRIF	€ 24.162.600,00	€ 16.958.000,00	1,33E+05	3,73E+05	2,5	€ 42.395.000,00
Main Area	phosgene reactor	DHE TEMA EXCH	€ 4.179.500,00	€ 3.081.500,00	1,67E+05	2,01E+05	3,5	€ 10.785.250,00
Main Area	catalyst	EPAKPACKING	€ 470.900,00	€ 75.000,00	0,00	0,00	2,5	€ 187.500,00

Main Area	mea cooler	DHE TEMA EXCH	€ 651.400,00	€ 139.000,00	9,00E+03	3,11E+04	3,5	€ 486.500,00
phosgene	phosgene destroyer	DVT	€ 737.000,00	€ 99.500,00	8,00E+03	4,13E+04	4	€ 398.000,00
destruction		CYLINDER						
phosgene	HCl condenser	DHE TEMA	€ 725.300,00	€ 99.500,00	8,50E+03	3,44E+04	3,5	€ 348.250,00
destruction		EXCH						
phosgene	HCl destroyer	DVT	€ 488.800,00	€ 76.500,00	6,00E+03	1,97E+04	4	€ 306.000,00
destruction		CYLINDER						
phosgene	phosgene storage	DHT HORIZ	€ 708.600,00	€ 77.000,00	6,00E+03	3,50E+04	4	€ 308.000,00
destruction	vessel	DRUM						
phosgene	steam blower	DGC CENTRIF	€ 3.194.200,00	€ 2.391.500,00	1,35E+04	5,27E+04	2,5	€ 5.978.750,00
destruction								
SO2	SO ₂ scrubbing tower	DVT	€ 7.301.200,00	€ 3.229.000,00	2,04E+05	3,56E+05	4	€ 12.916.000,00
scrubber		CYLINDER						
SO2	reaction mixture tank	DHT HORIZ	€ 983.700,00	€ 178.500,00	2,10E+04	6,03E+04	4	€ 714.000,00
scrubber		DRUM						
SO2	limestone ball mill	EM BALL	€ 7.064.300,00	€ 6.223.000,00	6,98E+05	7,71E+05	2,5	€ 15.557.500,00
scrubber		MILL						
SO2	slurry pump	DCP CENTRIF	€ 5.733.100,00	€ 2.542.500,00	6,65E+04	3,51E+05	4	€ 10.170.000,00
scrubber								
SO2	oxygen blower	DGC CENTRIF	€ 2.838.900,00	€ 2.302.500,00	1,30E+04	3,19E+04	2,5	€ 5.756.250,00
scrubber								
SO2	slurry mixer	EMX MULLER	€ 171.600,00	€ 124.000,00	4,55E+03	5,77E+03	2,5	€ 310.000,00
scrubber		EXT						
SO2	gypsum filter	DF ROTY	€ 746.900,00	€ 446.500,00	9,50E+03	2,04E+04	2,5	€ 1.116.250,00
scrubber		DRUM						
SO2	after column	EGC RECIP	€ 18.912.600,00	€ 12.397.000,00	3,49E+05	9,44E+05	2,5	€ 30.992.500,00
scrubber	compressor	GAS						
section 3	desiccating towers	EAD AIR DRYER	€ 3.260.200,00	€ 2.549.000,00	0,00	6,35E+04	4	€ 10.196.000,00
section 3	desiccating tower packing	EPAKPACKING	€ 782.400,00	€ 684.000,00	0,00	0,00	2,5	€ 1.710.000,00

section 3	PSA1	DTW PACKED	€ 809.929.984,00	€ 603.014.400,00	4,50E+07	2,00E+08	4	€ 2.412.057.600,00
section 3	pre desiccating towercomp	DGC CENTRIF	€ 248.780.000,00	€ 225.134.016,00	1,69E+06	3,90E+06	2,5	€ 562.835.040,00
section 3	after psa turbine	ETURNON COND	€ 69.501.000,00	€ 42.499.200,00	1,30E+06	4,11E+06	2,5	€ 106.248.000,00
section 3	storage vessel	DVT CYLINDER	€ 131.420.000,00	€ 40.082.400,00	7,09E+06	2,57E+07	4	€ 160.329.600,00
CO2 absorption	preCO ₂ abscompressor2	DGC CENTRIF	€ 748.080.000,00	€ 692.917.504,00	5,24E+06	7,45E+06	2,5	€ 1.732.293.760,00
CO2 absorption	MEA/CO ₂ absorber2	DTW TRAYED	€ 2.517.400,00	€ 1.098.500,00	4,55E+04	1,19E+05	4	€ 4.394.000,00
CO2 absorption	MEA/CO ₂ stripper2	DTW TRAYED	€ 1.434.200,00	€ 723.500,00	5,45E+04	1,11E+05	4	€ 2.894.000,00
CO2 absorption	amine pump 2	DCP CENTRIF	€ 163.600,00	€ 31.000,00	450,00	4,13E+03	4	€ 124.000,00
Missing equipment			€ 64.776.000,00	€ 10.440.065			3	€ 31.320.195,00
		total	€	€				€ 5.327.881.445,00
			2.239.006.984,00	1.723.471.085,00	6,34E+07	2,47E+08		

L. Pumps

L.1 Pump selection chart [94]



CPKN

Selection Charts



L.2 Impeller curve [95]



Laufradaustrittsbreite/Impeller outlet width/Largeur à la sortie de la roue 7 mm Luce della girante/Waaier uittredebreedte/Anchura de salida rodete 7 mm

22

M. SO₂ scrubber sizing calculations

# droplets	flow rate slurry (m³/h)	Droplets per second	[SO2]out (mol/m³)	efficiency out/in	number of nozzles per tower	water pumped around (kg/h)	gypsum (kg/h)
1	5.44E-05	0.45	1.21E-02	1.0000	5.39E-08	0.052	7.54E-05
1.00E+08	5.44E+03	4.50E+07	6.75E-05	0.0056	5.39	5.17E+06	1.45E+03
1.10E+08	5.98E+03	4.95E+07	4.02E-05	0.0033	5.93	5.69E+06	1.45E+03
1.20E+08	6.52E+03	5.40E+07	2.39E-05	0.0020	6.47	6.21E+06	1.45E+03
1.30E+08	7.07E+03	5.85E+07	1.42E-05	0.0012	7.01	6.73E+06	1.45E+03
1.40E+08	7.61E+03	6.30E+07	8.48E-06	0.0007	7.55	7.24E+06	1.45E+03
1.50E+08	8.15E+03	6.75E+07	5.04E-06	0.0004	8.09	7.76E+06	1.45E+03
1.60E+08	8.70E+03	7.20E+07	3.00E-06	0.0002	8.63	8.28E+06	1.45E+03
1.70E+08	9.24E+03	7.65E+07	1.79E-06	0.0001	9.17	8.80E+06	1.45E+03
1.80E+08	9.79E+03	8.10E+07	1.06E-06	0.0001	9.71	9.31E+06	1.45E+03

oxygen (kg/h)	water in gypsum (kg/h)	unbound water in gypsum wet cake (kg/h)	total limestone to be added to the process (kg/h)	water to be added (kg/h)	CO ₂ released (kg/h)	pumped around mass flow rate (kg/h)	density slurry kg/m³)	pressure drop slurry pumped (Pa)	Pressure drop gas (bar)
7.01E-	1.58E-	4.3822E-	4.09E-	1.93E-	5.75E-	1.06E+0	2.07E+0	7.59E-	1.88E-
06	05	05	05	05	02	3	5	04	05
1.34E+0	3.02E+0	8.40E+02	7.84E+0	3.69E+0	5.75E+0	1.06E+0	2.07E+0	7.59E-	3.61E+0
2	2		2	2	6	3	5	04	2
1.35E+0	3.03E+0	8.42E+02	7.86E+0	3.70E+0	6.32E+0	1.06E+0	2.07E+0	7.59E-	3.62E+0
2	2		2	2	6	3	5	04	2
1.35E+0	3.03E+0	8.43E+02	7.87E+0	3.71E+0	6.90E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.44E+02	7.87E+0	3.71E+0	7.47E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.44E+02	7.88E+0	3.71E+0	8.05E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.44E+02	7.88E+0	3.71E+0	8.62E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.44E+02	7.88E+0	3.71E+0	9.20E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.44E+02	7.88E+0	3.71E+0	9.77E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	6	3	5	04	3
1.35E+0	3.04E+0	8.45E+02	7.88E+0	3.71E+0	1.03E+0	1.06E+0	2.07E+0	7.59E-	1.45E+0
2	2		2	2	7	3	5	04	3

Used formulas:

$$\begin{aligned} \tau_{droplet}(s) &= \frac{H_{tower}}{v_{droplet}} \\ \phi_{v, \ slurry}(m^3h^{-1}) &= \frac{V_{droplet}}{\tau_{droplet}} n_{droplets} * 3600 \\ n_{droplets \ per \ second} &= \frac{n_{droplets}}{\tau} \\ [SO_2]_{out} &= [SO_2]_{in} * \exp(\frac{-k_g * A_{droplet} * H * n_{droplets}}{\phi_v/_5}) \\ \eta &= \frac{[SO_2]_{out}}{[SO_2]_{in}} \\ n_{nozzles} &= \frac{\phi_{v, \ slurry}}{\phi_{v, \ nozzle}} \end{aligned}$$

 $\phi_{m, water pumped around} = n_{droplets per second} * 3600 * m_{water in droplet}$

$$\phi_{m,gypsum} = ([SO_2]_{in} - [SO_2]_{out}) \phi_{v,gas} * 3600 * \frac{M_{gypsum}(\frac{kg}{kmol})}{1000}$$

$$\phi_{m,oxygen} = \frac{\phi_{m,gypsum}}{M_{gypsum}} * M_{oxygen} * 0.5$$

$$\phi_{m,water in gypsum} = \frac{\phi_{m,gypsum}}{2M_{water}} / M_{gypsum}$$

$$\phi_{m, unbound water in wet cake} = rac{\phi_{m,gypsum}}{3} * 4 - \phi_{m,gypsum}$$

$$\phi_{m, limestone to be added to the process} = rac{\phi_{m,gypsum}}{M_{gypsum}} M_{limestone}$$

 $\phi_{m, \,\, water \,\, to \,\, be \,\, added \,\, to \,\, the \,\, process}$

$$= \phi_{m, unbound water in wet cake} + \frac{\phi_{m, limestone to be added to the process}}{M_{limestone}} * 2 * M_{water}$$

$$\phi_{m, CO2 \ released} = ([SO_2]_{in} - [SO_2]_{out}) \phi_{v,gas} * 3600 * \frac{M_{CO_2}}{1000}$$

 $\phi_{m, total pumped around} = \phi_{m, water pumped around} + \frac{\phi_{m, water pumped around}}{9}$

$$\rho_{slurry} = \frac{\phi_{m, \ total \ pumped \ around}}{\phi_{v, \ slurry}}$$

 $\Delta P_{slurry}(Pa) = 9.81 * H_{tower} * \rho_{slurry}$

$$\Delta P_{gas}(bar) = 9.81 * H_{tower} * \frac{\frac{\phi_{m, gas average}}{\phi_{v, gas}/gas flow correction (= 0.2) * 3600}}{100000}$$