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ACETIC ACID PRODUCTION FROM STEEL MILL OFF-GAS

Bachelor Thesis Chemical Engineering

Abstract

This project was undertaken to design a process for the production of acetic acid from the carbon monoxide content of a steel mill's off-gas stream and evaluate its reachability. To purify the off-gas stream, the LO-CAT™ process, limestone wet scrubber and COSORB™ process were used. The Acetica™ process was chosen for the carbonylation reaction between CO from the off-gas and purchased methanol. Aspen Plus™ was used to model the process and identify equipment specifications. Important assumptions made in the modelling phase of the project included omitting the catalyst from the COSORB™ process and drastically simplifying the reactor model in the Acetica™ process. A process safety analysis was performed via a HAZOP study and P&ID's for the plant were developed. From the cost analysis, it was shown that the overall process could be profitable after less than 4 years. However, the extraordinarily large feed stream used necessitated the acceptance of some assumptions in the calculation of the investment- and production costs.

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1. Introduction

Steel is the world's most often used metal and the steel sector is one of the largest global industries. During the recent decades, industrialization and urbanization have boosted the global steel demand. At present, the steel sector contributes 9% to the global energy- and process related carbon emissions.¹ Most often, steel is produced using blast- and basic oxygen furnaces with a strong reducing agent. A commonly used reducing agent is coke, which results in the high carbon intensity of the process.² One steel plant may consist of up to five blast furnaces, each emitting large amounts of carbon containing off gas. Blast furnace off gas typically consists of a mixture of CO₂, CO, N₂ and H₂. The concentration of both CO₂ and CO is typically about 20%.³

Most often, off gases generated in steel production are used as fuels in process units within the plant. Other uses of these off gases include their supply to a power or combined heat and power plant on the site for the production of steam, power or heat. Although utilization of these gases for heat or power generation already proves advantageous, it is of great interest to find methods of recovering their carbon-content.⁴ Not only is it preferable to use this carbon for the generation of higher-value products, also the reduction of greenhouse gas emissions is a pressing issue. Capturing and recovering carbon from carbon monoxide (CO)-rich off gas from steel mills is an efficient way of reducing further greenhouse gas releases.⁵

A well-documented use of carbon monoxide is in the production of acetic acid through carbonylation of methanol.^{2,6-9} Around 80% of the 13 million ton global annual production of acetic acid in 2013 originated from these liquid-phase catalysed methanol carbonylation reactions.⁶ Acetic acid is a widely used platform chemical in all areas of the chemical industry. It is a raw material for the synthesis of polymers such as poly vinyl acetate and can also be used as a solvent or in the production of vinegar.⁶ It is thus self-evident that research towards a synthetic route from low-value chemicals is essential for a wide range of technologies. The carbonylation reaction of methanol using waste carbon monoxide is an important example of such a synthetic route.

A methanol carbonylation reaction is commonly performed using methanol with an excess of carbon monoxide, according to Eq. 1. Operating at higher pressure and lower temperature can increase the equilibrium conversion. This selective liquid phase reaction of CO and methanol to acetic acid can be catalysed by a variety of transition metal catalysts. Additionally, halogen promoters such as iodide are needed to activate the methanol into methyl iodide, which subsequently reacts with CO to form acetic acid. Examples of processes designed for the liquid-phase conversion of CO and methanol to acetic acid using a homogeneous catalyst include the BASF-, Monsanto-, Celanese-, Cativa- and Acetica Process. The Chiyoda™/UOP Acetica Process has the significant advantage that its catalyst is immobilized and thus heterogeneous.⁶



The most important improvement of the Acetica process as compared to the aforementioned processes is the usage of an immobilized rhodium complex on polyvinyl pyridine (PVP) resin. The immobilized catalyst showed a high activity, long-term stability under elevated temperature and pressure and no significant rhodium loss. Since Rh metal is expensive, confining the catalyst to the reactor rather than losing it downstream is very beneficial. Furthermore, the reactor capacity is no longer governed by catalyst solubility as in the homogeneous systems. Instead, the reaction rate is limited by the resin's metal capacity, allowing for a significantly increased reaction rate.⁸

1.1 Process Goals

The main objective of this research is the design of a process to convert the CO content of a defined off-gas stream from the steel industry to acetic acid using the Acetica™ process. First, a model will be created using the Aspen Plus® software (version 8.6).¹⁰ This model gives an impression of the equipment, streams and energy needed in the manufacturing procedure. After this process simulation has been optimized, P&ID diagrams will be derived and a HAZOP analysis will be performed. The dimensions of all the equipment used in the model will be calculated. The costs of the design will be briefly investigated using these calculated dimensions and prices of feedstock and products. After this, overall conclusions can be drawn regarding the profitability of the process and its reachability.

The CO containing feed stream obtained from the steel mill contains 15% H₂, 35% N₂, 30% CO, 14% CO₂ and 5% CH₄. Additionally, the feed stream contains sulphurous contaminants. Although the Acetica™ process can operate with low purity industrial CO feedstock, it is desirable to obtain a higher purity CO stream.⁸ Therefore, a purification step is included before the CO stream enters the reactor. The most important objective of this additional purification step is the removal of the sulphurous contaminants, since sulphur species are well-known catalyst poisoners.¹¹⁻¹³ Moreover, including a purification step before the carbon monoxide enters the reactor will make the reaction more efficient due to a higher effective CO concentration.

2. Process overview

The acetic acid production consists of two primary parts, each of which will be treated separately. The first section contains the purification of the CO-containing feed stream. This purification includes a sulfuric contaminants removal step and a subsequent CO purification step using the COSORB process.^{14,15} The second part consists of the reaction itself. The reaction section starts with the bubble column reactor in which the acetic acid formation takes place, after which the low purity acetic acid is converted to high purity product in several columns. The general process flow diagrams for both sections are taken from literature, but some modifications were included. A schematic overview of the process is given in figure 1 and a brief description of each part of the equipment is given below. All Aspen simulations were done using the NRTL-RK base method, since this is well-suited for non-ideal chemical systems and can be used for vapor-liquid and liquid-liquid equilibrations¹⁶.

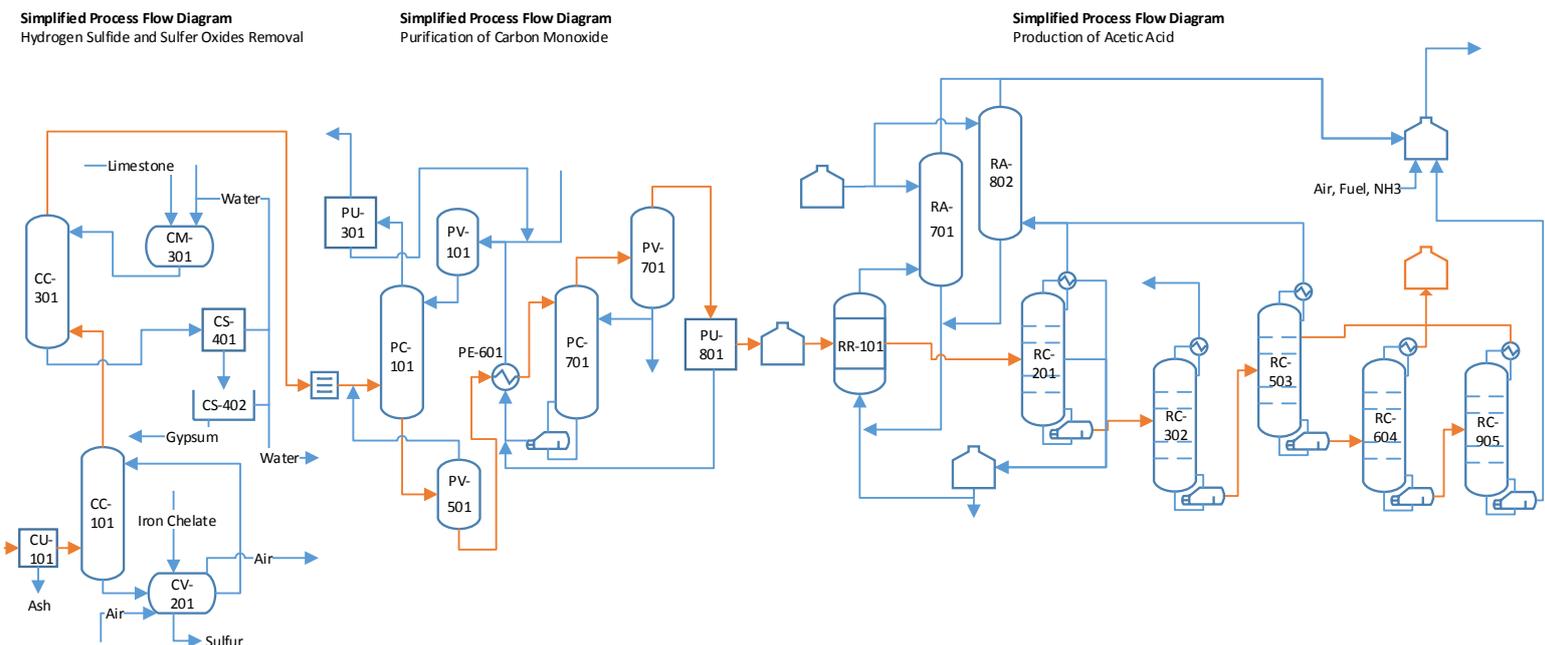


Figure 1: Simplified PFD of entire process. See Appendix 1 for enlarged version.

2.1 Feed stream purification section

2.1.1 Feed gas contaminants

The carbon monoxide feedstock is obtained from the off-gases from steel mills. These gases are coke gas, blast furnace gas and converter gas. A combination of these three gases has been defined as the feed gas used to obtain the used carbon monoxide. The exact composition of this gas has not been given, as one volume percent has been left undefined with the notice that it could contain sulfurous contaminants. Literature study has shown that contaminants such as hydrogen sulfide (H₂S), sulfur oxides (SO₂ and SO₃), nitrogen oxides (NO and NO₂, or NO_x), particulate matter and many hydrocarbons are all commonly found in coke oven gas and in other coal fired plant waste gases.¹⁷ Each one of these components will be reviewed below. Their source as well as their quantity will be discussed.

The contaminants containing sulfur all have an origin in the fuel that is used in the steel mill's furnaces. For the coke oven, this fuel consists of coke, which is produced by heating bituminous coal to a temperature of 1000°C in the absence of air. Coal contains sulfur, which comes from the parent plant material. The sulfur content in coal is not a fixed value and therefore distinction has

been made in low-sulfur (< 1% S), medium-sulfur (1 to < 3% S) and high-sulfur (\geq 3% S) coal.¹⁸ Further study has to determine what sort of coal is used for the steel mills and what the exact composition of the gas contaminants is. However, for the composition of the gas, literature values were used to obtain a realistic design.

The presence of hydrogen sulfide in the off-gases originates from the formation of hydrogen sulfide when sulfur comes into contact with organic material at high temperatures. This is a highly poisonous gas that can cause symptoms such as headaches and nausea from a concentration of 2 ppm in air and can be deadly at a concentration of 500 ppm after half an hour of exposure.¹⁹ Not only is the gas a very serious health hazard, it also causes corrosion of stainless steel and is poisonous to the catalyst used in the Acetica process further downstream.¹¹ It is therefore clear that the concentration of hydrogen sulfide has to be reduced to almost zero.

For the concentration of hydrogen sulfide in the off-gases, several literature values were compared. The Journal of Chemical Engineering of Japan states that coke oven gas contains a H₂S concentration in the order of hundreds of ppm.²⁰ A process manual for analyzing equipment states that flue gases contain typically between 0 and 300 ppm H₂S by volume.²¹ The off-gas used as our feed gas is not pure coke oven gas, as it was presumably mixed with blast furnace gas and converter gas. Therefore, the amount of hydrogen sulfide in our feed gas was assumed to be 300 ppm by volume. By doing this, the process will be designed for a relatively high concentration of H₂S and should therefore be able to handle a high variation of concentrations of sulfide in the off-gases.

Hydrogen sulfide is not the only sulfuric compound present in the off-gases from steel mills. Two others are the sulfur oxides SO₂ and SO₃. Sulfur oxides are major air pollutants and can have significant impacts on human health.²² During the combustion of coke, the elemental sulfur can oxidize to sulfur dioxide, which in turn oxidizes to sulfur trioxide.



In general, about one to five per cent of the SO₂ is oxidized to SO₃.²³ Again, literature values of sulfur oxide concentrations in flue gases do not coincide. An article on the combustion products of coal states that the concentration of SO₂ in the flue gases is 204±13 ppm²⁴ and another article on the typical flue gas composition of a coal fired power plant states that the flue gas contains up to 162 ppm of SO₂ by volume.²⁵ The same process manual as cited for H₂S, also stated that the typical sulfur dioxide concentration is between 0 and 300 ppm by volume.²¹ As for the hydrogen sulfide concentration, 300 ppm SO₂ by volume was assumed as a relatively high sulfur content scenario value. The SO₃ concentration, taken as five percent, will then be 15 ppm by volume. The designed process will be able to handle a good variation of inlet sulfur oxide concentrations.

Nitrogen oxides in the steel mill's off-gases are common contaminants from combustion. Nitrogen monoxide is thermally formed at the high temperatures in the steel mill according to the following set of reactions, known as the extended Zel'dovich mechanism.²⁶



Nitrogen dioxide can be formed by further oxidation of nitrogen monoxide.



These NO_x gases contribute to the destruction of ozone and are, together with sulfur oxides, responsible for acid rain. The literature source on the combustion products of coal states that the corresponding flue gas contains 289 ± 8.4 ppm of NO by volume.²⁴ Another literature source gives that the NO_x concentration in the flue gas from a coal-fired power plant has a value of 179 to 310 ppm by volume.²⁵ The molar ratio of NO to NO_2 for a combustion process is typically more than 20 to 1 in a flue gas.²⁷ From these literature sources, the concentration of NO was assumed to be 300 ppm by volume and the concentration of NO_2 to be 15 ppm by volume.

Solids present in the gas stream are composed of fine particles originating from the burnt coal fuel. The composition of this so-called fly ash depends on the composition of the coal burnt, the most common components being SiO_2 , Al_2O_3 , Fe_2O_3 and CaO. These solids could start accumulating over time in the process equipment and can create a risk of clogging. They also contain toxic substances which can negatively impact the human body.²⁸ TATA steel has about 83 mg/m³ fly ash in their coke oven stack.²⁹ Although the coke oven gas is mixed with the blast furnace gas and converter gas, this concentration was assumed to be identical in the off-gas.

The remainder of the undefined one percent is assumed to consist mainly of a variety of hydrocarbons that originate from the fuel. They did not combust in the steel production process and are now left over in the gas. They are assumed to be unreactive and are neglected entirely from now on.³⁰

An overview of the contaminant concentrations, flow rates, and ELV values can be found in table 1. The ELV values for SO_3 and NO_2 are not precisely defined, as they are dependent on SO_2 and NO respectively.

Table 1: Contaminant Concentrations in the feed gas

Component	PPM by vol.	Vol.%	Flow rate in feed (m ³ /h) (25 °C)	Mol/h	EU emission limit value ³¹ (ELV) (ppm)
H₂S	3.00E+02	3.00E-02	3.56E+04	1.59E+00	
SO₂	3.00E+02	3.00E-02	3.56E+04	1.59E+06	1.24E+02
SO₃	1.50E+01	1.50E-03	1.78E+03	7.95E+04	
NO	3.00E+02	3.00E-02	3.56E+04	1.59E+06	1.51E+02
NO₂	1.50E+01	1.50E-03	1.78E+03	7.95E+04	
Dust	8.30E+01 (mg/m ³)		9.85E+01 (kg/h)		2.00E+01 (mg/m ³)

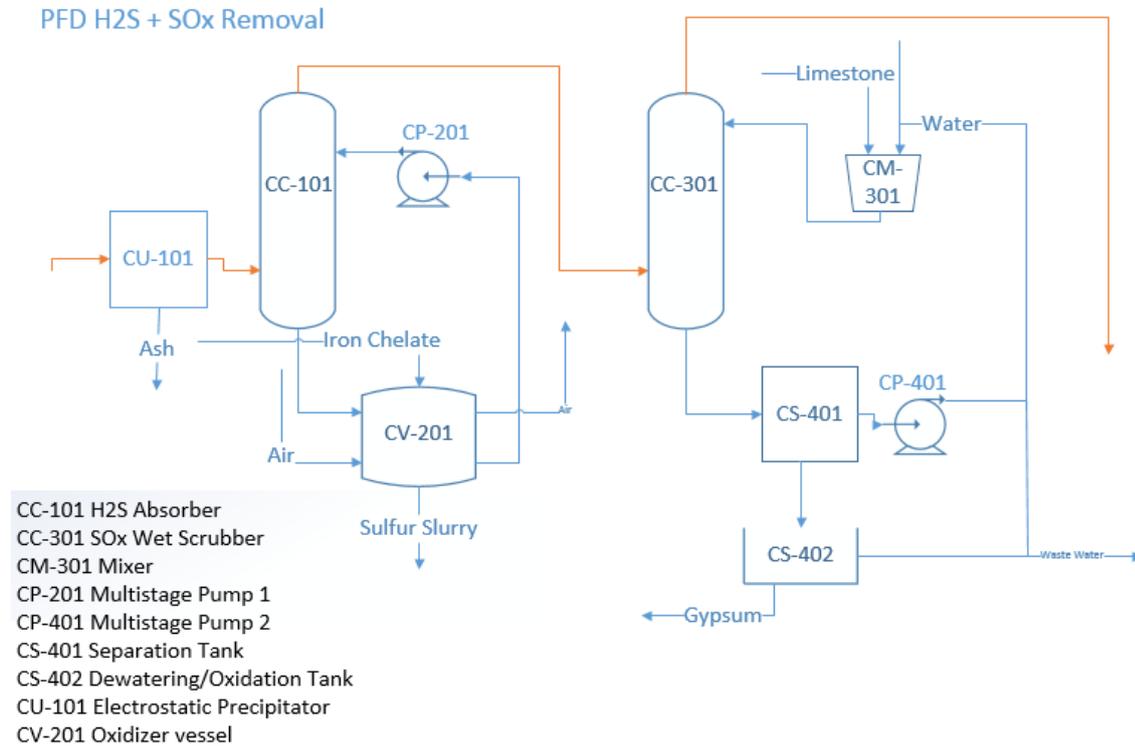


Figure 2: PFD Cleanup

2.1.2 Selected processes and equipment for contaminant removal

For each of the contaminants that needed to be removed for process specific reasons or for environmental regulations, the choice of process and equipment can be found below. The consecutive process order is also used here. The calculations for the cleanup flows were based on literature values (e.g. for conversion, stoichiometric ratios, operating conditions etc.) rather than on values from Aspen. Their impact on the main gas stream was minimal as the contaminants that were removed totaled to less than 0.1 vol% of the total flow and was therefore neglected. For the COSORB and Acetica processes however, quite reliable Aspen models were made.

Electrostatic precipitator (ESP) to remove particulate matter

An electrostatic precipitator was placed at the process inlet in order to get rid of particulate matter. The further upstream used wet scrubber can also remove solid particles, however, the ESP is able to remove effectively all particles down to 1 μm and even large portions of particles down to 0.05 μm .³² The precipitator first filters the largest particles. It subsequently ionizes the gas stream using high voltage and the free electrons created attach to the solid particles. These will then get stuck to the positively charged plates present in the precipitator. By vibration of the plates, the particles move down to be collected by a hopper.

Frequently, electrostatic precipitators are designed for an operating temperature of about 150 °C. One reason for this is that inlet gas streams are directly acquired from the plant they originate from and are still at elevated temperature. Another reason is that the electrical resistivity of coal-based fly ash is typically near the maximum at this temperature for low sulfur coals.³³ The inlet gas used in this process is unfortunately only 25 °C. Another article suggests that an operating temperature of 90 °C does not significantly decrease the ESP's efficiency in removing fly ash.³⁴ For the energy efficiency of the process it was therefore assumed that the ESP designed has an operating temperature of 90 °C and effectively achieved complete conversion. The obtained ash from the ESP, which is about 100 kg/h, can also be re-used for making concrete, bricks and

wallboards.³⁵ In combination with the gypsum from the SO_x limestone wet scrubber downstream, fly ash bricks can be made. This could reduce disposal costs for both the substances.

LO-CAT® process to remove H₂S

For the almost complete removal of hydrogen sulfide from the steel mill's off-gases the LO-CAT® process was used.³⁶ This process uses a catalytic iron chelate catalytic solution in order to convert H₂S to solid elemental sulfur by direct oxidation of H₂S. A chelant is a component that can form a coordination compound with metal ions. In this process, the chelant is nitrilotriacetic acid, or NTA. The liquid solution is inert to all the other gases in the inlet gas stream. A high conversion of 99.9% can be reached and the operating conditions are very mild with a temperature range of 20 to 60 °C and a pressure of 1 bar. The equipment consists of an absorber and an oxidizer. The reactions that take place in this process are listed in Table 2 below.

Table 2: Reaction overview LO-CAT system

#	Reaction ³⁶	Location
1	$\text{H}_2\text{S (g)} + \text{H}_2\text{O (l)} \leftrightarrow \text{H}_2\text{S (Aq)} + \text{H}_2\text{O (Aq)}$	Absorber
2	$\text{H}_2\text{S (Aq)} \leftrightarrow \text{H}^+ + \text{HS}^-$	Absorber
3	$\text{HS}^- + 2\text{Fe}^{+++} \rightarrow \text{S}^0 + 2\text{Fe}^{++} + \text{H}^+$	Absorber
4	$\text{O}_2 \text{ (g)} + 2\text{H}_2\text{O (l)} \leftrightarrow \text{O}_2 \text{ (Aq)} + 2\text{H}_2\text{O (Aq)}$	Oxidizer
5	$\text{O}_2 \text{ (Aq)} + 2\text{H}_2\text{O} + 4\text{Fe}^{++} \rightarrow 4 \text{OH}^- + 4\text{Fe}^{+++}$	Oxidizer

In the LO-CAT process, the incoming gas flow is introduced at the bottom of a liquid-vapor absorber vessel. The liquid flow is introduced at the top of the vessel, where after it meets the gas flow counter currently. The hydrogen sulfide is absorbed and ionized in the liquid phase, reactions one and two, and afterwards oxidized to elemental sulfur while the active ferric iron is reduced to the inactive ferrous state which resembles reaction three. Reaction three is very rapid while number one is relatively slow, making reaction one the rate determining step. The treated gas leaves the absorber at the top, where it continues to the sulfur oxide removal section. The liquid containing the elemental sulfur leaves the absorber at the bottom to continue to the oxidizer.

Reactions four and five occur in the oxidizer vessel. Oxidizing air is led through the vessel and the inactive iron is oxidized back to its active state. The oxidizer is designed not to contaminate the product gas stream with oxidizing air. Sulfur settles at the bottom section of the oxidizer where it is concentrated into slurry and led to a sulfur recovery system where after it can be sold.

The chelating agent, NTA, does not appear in any of the reactions but is nevertheless an important component in this process. It wraps the iron ions and keeps them in solution as they would otherwise precipitate to Fe(OH)₃ or FeS. The degradation of the chelating agent NTA itself is reduced by adding sodium thiosulphate.³⁷ Nevertheless, little amounts of iron can still precipitate even in the presence of a chelating agent. To compensate for the loss of reaction components new chemicals are added to the oxidizer to keep their concentration constant.

It was found that the absorption could achieve the highest efficiency at a molar ratio of Iron(III) to H₂S of 2 : 1 in the absorber itself³⁸ with an iron ion concentration of 10000 ppm.³⁷ The NTA chelant to iron ion molar ratio is optimal at 2 : 1.³⁷ The sodium thiosulphate added to reduce the degradation of the chelant itself was added as 10 mol% to NTA.³⁷ Almost the entire liquid flow is recycled as none of the chemicals are directly consumed. The chemical and utility price for LO-CAT was therefore based on literature that stated that the costs per pound of sulfur removed would be \$0.20 including new chemicals to be added and power consumption.³⁹ The resulting composition and flow of the LO-CAT solution fed to the absorber can be seen in Table 3 below. Aspen was used for the calculation of the mass flows. The process temperature and pressure were set at 25 °C and 1 bar.

Table 3: Composition and flows from LO-CAT system

Component	ppm	kmol/h required	Molar mass (g/mol)	Mass flow (kg/hr)
Water	9.68E+05	3.08E+05	1.80E+01	5.54E+06
Fe(III)	1.00E+04	3.18E+03	5.59E+01	1.78E+05
Chelant (NTA)	2.00E+04	6.36E+03	1.91E+02	1.22E+06
Sodium thiosulphate	2.00E+03	6.36E+02	1.58E+02	1.01E+05
Total	1.00E+06	3.18E+05	2.22E+01	7.04E+06

Wet limestone scrubbing to remove SO_x

The next contaminants to be treated are the sulfur oxides. For their removal the wet limestone scrubber process was selected as most suitable as it has several advantages. First of all, it treats both SO₂ and SO₃. The operating conditions are mild with a temperature of anywhere between 5 and 80 °C at a pressure of 1 bar. Limestone and water are relatively cheap and also a high conversion of up to 97% is possible. The conversion is based on the liquid to gas (L/G) ratio that uses the units of gallons per 1000 actual cubic feet or liters/cubic meter. The higher the conversion, the more water is used that will need to be treated before it can be disposed.⁴⁰

The most important piece of equipment is the wet scrubber, where the liquid slurry is sprinkled over the gas. The liquid then continues to a separator tank where the heavy slurry is separated from the lighter water and limestone that are recycled. The reactions can be found in Table 4 below. The reactions for SO₃ are similar.

Table 4: Reactions in Wet Scrubber

#	Reaction ⁴¹	Location
1	$\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{++} + \text{HCO}_3^- + \text{OH}^-$	Wet scrubber
2	$\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+$	Wet scrubber
3	$\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O}$	Wet scrubber
4	$\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}_2\text{O} + \text{CO}_2$	Wet scrubber
5	$\text{CaCO}_3 + 2 \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{++} + \text{CO}_2 + 2 \text{HSO}_3^-$	Wet scrubber
6	$\text{CaCO}_3 (\text{s}) + 2 \text{HSO}_3^- + \text{Ca}^{2+} + \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 2\text{H}_2\text{O} (\text{s}) + \text{CO}_2$	Wet scrubber
7	$2 \text{CaSO}_3 \cdot 2\text{H}_2\text{O} (\text{s}) + \text{O}_2 \rightarrow 2 \text{CaSO}_4 \cdot 2\text{H}_2\text{O} (\text{s})$	Dewatering tank

In reaction one, limestone (CaCO₃), creates an alkaline environment in water. This cancels out the acidity formed by the dissolved SO₂ and is resembled by reaction two and three. The HCO₃⁻ and H⁺ form an equilibrium with H₂CO₃ which forms an equilibrium itself with water and carbon dioxide, reaction four. The overall result is reaction number five. In reaction six more limestone reacts with HSO₃⁻, Ca²⁺ and water to CaSO₃·2H₂O, which is a solid that precipitates. In both reactions five and six, carbon monoxide leaves the solution as a gas. Reaction seven shows the oxidation of calcium sulfate dihydrate to calcium sulfate dihydrate, also known as gypsum. The fact that SO₂ dissolved in the liquid directly reacts to bisulfite makes room for more SO₂ to be dissolved in the liquid. This has a large positive effect on the amount of sulfur oxides able to dissolve in the liquid simultaneously.

The focus for this process design is on the wet scrubber as for the surrounding equipment assumptions were made. An efficiency of 80% was chosen to be sufficient, as the wet scrubber then only uses 4.01 L/m³ of limestone water slurry. This compares to water flows almost five times as large to achieve 97% sulfur oxide removal.^{40,42} This flow is defined as the incoming liquid

flow of the wet scrubber. The stoichiometric ratio in the scrubber is 1.2 based upon inlet SO_x .⁴² A large part of the water flow is recycled with a purge of about 16%.⁴² It was assumed the price as if the flow consisted entirely of fresh water would be comparable to the price to clean the contaminated purge. The price for the gypsum sold was also neglected as these streams and prices are negligibly small compared to those the CO purification and acetic acid production. The resulting composition and flow of the solution fed to the wet scrubber can be seen in Table 5 below. Aspen was used for the calculation of the mass flows. The process temperature and pressure were set at 25 °C and 1 bar.

Table 5: Composition and flow of flow to wet scrubber

Component	kmol/hr required	Molar mass (g/mol)	Mass flow (kg/hr)
Water	2.64E+05	1.80E+01	4.76E+06
Limestone (CaCO ₃)	2.00E+03	1.00E+02	2.00E+05
Total	2.66E+05	1.86E+01	4.96E+06

SNCR (in incinerator) to remove NO_x

Selective Non-Catalytic Reduction is a widely used technique to reduce the amount of nitrogen oxides in off-gases. The process involves the injection of ammonia onto the firebox of the incinerator at a point where the gas has a temperature of between 760 and 1090 °C. The ammonia reacts with the nitrogen oxides to molecular nitrogen and water.

For a conversion of 90%, the molar ratio of NH_3 to NO_x has an optimum at a value of 1.5 to 1. A lower ratio decreases the conversion and a higher value sharply increases the concentration of NH_3 in the outlet gas.⁴³ The reactions can be found in Table 6 below and are self-explanatory. The ammonia mole flow is based on the molar ratio used and the number of moles of NO_x in the gas and can be found in Table 7 below.

Table 6: Reactions in SNCR system

#	Reaction ⁴⁴	Location
1	$4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$	Incinerator
2	$2 \text{NO}_2 + 4 \text{NH}_3 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$	Incinerator

Table 7: calculation of Ammonia flow

Component	kmol/hr required	Molar mass (g/mol)	Mass flow (kg/hr)
Ammonia	2.50E+03	1.70E+01	4.26E+04

2.1.3 COSORB process

The process chosen for the purification of carbon monoxide is a process known as COSORB™.¹⁵ Tenneco developed the process in the late seventies. It was later sold to Kinetics Technology International. Through the years improvements have been made to increase the yield and purity of the obtained carbon monoxide concentration as well as improvements on the lifetime of the COSORB™ absorption solution.

The most important equipment used in the process are an absorber and a stripper. In the absorber, the carbon monoxide is purified by temporally trapping it with a COSORB™ solution consisting of toluene which contains a cuprous aluminum chloride complex (CuAlCl_4). The COSORB™ solution is then transferred via pumps to the stripper, where the carbon monoxide is released from the copper complex upon heating the solution. Other important techniques used are drying - and solvent recovery. Aspen plus was used for modeling the COSORB™ process. The base method used is the NRTL-RK method. The most important information gathered about the

process are the stream sizes and information regarding duties used in the heat exchangers, pumps and compressors.

The major benefits of this process over other commercially available processes, such as cryogenic separation and pressure swing absorption (PSA), are the lower running- and investment costs and the capability to remove carbon monoxide from feed gasses that contain relatively large fractions of hydrogen, carbon dioxide, nitrogen and methane.⁴⁵ This is not possible with cryogenic separation without pretreatment, due to similar boiling points of molecular nitrogen and carbon monoxide. The COSORB™ process can operate under mild pressures and temperatures, thus resulting in lower electricity costs. Building costs will also be lower as the vessels and piping do not need to be as strong as with processes like PSA. Ordinary carbon steel can be used for the piping, columns and vessels, due to the non-corrosive character of the solvent. This further reduces the investment costs. The COSORB™ process can typically achieve yields and purities of respectively 98% and 99%.¹⁴ This enables the acetic acid production to be more efficient.

However, the process has been criticized for its major drawbacks and challenges, such as loss of solvent, degradation of the cuprous aluminum chloride complex due to impurities and solid buildup in the reboiler of the stripper column. To reduce the loss of solvent, the toluene that naturally evaporates in the absorption - and stripping tower is cooled down to -50°C. The toluene condenses and is recycled to the main inlet stream. Contaminants such as SO₂ and SO₃ are removed in the cleaning part of the purification. Furthermore, water is removed in a dryer before the gas enters the absorber. By removing the impurities and water, longer cuprous aluminum chloride complex lifetimes can be achieved. It was assumed that the cleanup section of the plant, cleans the gas in a sufficient manner that no side reactions would occur. Self-cleaning reboilers could be used to remove the particles that build up in the stripper reboiler and reduce the effects of fouling.⁴⁶ An overview of the PFD of COSORB™ can be seen in figure 3.

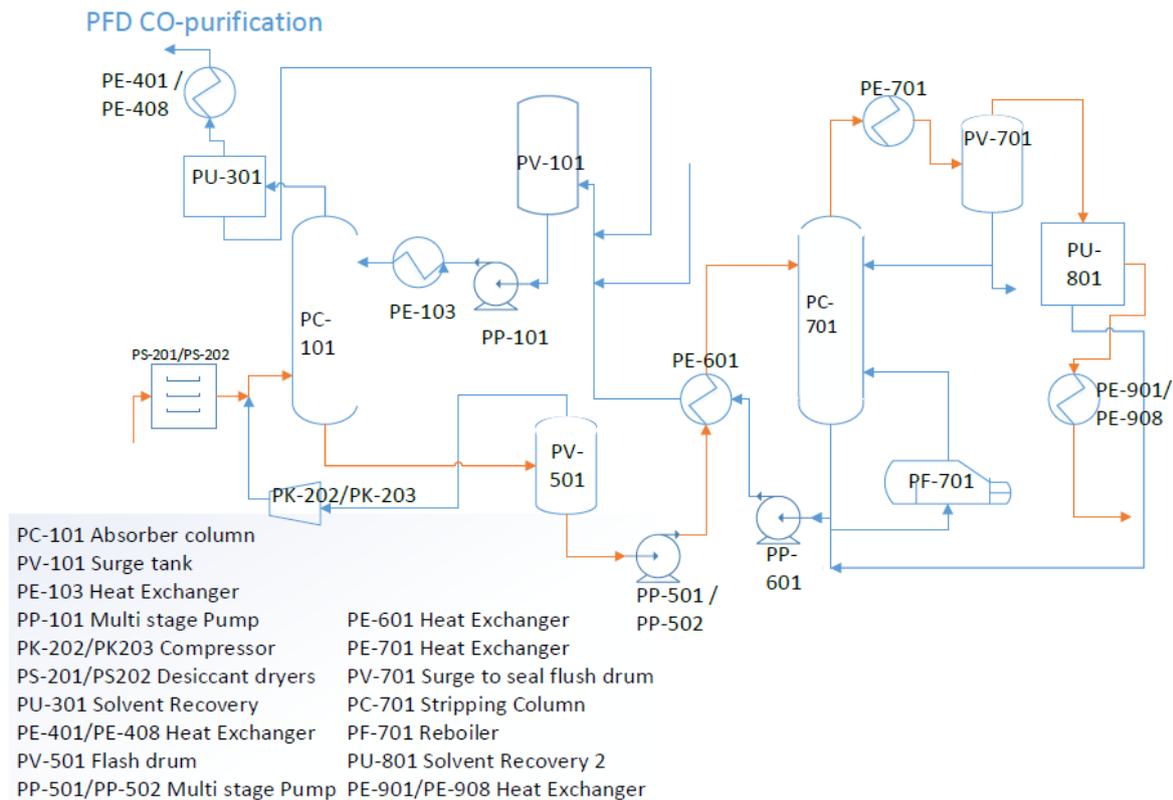


Figure 3: PFD COSORB™

2.1.4 Dryer

Before carbon monoxide can be separated from the cleaned off-gas stream, it must be dried in a dryer. This needs to be done to prevent water from damaging the cuprous aluminum chloride complex by irreversibly reacting with it. The goal of this dryer is to reduce the water level to ppm scale, while retaining all other compounds in the gas. The dryer chosen for this process is an externally heated regenerative dryer. It consists of two dryer vessels filled with layers of activated alumina desiccant. Only one of the two drying vessels is operational at any time. The other column is being regenerated by forcing hot nitrogen purge gas through the layers of activated alumina desiccant under sufficient pressures. The use of two vessels allows continuous drying of the CO containing gas. Besides water, also oxygen is harmful for the cuprous complex and reduces its lifetime. Therefore, nitrogen gas is used as purge gas instead of air for regeneration because oxygen molecules from the air could remain in the vessel. This would then end up in the main gas stream when the vessel is used for drying.

2.1.5 Absorbers (PC-101 and CO-ABS)

In order for carbon monoxide to be separated from the other gasses it needs to be absorbed. This is done by passing carbon monoxide containing gas past toluene, containing cuprous aluminum chloride. Depending on the ratio of mixing of the two compounds, the cuprous aluminum chloride will either be surrounded by one or two toluene molecules. The copper salt can dissolve a maximum of 1 mole of carbon monoxide per mole of CuAlCl_4 complex.¹⁴ This complex formation is exothermic, with a heat of formation, of -6.8kJ/mol .⁴⁷ All other gasses are inert with the complex. Therefore, a possible overall reaction can be written as in Equation 8. No data on the kinetics for the conditions used were available, so the amount of toluene needed was calculated from equilibrium data.



The equilibrium concentration of $\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}$ varies with temperature, partial pressure of CO and is proportional to the concentrations of CuAlCl_4 dissolved in toluene. For the absorption process a pressure of 3 bar was chosen at a temperature of 25°C . By increasing the pressure in the column to 3 bar, the concentration of CO in the gas phase becomes $40\text{ mol}\cdot\text{m}^{-3}$. It is assumed that the feed gas behaves as an ideal gas. From literature, it is known that at this concentration and temperature, 1.7 M CuAlCl_4 forms a complex with 1.2 M CO to form 1.2 M $\text{CuAlCl}_4 \cdot \text{tol} \cdot \text{CO}$ in equilibrium.¹⁴ This means that in order for all the CO to react, when the reaction reaches equilibrium, the mole ratio of CuAlCl_4 :CO must be 1.42:1. To have a 1.7 M CuAlCl_4 solution with toluene, the CuAlCl_4 :toluene molar ratio should be 1:5.54. This means that for every mole carbon monoxide in the feed gas, 1.42 mole of CuAlCl_4 and 7.86 mole toluene should be added.

Next the absorption column was modeled in Aspen. Aspen did not have the CuAlCl_4 component in its library. Therefore, the actual reaction of CO with $\text{CuAlCl}_4 \cdot \text{tol}_2$ could not be modelled. Despite this, still some useful information could be obtained from the Aspen model. To achieve this, the absorption column was actually modeled as two separate columns with two different functions. The pressure and temperature of the modeled columns are equal to the earlier stated equilibrium conditions. The first column, called PC-101, is modeled to give an impression of the amount of toluene that would evaporate in the actual absorption column and the amount of gasses that dissolve naturally in toluene.

The inlet toluene flow of the absorber was based on the inlet CO mole flow and the equilibrium ratio of toluene to CO that was stated above. From this ratio, it can be calculated that the toluene flow in the model should be about 198281 l/min ($=112123\text{ kmol/hr}$). Notice that this does not mean that this amount of toluene is added to the COSORB™ plant every hour. As it is the amount of toluene that has to enter the absorber, it consists almost completely of toluene pumped back from the stripper and a small amount of fresh toluene added to compensate for any losses. Both the feed gas and toluene are at 25°C and 3 bar. The feed gas and toluene flow counter currently through the column, resulting in the desired evaporation and natural absorption.

The gas leaving PC-101 is separated into two flows; toluene gas and the bulk of the gasses that did not dissolve in toluene, called GASABSIN. This is fed to column CO-ABS. The toluene gas is brought to the solvent recovery. The bottom flow of PC-101 is fed to a flash column, here some of the absorbed gasses at 3 bar are desorbed at a lower pressure of 1 bar. The gasses flow back to the PC-101 column to recycle them. All the liquid toluene, still containing some absorbed gasses, is brought back to 3 bar and fed to the CO-ABS column. The CO-ABS column thus receives all the gasses that did not dissolve in toluene and all the toluene that is still in the liquid phase besides some absorbed gasses. The function of the CO-ABS column is to mimic the actual reaction by forcing 99% of the CO in the gas phase to the toluene liquid phase, so in Aspen it is actually just a separator. Also, all the earlier naturally absorbed gasses are forced to stay with the toluene flow. This liquid flow, called CO+TOL is fed to the stripper.

To model the absorber, two assumptions were made. The first is that in the real column all the liquid toluene with approximately 1.7 M CuAlCl_4 will remove 99% of the CO mole from the non-absorbed gas feed according to the earlier stated ratio, and will thus almost reach equilibrium. This means that effort should be put in to maximize the CO flux from the gas - to the liquid phase, so that equilibrium concentrations can be reached. This is done by maximizing the contact area of the gas and liquid phase. Moreover, the operating temperature should be quite low and the pressure should be slightly increased. The assumption that equilibrium is reached is probably justified as the chosen conditions and concentrations of the column mimic the equilibrium conditions of the literature. The gas flow going up will have a lower concentration near the top of the column. However, the gas concentration of CO in the gas phase in the column near the gas feed inlet is expected to stay at 40 mol/m^3 , as this is continuously fed with new gas feed with this concentration. Therefore, the conditions at the bottom of the column are expected to stay at equilibrium condition. Several companies state that yields of 99% were achieved, implying that the 99% removal of CO is accurate.¹⁵

Additionally, it was assumed that dissolved gasses in toluene do not influence the capability of the COSORB solution to reach to the CuAlCl_4 .tol.CO equilibrium concentration. This is probably justified as CuAlCl_4 has a very high selectivity for CO. The mole balances from Aspen over both columns, including the solvent recovery can be found in Appendix 48. A mole balance, with CuAlCl_4 added to the toluene inlet flow, was made in excel to give an idea what mole flows should be expected with regard to the expected reaction equilibrium in the actual column in Appendix 49. The overall balances can be found in the 'BalancesFinal' excel file.

From this data, it can be seen that the in - and outgoing gas flows in both tables are very similar. These should be quite similar to the actual process. The big differences are the liquid flows. The second table shows that when the CuAlCl_4 is added to the toluene stream, some of the toluene forms a complex with the copper salt. This is based on an complex ratio of CuAlCl_4 :toluene of 1:2,¹⁴ leaving less unbound toluene in the feed. By having less free toluene, also less gas would be absorbed naturally. Because the amount of naturally absorbed gas is very small in comparison with the main flows, this was ignored in Aspen. Another shortcoming of this model is that the densities of the liquid flows are different than the actual flows with the copper salt added to it, especially for the CO+TOL flow in Aspen. It consisted of a toluene flow with CO forced into it. This is clearly not realistic compared to the real flow of carbon monoxide bound with CuAlCl_4 . The density that Aspen shows for this stream is 54.8 kg/m^3 , because a fraction of the CO is in the gas phase.

Besides this, efforts were done to validate the calculations performed with the density from Aspen. From literature data the following equation was used to calculate the density of the COSORBTM solution; $\rho = 866.4 + 0.1561 \cdot [\text{CuAlCl}_4 \cdot \text{tol}_2]_0$ ¹⁴. Where ρ is in mol.m^{-3} . It was calculated that the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration is about 1700 mol.m^{-3} . To calculate the density in kg.m^{-3} , 866.4 was multiplied by the molar mass of toluene ($=0.92\text{E-}01 \text{ kg.mol}^{-3}$). 0.1561 was multiplied by the $\text{CuAlCl}_4 \cdot \text{tol}_2$ concentration and molar mass of $\text{CuAlCl}_4 \cdot \text{tol}_2$ ($=0.416 \text{ kg.mol}^{-3}$). Using this method, the density calculated resulted in about 190 kg.m^{-3} . This value is about 4.5 time lower than the density of toluene alone, this seems very unrealistic. Therefore calculations were still based on densities from AspenTM and validations by literature data could not be done. The calculations with respect to density of the liquid phase are thus expected to be less accurate.

Because the actual reaction was not modeled, heat of formations in the absorber due to complex formation was also not taken into account. As the formation is exothermic, some heat will be produced in the absorber.⁴⁷ This amount is quite low and will only increase the temperature of the gasses and fluids in the column with 3°C . It was not taken into account for the Aspen model. Despite these inaccuracies of the modeled absorber, it still gives an impression of what toluene flows to expect. Because liquid flows in the actual process are largely toluene, the Aspen model

can still be useful to indicate what sizes of equipment to expect. Furthermore, duties that are used in the heating, cooling and pumping equipment can be calculated quite accurately from this model.

2.1.6 Solvent Recovery

Because of natural evaporation in the absorber and evaporation of toluene in the reboiler of the stripper, solvent recoveries were implemented in the Aspen model. The recoveries consist of a cooler followed by a flash column. The first solvent recovery is placed on the toluene gas flow of the absorber. This is the heat exchanger PE-301 and flash column PV-301. The other solvent recovery is placed on the CO gas leaving the stripper. This consists of the heat exchanger PE-801 and flash column PV-801. To condensate a large fraction of the toluene, the heat exchangers cooled to -50 °C at 1 bar. By doing so, the toluene that is still in the gas phase is reduced to a toluene flow 745 kg/hr for both solvent recoveries. In Aspen, this flow is called TOLLOST and leaves the factory. The liquid toluene from both solvent recoveries is fed to the main toluene flow, coming from the stripper. This is then used again in the absorber.

2.1.7 Vessel PV-101

Vessel PV-101 is actually a surge tank in the COSORB™ process. The function of this tank is to reduce the pressure differences that can occur, due to flow velocity changes in the toluene flow. The toluene flow in the system is closed. So when at some point in the system a pump will fail, the momentum of the flow has to be reduced in order to avoid high pressure build up in the piping.⁴⁸ This is done by using the momentum of the flow to rise the toluene level inside the tank. This way the momentum is “absorbed” in the tank. The overall benefit of the tank is that it makes the process safer in case of a pump failure, by reducing the chance of leakage due to lower pressure buildup. The tank should have a movable roof that follows the level of toluene inside the tank, to prevent evaporation from toluene. No accurate calculations were performed on its size, but it should be able to contain at least the amount of toluene that is circulating in the system.

2.1.8 Heat Integration

To reduce the total amount of heat required in the COSORB™ plant, at some point heat integration was implemented. The biggest opportunity for this lay in counter current shell-and-tube heat exchanger, called PE-601, between the absorber and the stripper. In this heat exchanger, hot toluene fluid coming from mainly the stripper liquid outlet is flown counter currently past the colder toluene flow from the absorber. This saves energy is two ways, the first is that the toluene, TOL+CO flow, going to the stripper is pre-heated to almost the reboiling temperature of the stripper. The second is that it also saves energy by cooling toluene from the stripper to nearly the temperature that is required to maintain equilibrium conditions in the column. A significant amount of duty needed could be recovered via this construction.

Besides this heat integration, other areas were examined for their capability to integrate duties. Three streams were found to have potential to save energy in the system, especially the cold flows coming from the solvent recoveries seemed promising. All the heat values were based on data from the Aspen model of the COSORB™ process. Before the feed gas enters the first absorption column it was compressed to 3 bars. By doing so the temperature of the stream was increased to 166 °C. Before this gas enters the absorber, it must be cooled back to the equilibrium temperature of 25 °C. This is done by using the cold gas streams exiting the solvent recoveries (PU-301 and PU-801). Both these flows are at -50 °C, when leaving the flash columns. These cold streams are used in heat exchangers PE-205 and PE-206 to cool down the aforementioned feed gas into the absorber. This resulted in a temperature decrease of 72°C.

Another stream that was cooled by using heat integration is the gas stream leaving the stripper column. This gas is at 63 °C when leaving the column. As mentioned before, the stream then goes through a heat exchanger and a flash column, which make up the solvent recovery (PU-801). To cool this flow down before the heat exchanger of the solvent recovery, it was first cooled by the

cold toluene flow leaving the same solvent recovery unit, as seen in the Appendix 24. This made the process more efficient in two ways. First, it reduced the amount of heat that was needed to cool down the gas leaving the stripper as mentioned before. It also increased the temperature of the cold toluene before it is fed to the main toluene flow leaving the bottom of the stripper. The reason this is favorable is that this toluene flow is used to give off heat to the incoming colder toluene flow, as mentioned in the first paragraph of the heat integration section. By increasing the temperature difference between the two toluene flows of the PE-601 heat exchanger, even more heat could be transferred to the toluene flow to the stripper.

After it was known how much heat could be recovered by heat integration, effort was put into designing an ethanol cooling flow. Ethanol was used for the cooling flows as this is relatively cheap and still has a low viscosity at temperature around -80°C . The goal was to use cold ethanol from the COSORBTM process that already received heat from the process, to cool down flows of other processes such as the AcitecaTM - and dust removal process, i.e. electrostatic precipitator. Especially finding the right sequence for the ethanol to cool the flow streams proved to be challenging. This is due to the fact that a heat exchanger cannot cool the hot inlet flow any further than to the temperature of the incoming cold flow. Therefore, when the ethanol is already heated above the temperature of the desired outgoing hot flow in the next heat exchanger, the desired heat transfer cannot be achieved. In Aspen an ethanol cooling flow was made successfully. By combining the several cooling streams into one cooling flow, the process was made more efficient.

The cooling ethanol flow starts its cycle at heat exchanger PE-310. This cools down the ethanol coming from the heat exchangers CE-102 and RE-104, from respectively the cleanup- and AcitecaTM process. The flow is then split into two flows; one going through the COSORBTM process to the cleanup - and AcitecaTM section, the other to the AcitecaTM process directly. Here the ethanol takes up heat from hot streams in these processes. The now warmed up ethanol is fed to the heat exchanger where it is cooled again, thus completing the cycle. The information about the flows can be found in the Appendix 45. A detailed model of the actual ethanol cooling flows can be found in the aspen model of the COSORBTM- and AcitecaTM process.

Another reason for the use of an ethanol stream for the cooling in the process, is that the sizing could be made more accurate. This is because Aspen does not give densities and flows of the refrigerant when using a simple heater. When using a process exchanger in Aspen, velocities and pressure drops on both the tube- and shell side could be calculated as explained in the sizing of heat exchangers section, 3.1.2.

2.2 Reaction section

The methanol feed stream used in the AcitecaTM process is purchased commercially. Technical grade methanol is used, which means that it contains 5 vol% water. Since the AcitecaTM process operates at a water content of maximum 8 wt%, most of which is formed in the reaction, the water content in the methanol feed should not cause any problems. Technical grade methanol is significantly cheaper than pure methanol, making it a better choice. It is assumed that water is the only impurity present in the methanol. The amount of methanol is chosen such that carbon monoxide is fed with an excess of 40%. In literature, it was found that CO always has to be present at high partial pressure, so it is generally the excess reagent. This excess has to be enlarged for less pure CO feed-streams.⁸ Additionally, the CO is obtained for free, while the methanol costs are relatively high. Therefore, it is beneficial to attempt to achieve a methanol conversion that is as high as possible.

2.2.1 Reactor

A bubble-column reactor is chosen in the AcitecaTM process for its excellent three-phase contacting, thus minimizing loss of catalyst activity.⁸ Both reactant feed streams are introduced at the bottom of the reactor, along with a recycle liquid stream. These streams flow up the riser

section of the reactor, where most of the CO is converted in the carbonylation. The density difference between the CO-rich riser and the CO-depleted downcomer drives reactor circulation, thus eliminating the need for a moving impeller to ensure mixing. At the top of the reactor, off gas is vented from the reaction mixture. The low purity product is passed through a filter to prevent catalyst loss and sent to downstream purification. The remaining reaction slurry is cooled and returned to the bottom of the reactor to maintain circulation and absorb the large heat of reaction.

Due to insufficient kinetics information and the irreversibility of the catalysed reaction,⁴⁹ the Aspen Plus RStoic reactor at 180°C and 60 bar is used to model the bubble column reactor. The fractional conversions of all defined reactions are tweaked such that the outlet concentration of all reactants and products are approximately in the ranges as found from literature. An overview of all defined reactions and their fractional conversions can be found in Table 8. Additionally, the outlet concentrations of all compounds and their literature values are shown in Table 9. The outlet stream is split into a gas and liquid stream using a two-outlet flash at 0 kW duty and 0 bar pressure drop, thus imitating a reactor with both a vapour- and liquid outlet stream.

It can be seen that, compared to the amount of acetic acid formed, 100.93 % CO has reacted. This means that 0.93 % of this feedstock reacts to side products. For methanol, only 0.79 % reacted to side products. Both these values are less than 1 %, thus meeting one of the characteristics of the Acetica™ Process. Conversely, the water content in the reactor is slightly higher than the specified range. In an earlier model, the water content remained perfectly below 8%. However, when the column reflux- and boil-up ratios were edited to obtain reasonable column dimensions, the final water content increased. A change in the resulting recycle streams probably caused more water to enter the reactor. Since all column- and reactor sizes were already calculated based on the final streams, it was not considered feasible to attempt to obtain a lower water content in the Aspen reactor model.

An option to lower the water content would be to distil out the water added via the methanol feed stream. However, this process is quite costly. Most aforementioned processes using the methanol carbonylation reaction other than the Acetica™ process operate at higher water content, implying that the reaction is not hindered by the presence of water. The main disadvantage of a higher water content is the possible formation of more side-products. However, the final product obtained in the designed process is of very high purity. Additionally, it was seen during the manufacturing of the model that a lower water content could easily be generated by disposing more of the bottom recycle streams in the purge. However, this was considered unfeasible since it would mean that all the sizing calculations would have to be redone.

In the Acetica™ process, CH₃I promotor is used to form acetic acid according to Eq. 9-11.⁸ Combining the reactions in Equation 2-4 while assuming no accumulation of any of the iodide species gives Equation 1, which is implemented in the Aspen Plus model. In this model, the involvement of CH₃I and HI is thus ignored, since it is mostly confined to the reactor. All CH₃I and HI leaving the reactor will immediately be returned via the two absorbers, thus eliminating the need for their explicit modelling. Any CH₃COOI formed will instantly be converted to acetic acid, thus this reaction can also safely be left out of the Aspen model. Ignoring these compounds simplifies the model drastically, which makes it more stable and controllable.

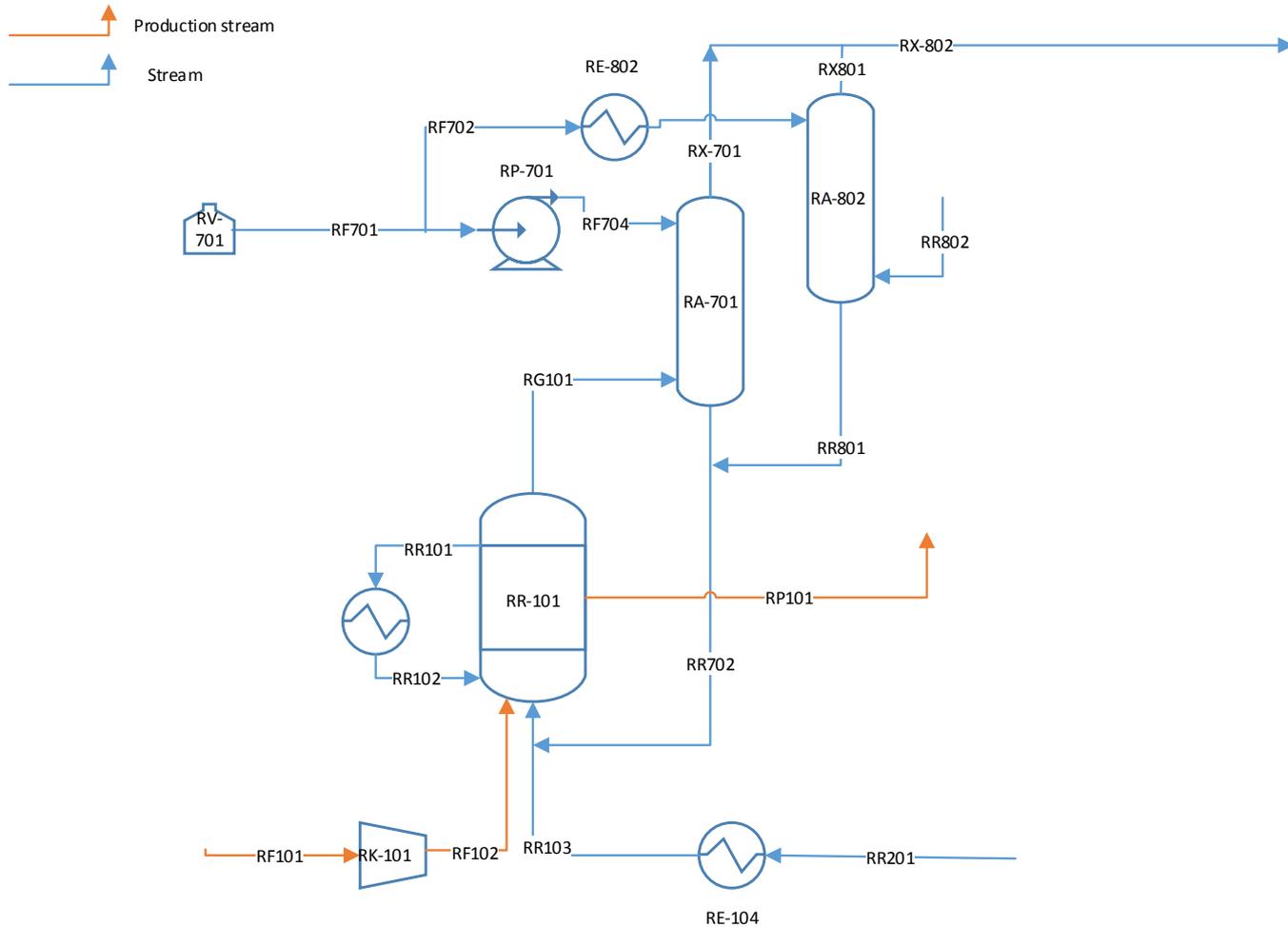


Table 8: Reactions and fractional conversions as specified in RStoic

Reaction	Fractional Conversion (%)	Of component
$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$	98.5	CH_3OH
$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$	0.100	CH_3OH
$2 \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{OCH}_3$	0.100	CH_3OH
$\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2$	0.500	CO
$\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	0.300	CH_3OH
$2 \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$	0.300	CH_3OH
$\text{H}_2\text{O} + \text{CH}_3\text{OCH}_3 \rightarrow 2 \text{CH}_3\text{OH}$	1.00	CH_3OCH_3
$\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$	20.0	$\text{CH}_3\text{COOCH}_3$

Table 9: Outlet conditions in the product mixture stream (RPMIX) that contains the mixture of products from the reactor.

Component	Mole fraction (%)	Mass Fraction (%)	Moles formed relative to AA (%)	Literature range ⁶⁻⁸
CH_3COOH	5.25E+01	7.39E+01	1.00E+02	99% final yield from CH_3OH
$\text{CH}_3\text{COOCH}_3$	1.00E-02	1.60E-01	4.00E-02	
H_2O	2.71E+01	1.15E+01	-1.90E-01	3-8 wt% in reactor
CH_3OCH_3	1.10E-01	1.10E-01	5.00E-02	
$\text{CH}_3\text{CH}_2\text{COOH}$	5.00E-02	9.00E-02	1.50E-01	<0.16 mole% relative to AA
CH_3OH	2.20E-01	1.60E-01	-1.01E+02	
CO	1.29E+01	8.47E+00	-1.01E+02	
CH_4	1.55E+00	5.80E-01	3.10E-01	<1% loss of CO and CH_3OH
H_2	3.20E-01	1.00E-02	4.30E-01	<1% loss of CO and CH_3OH
N_2	6.20E-01	4.10E-01	0.00E+00	-
CO_2	4.47E+00	4.61E+00	7.40E-01	<1% loss of CO and CH_3OH

Process Flow DiagramProduction of Acetic Acid (AA)
Reactor and absorbers**Legend**

RA-701 High Pressure Absorber
 RA-802 Low Pressure Absorber
 RK-101 Multistage Compressor
 RP-701 Hydraulic pump
 RR-101 Bubble-Column Reactor
 RE-802 Heat Exchanger
 RE-104 Heat Exchanger
 RV-701 Methanol drum

Figure 2: PFD of Reactor and Absorbers

2.2.2 Absorbers

The methanol feed stream is split and fed to two counter current absorber columns, to maximize the recovery of methyl acetate and methyl iodide. In a high-pressure absorber at 60 bar, the first part of the methanol is contacted with the reactor off-gas. The rest of the methanol is contacted with light gases from the purification columns in a low-pressure absorber at 1 bar. The streams exiting the bottom of the absorbers are recombined with the recycle stream and charged to the bottom of the reactor. This way, no valuable by-products are lost via the vent gas. The two absorbers in Aspen mainly serve to recharge methyl acetate and dimethyl ether to the reactor.

In modelling these two absorbers, the literature PFD was followed as closely as possible to make sure that the bottom products would contain most of the methyl acetate and dimethyl ether. In Aspen this was readily achieved, although problems arose at the top products: a lot of methyl iodide, unreacted methanol and acetic acid was thrown away via these gaseous streams. After

failing to specify the columns to get more of these precious materials in the bottom stream, methyl iodide was left out of the model. Now, the top product consists mainly of waste gases, almost no methyl acetate, dimethyl ether or acetic acid. Some methanol remains, but this is less than 1% of the total methanol feed.

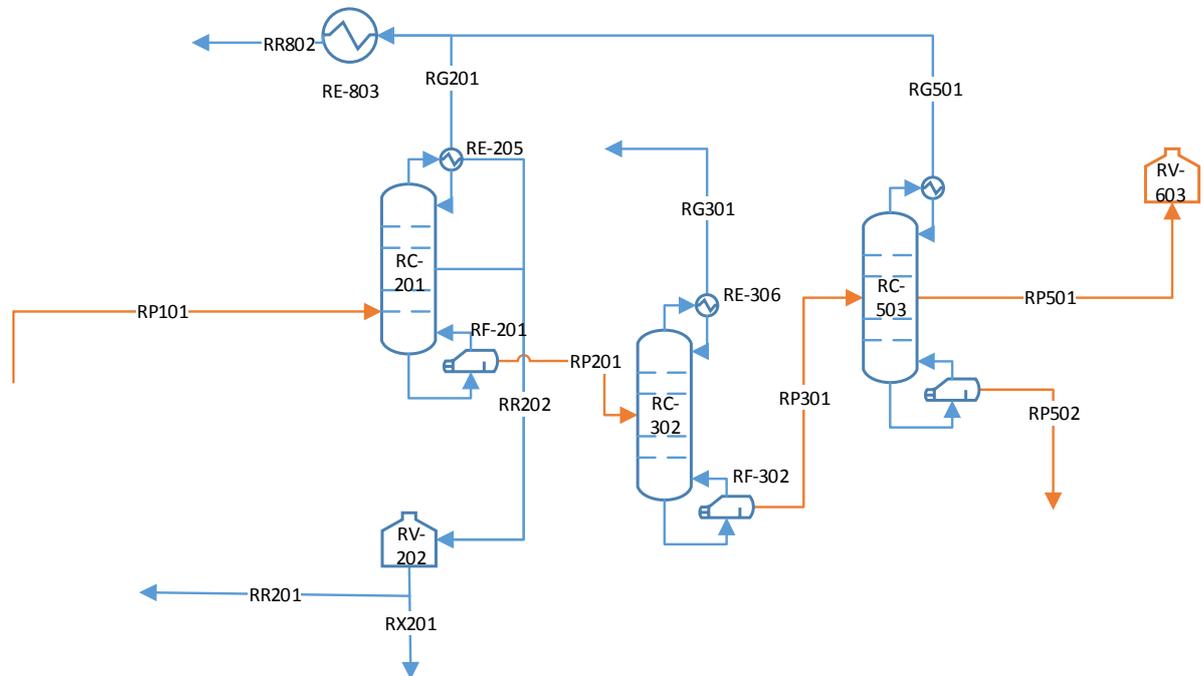
2.2.3 Flush Column (C1)

The liquid reaction product is sent to a flush column, where the crude acetic acid is separated from the dissolved gases. The gas stream exiting the overhead vaporizer contains mainly CO and CO₂ and is led to the low-pressure absorber. The lighter liquids from the overhead condenser are combined with a liquid side stream from the top of the column and sent to the recycle surge drum. The crude acetic acid exiting the bottom of the flush column is completely free from light gases and is sent to the first dehydration column. The flush column operates at 40 bar and a condenser temperature of 120°C and was designed for maximum acetic acid recovery.

2.2.4 Dehydration Column (C2)

The acetic acid product from the bottom of the flush column enters the bottom of the dehydration column, which operates at 3 bar pressure and subcooled reflux and liquid distillate. The column removes 98.9 mole% pure water at its vapour outlet, hereby reducing the water content of the acetic acid product by 50%. The column specifications have been defined to ensure maximum water purity in the vapour, such that this stream can be discarded rather than recycled. In the literature PFD, a third outlet stream is defined that is connected to the recycle surge drum. Since the desired purity could also be reached without defining this stream, it was left out of the Aspen model.

The water vapour outlet (RG301) can be led to a biological water treatment unit. The main impurities in the stream are methanol, methyl acetate, dimethyl ether and some acetic acid. These can all be removed via either anaerobic or aerobic fermentation processes. This method is commonly known as an activated sludge process and is often used in wastewater treatment.⁵⁰ The same procedure can be applied to the waste stream exiting the purge of the bottom recycle surge drum (RX201). This stream contains more contaminants than RG301 (~10% non-water), but it should still be possible to clean it via biological treatment, since the impurities are mainly CO₂, methanol and some methyl acetate. RX201 exits at a pressure of 40 bar and 198°C, so if the temperature- and pressure drop over the connecting pipeline is not sufficient, the stream should be depressurized and cooled before entering the bio-treatment unit.

Process Flow DiagramProduction of Acetic Acid (AA)
RC-201, RC-302 and RC-503**Legend**

RC-201 Flush Column
 RC-302 Dehydration Column
 RC-503 Finishing Column
 RV-202: Collecting Drum
 RV-603: AA Drum
 RF-201 Reboiler RC-201
 RF-302 Reboiler RC-302
 RF-503 Reboiler RC-503
 RE-803 Heat Exchanger
 RE-205 Condenser RC-201
 RE-306 Condenser RC-302
 RE-507 Condenser RC

Figure 3: PFD of first three columns (C1, C2 and C3)

2.2.5 Finishing Columns (C3, C4 & C5)

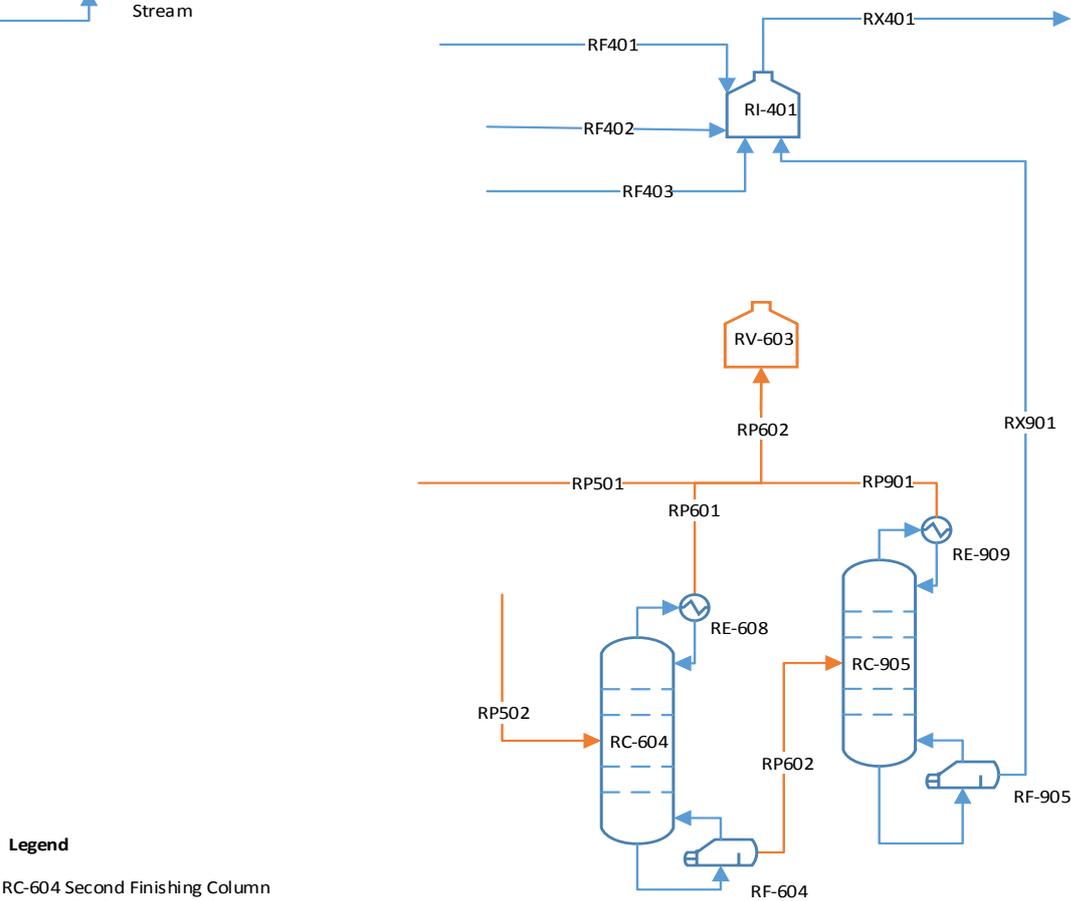
The liquid outlet stream of the dehydration column enters the first finishing column at the top. This finishing column removes all remaining water, methanol and methyl acetate via its vapour outlet stream, which is recycled. An essentially pure product vapour stream is removed from stage 17, thereby reducing the volume of the liquid outlet stream. The liquid outlet stream is led to a second finishing column, designed to remove the propionic acid from the acetic acid product. Since the amount of propionic acid is relatively low compared to the amount of acetic acid, this separation proved to be difficult and thus a high boil-up ratio was required. All finishing columns operate at 1 bar pressure and subcooled reflux and liquid distillate.

In the literature model, the last two finishing columns are not included. However, in order to remove all of the propionic acid, it was required in the Aspen model. A pure product could be obtained from C3, but a significant amount of acetic acid would then be discarded at the bottom. Therefore, it was chosen to implement a second finishing column to regain as much of this acetic

acid as possible. This column requires a very high boil-up ratio, since only a small volume of propionic acid needs to be removed from a large volume of acetic acid. Eventually, still a significant amount of acetic acid is discarded with the propionic acid as the bottom product. Nevertheless, the inclusion of this column improved the yield of pure product by almost 200%.

All columns were finalized by some minor modifications during the scaling stage of the project. It was found that for the original reaction part of the model, at least 85 parallel columns were needed to get reasonable column dimensions. Inherently, this can be explained by the extraordinarily large streams that are used in this process. Nevertheless, by tweaking the reflux- and boil-up ratio's and accepting a slightly less pure product, this number was reduced to 24 columns in total. In this modelling step, also another finishing column was added that further purifies the outlet stream of C4 to increase the yield. In this construction, a total of 4 columns is needed (three C4 in parallel and one C5), whereas without C5 six parallel columns C4 would be required for the same yield and degree of purity.

Process Flow Diagram
 Production of Acetic Acid (AA)
 RC-604, RC-905 and incinerator



- Legend**
- RC-604 Second Finishing Column
 - RC-905 Third Finishing Column
 - RI-401: Incinerator
 - RV-603: AA Drum
 - RF-604 Reboiler RC-604
 - RF-905 Reboiler RC-905
 - RE-608 Condenser RC-604
 - RE-909 Condenser RC-905

Figure 4: PFD of finishing columns C4 and C5

2.2.6 Discussion overall Reactor Section

The Aspen model adequately resembles the literature process with some exceptions. The first and main exception is that all iodide species were left out of the model. This implies that all iodide must be continuously recycled to the reactor via the two absorbers. It is undesirable to have any iodide species leftover in waste- or product streams, as it is improbable that these are removed in the bio-treatment of the waste streams. However, since literature clearly states that the two absorbers maximize the recovery of methyl iodide, it can safely be assumed that the iodide content of the liquid waste streams is negligible.⁸ Nevertheless, it is possible that the vent gas exiting overhead still contains some iodide species. In that case, iodide removal technology should be implemented before these enter the incinerator.

The second exception is the removal of the water stream exiting the dehydration column from the system. In the literature process, this stream is recycled to the reactor. In the Aspen model, it proved advantageous to consider this stream as waste and thereby reduce the water content of the reactor to the literature range. A lower water content reduces by-product formation, which is one of the main advantages of the Chiyoda process.⁸ The third exception is the elimination of the third outlet stream from the dehydration column, as it was possible to achieve the desired separation in Aspen without this stream. Excluding this recycle stream stabilized the model, since the dehydration column now does not require any recycle loops.

The fourth and last exception is the addition of the extra finishing columns. No good separation of propionic acid was achieved unless a fourth column was included. In the literature PFD, a liquid stream from the top of the finishing column is recycled to the dehydration column. This recycle stream is omitted in the Aspen model, since adding a fourth and fifth column made it unnecessary. This construction leads to an overall yield of 97.1% (from methanol) and a purity of 99.98 wt%, with propionic acid as the main impurity. In literature, sales specifications of acetic acid were found to require a minimum purity of 99.85 wt% and a maximum content of 0.05 wt% non-water.⁵¹ The product amply meets these requirements, since it only contains approximately 0.03 wt% impurities. All mass balances and incorporated final calculations can be found in the 'BalancesFinal' excel file.

2.2.7 Heat integration

To reduce the total heat required in the reaction section, options for heat integration were investigated. Since most of the distillation columns operate at a temperature around 118°C and a pressure around 1 bar, not many opportunities for heat integration were found. However, by combining the condenser of the flush column (RC-201) with the reboiler of the first finishing column (RC-503) in a shell-and-tube heat exchanger (HEXH12), a significant decrease in the total heat can be obtained. A similar approach was tested on other combinations of condensers and reboilers from different columns, but no efficient combinations were found. This leaves the option of using a single water stream in series through some of the consecutive condensers and reboilers, which could be investigated. This is yet to be completed and is thus left for further research.

The reactor heat can be used to generate medium pressure steam via the reactor cooling system. However, since no thermodynamic data on the catalyst is available, the heat of reaction as found by Aspen might not be absolute. Therefore, this option was only briefly explored. It was found that not enough high-pressure steam could be generated to significantly decrease the heat required for the reboiler of the flush column, which has the highest duty. Nevertheless, the generated steam was sufficient to eliminate the need for a reboiler in the second finishing column (RC-604) by adding another heat exchanger (HEXH11). This result should be considered conditional to the reliability of the reaction heat, as explained above.

Literature states that importation of steam during normal operation should not be required due to high heat recovery from both the reactor and as fuel value from waste streams.⁸ This

observation was not found in Aspen, although the burning of waste streams was omitted in the simulation. The heat obtained via this route cannot be studied without explicit modelling of the ignition process, which was not considered feasible. Due to the extraordinarily large feed streams, it is assumed that the literature statement is invalid and steam importation will be necessary. The utility costs will depend on the fuel value obtained from the waste streams, but the maximum can be calculated from the duties as found in Aspen.

3. Equipment Specifications

The scaling of the different parts of the Aspen model proved to be complicated. The inlet streams are unusually large, leading to the need for very large equipment. To obtain reasonable dimensions for the equipment, some streams had to be divided over multiple units in parallel. The number of units was tweaked together with their specifications until realistic dimensions for each constituent were found. This also resulted in the addition of some extra parts, as described above in the discussion of the reactor section. Not all parts were sized in Aspen, as it was more time-efficient to use literature procedures and good agreement with Aspen values endorsed their validity. For the same reason, some unit dimensions were estimated based on the calculated measurements of similar parts.

3.1 Purification section

3.1.1 Dryer

For the drying process, it is very important that the regeneration of the dryer vessel occurs faster than the water saturation in the operational vessel. The gas flow used is adjusted on the rate of water saturation of the operational tower. Aspen was not used for specifying the dryer, as its influence on mole fractions and flows of the inlet gas can be neglected. After the dryer beds, two activated carbon filters are implemented to filter out any particles that might leave the dryer. In order for the steel factory lean gas to pass through the dryers and filters it needs a pressure difference. This is created with compressors after the filters. The gas composition after the dryer can be regarded as unchanged in composition and flow.

3.1.2 Columns

Research has shown that the capture of carbon monoxide by $\text{CuAlCl}_4 \cdot \text{tol}_2$ occurs instantaneous in comparison with the mass transfer of CO in the gas phase to the toluene liquid phase. Therefore, the total absorption of CO in the copper salt is determined by mass transfer.¹⁴ The absorption tower may thus be based on maximizing the mole flux and total mole transfer from the gas phase to the liquid interface. The mole flux between two phases could be written as in Equation 12. To use this equation effectively, information on the equilibrium concentration (C^l and C^g) of the two phases, the diffusion coefficient (m) and the partial mass transfer coefficients (k^l and k^g) should be known. However, these values are not accurately known as the conditions described in literature are widely different from the conditions in the column. Moreover, the area between the gas and the liquid in the column is not known either. Therefore, it was chosen to base the size of the column on vapor flow rates as described below.

$$\Phi''_{mol,A} = \left(\frac{m}{k^g} + \frac{1}{k^l} \right)^{-1} (mC''_{A,f} - C'_{A,f})$$

Equation 12

Besides the dimensions of the absorber, also the dimensions of the stripper used in the COSORB process were calculated according to the method described below for the reaction section. All values can be found in Appendix 7. Because the Aspen model of the absorption column was not completely realistic, some assumptions had to be made during the calculation of its dimensions. It was assumed that the maximum vapour flow rate through the absorber equals its inlet flow rate. This assumption is justified by checking the size of the combined gaseous streams that make up the vapour outlet stream from the real absorber, which is smaller than that of the inlet stream. The vapour density was taken from the inlet stream as well, while the liquid density was that from the liquid outlet stream. This density did not differ significantly from the liquid inlet density, enabling the calculation of the column diameter.

The number of stages was chosen to obtain a length-to-diameter (aspect) ratio of at least three. In reality, the column height should be calculated from the mass transfer flux and the amount of CO absorbed. As described previously, detailed data on the mass transfer coefficient and catalyst concentration for the absorption process should be known to facilitate these calculations. These could be found via lab-scale experiments or an elaborate literature study. The methodology for calculating absorption rates and corresponding column sizes for the COSORB process has been described in literature.¹⁴ For the current project, this was not considered feasible and the absorber dimensions were only roughly estimated to enable the analysis of the process costs. The dimensions of the stripper were calculated more reliably based on the Aspen data, although similar assumptions had to be made.

3.1.3 Heat Exchangers

For the design and specification of the heat exchangers a combination of literature values⁵² and data from the aspen model on heat integration was used. The basic design procedure that was used is based on the area needed for heat exchange between the hot- and cold side of the actual heat exchanger. Equation 13 was used for the calculation on heat exchange.⁵² Here, Q is duty in kW, U is the overall heat coefficient in W/(m².°C), A is the area of heat exchange in m² and ΔT(m) is the mean temperature difference. To simplify the calculations and make them more time efficient an excel file was made.

$$Q = U.A.\Delta T(m) \quad \text{Equation 13}$$

To calculate the area, values of the duty, heat coefficient and temperatures of the hot- and cold flows were found from Aspen. The heat coefficient was assumed to be constant in the heat exchanger and also the effect of fouling overtime was not taken into account. For the calculation of the mean temperature difference equation 14 was used⁵², where ΔT(A) is T(hot_in)-T(cold_out) and ΔT(B) is T(hot_out)-T(cold_in). All temperatures are in degrees Celsius.

$$LMTD = \frac{\Delta T_A - \Delta T_B}{\ln\left(\frac{\Delta T_A}{\Delta T_B}\right)} = \frac{\Delta T_A - \Delta T_B}{\ln \Delta T_A - \ln \Delta T_B} \quad \text{Equation 14}$$

After the area of each exchanger was calculated using excel, some specifications could be made with respect to the design of the exchangers. It was chosen to use a BEM shell-and-tube heat exchanger type for all the heat exchangers in the system. This choice was based on the fact that these exchangers are the most common type of exchangers used.⁵² For all but one heat exchanger, the number of tube passes was chosen to be one. All the dimensions used are based on the TEMA standards for heat exchangers.

Next some choices were made with respect to the tube diameter, thickness and length. For the initial guess of dimensions an outside diameter of 25 mm and length of 6.10 m was chosen. All heat exchangers used a tube thickness of 2.1 mm, as this is justified by literature.⁵² Based on this the excel file calculated the heat exchanger area per tube, which was done by multiplying the circumference by the length of the tube. By dividing the total area of exchange by the exchange area per tube the number of tubes could be calculated.

By calculating the cross-sectional area per tube, based on the inner diameter, the total cross-sectional area could be calculated. The number of tube passes per heat exchanger was set to 1, as this greatly simplified the calculations on the total cross-sectional area. By choosing only one tube passing, the correction factor for the mean temperature difference was also set to 1. This choice is justified, as including a correction factor was not needed to achieve reasonable values with respect to velocities and pressure drops for the tube side. Through dividing the volumetric flow by the cross-sectional area of all tubes, a velocity could be calculated. The volumetric flow was

obtained from the Aspen model. The first velocity calculated was based on the initial tube dimension guesses. When the tube velocity was not satisfactory as compared to the typical tube velocities, the initial dimensions were changed to result in satisfactory velocities. The satisfactory ranges for all velocities are found in table 10.

Table 10: typical values on velocity and pressure drop of shell and tube heat exchangers⁵²

	Tube-side velocity (m.s ⁻¹)	Shell-side velocity (m.s ⁻¹)	Tube-side pressure drop (bar)	Shell-side pressure drop (bar)
Liquids				
<1 mN s/m ²	1 to 2, max 4	0.3 to 1	0.35	0.35
1 to 10 mN s/m ²	1 to 2, max 4	0.3 to 1	0.5 to 0.7	0.5 to 0.7
Vapors				
1 to 2 bar	10 to 30	10 to 30	0.5 x gauge pressure	0.5 x gauge pressure
Above 10 bar	5 to 10	5 to 10	0.1 x gauge pressure	0.1 gauge pressure

Following the calculated velocity, also the pressure-drop over the tube side (ΔP) could be calculated. This is done using equation 15, where J_f is the dimensionless friction factor, L' is the pipe length in m, ρ is the density in kg/m³ of the flow through the tube side and u_t the velocity on the tube side. Also the pressure drop was preferred to be within the typical values found in table 10. When pressure drops were too high, they were adjusted by changing the velocity, as the pressure drop depends quadratically on velocity. The friction factor was chosen based on the Reynolds number inside the tube. Values of the friction factors corresponding to Reynold numbers are found in literature.⁵² All densities were taken directly from the aspen model. As stated in chapter 2, the pressure drop calculation could be less accurate for the liquid flows. Velocities of liquid flows are however much less dependent on density, so the calculations on velocity are still accurate. Because pressure drop is quadratically dependent on velocity, the calculations on pressure drops are probably still justified.

$$\Delta P = 8J_f \left(\frac{L'}{d_i}\right) \frac{\rho u_t^2}{2} \quad \text{Equation 15}$$

Subsequently the velocities and pressure drops on the shell side of the heat exchanger were calculated. For calculating the velocity, the cross area of the shell side (A_s) needed to be calculated. This was done using the Kern's method⁵². It was chosen to use a square pitch configuration of tubes in the shell side for all heat exchangers, as this usually results in lower pressure drops. Equation 16 was used for the calculation of the cross-sectional area.⁵² Here, p_t is the tube pitch ($=1.25d_o$) in mm, d_o is the outside tube diameter in mm, D_s is the shell inside diameter in m and l_b is the baffle spacing in m. The initial baffle spacing was chosen to be 80% of the shell inside diameter. The shell inside diameter was based on the bundle shell diameter (D_b) of the tubes plus 5%. The bundle diameter can be calculated using the equation 17. N_t is the number of tubes per heat exchanger as explained above. K_1 and n_1 are constants and equal respectively 0.215 and 2.207 for the chosen specifications of a 1 tube pass and square pitch configuration for the heat exchangers.⁵²

$$A_s = \frac{(p_t - d_o) D_s l_b}{p_t} \quad \text{Equation 16}$$

$$D_b = d_0 \left(\frac{N_t}{K_1} \right)^{1/n_1} \quad \text{Equation 17}$$

Finally, the velocity of the shell side could be calculated by dividing the volumetric flow by the cross-sectional area. The volumetric flow was derived from the Aspen model. Next the Reynolds number could be calculated following a similar method as for the Reynolds calculation on the tube side. The Reynolds number could then be used to find the corresponding friction factor, j_f . This was used to calculate the shell-side pressure drop (ΔP) as explained in equation 18. u_s is the shell side velocity in m.s^{-1} , L is the tube length in the shell in m. To use this equation the shell-side equivalent diameter, d_e , for a square pitch should also be calculated. This can be done with equation 19. As with the velocity and pressure drop on the tube side, effort was put into finding values of typical velocities and pressure drops as seen in table 10.⁵²

$$\Delta P = 8j_f \left(\frac{D_s}{d_e} \right) \left(\frac{L}{l_B} \right) \frac{\rho u_s^2}{2} \quad \text{Equation 18}$$

$$d_e = \frac{1.27}{d_0} (p_t^2 - 0.785d_0^2) \quad \text{Equation 19}$$

Overall the choice was made to let the highest volumetric flows flow through the shell side, as it was found to be easier and more realistic to decrease flow velocity and pressure drops on the shell side using the Excel file. Because of very large gas flows, almost every heat exchanger had to be put in parallel to retain acceptable values on velocity and pressure drop. The baffle spacing used on the shell side is higher than the recommended values in literature.⁵² The reason for this is that it significantly reduced the amount of heat exchangers needed in parallel to obtain reasonable values for pressure drop and velocities. Since the Reynolds numbers are still high, the flow inside the shell is still quite turbulent, even at this large baffle spacing. This will still result in sufficient heat transfer. To check if the heat exchangers are reasonable in size, the maximum diameter was set to about 2 meters. Furthermore, it was preferred to have a tube length to shell diameter ratio between 5 and 10, as this is considered the optimum ratio.⁵² A detailed overview of the specifications and results of the sizing are found in the Excel file 'HEATexchanger sizing final'.

3.1.4 Pumps & Compressors

Pump sizing was done with the use of formula's from Towler & Sinnott.⁵² The formula stated below for work required from the pumps shows the contributions of the difference in elevation, difference in system pressures and pressure drop due to equipment in that order. Due to the fact that piping was not taken into account in this process design, only pumps and compressors that either increase the system pressure and/or have to overcome pressure drop in equipment were considered in this section.

$$g\Delta z + \Delta P/\rho - \Delta P_f/\rho - W = 0 \quad \text{Equation 20}$$

From the sizing of the heat exchangers their pressure drop was obtained. After the heat integration and heat exchanger sizing, extra pumps were added to the process that had to overcome pressure drops in the heating or cooling streams. This was only done for COSORB. For the pumps, the power needed was manually calculated and compared to the Aspen values using the following formula from Towler & Sinnott.

$$\text{Power} = (W \times m) \times 100/\eta_p \quad \text{Equation 21}$$

Setting the pump efficiency to 79%, which is the same value Aspen uses, corresponding data was obtained. The Aspen power values did however not contain the power needed to overcome the

pressure drop in the heat exchangers. The pump data in Appendix 11 also shows the total pressure difference that does include both pressure differences. From the total pressure difference the liquid head was calculated using the formula below.

$$\text{Pressure head} = P/(\rho g) \quad \text{Equation 22}$$

For the calculation excel sheet including formula's, see the excel file 'Pump Sizing'. The results for all the pumps can be found in Appendix 11. This data was used for the cost analysis of the pumps using Aspen Economic Analyzer.

The compressor power for system pressure differences was taken directly from Aspen. Additionally, the heat exchanger pressure drop was taken into account by a fractional power increase estimation. Appendix 12 shows the results for the compressors. This data was used for the Aspen Economic Analyzer as cost estimation for the compressors.

3.2 Reaction section

3.2.1 Reactor

The reactor dimensions are roughly estimated based on literature information combined with Aspen results. Depending on the gas velocity and column diameter, different flow regimes arise in bubble column reactors.⁵³ The exact boundaries associated with the transition regimes depend on the system studied, but in large reactors operating at high pressure and temperature, the churn turbulent flow regime prevails.⁵⁴ This regime generally occurs at a minimum superficial gas velocity of 0.05 m/s. By combining this value for the superficial gas velocity (v_g , m/s) with the gas inlet volumetric flow (φ_g , m³/s) as obtained from Aspen in equation 23, an estimate for the column diameter (d , m) can be calculated.

$$d = \sqrt[4]{\frac{\varphi_g}{v_g * \pi}} \quad \text{Equation 23}$$

Inserting the data as displayed in the third column of Appendix 5 into Equation 23 leads to a column diameter of 7.6 m. Industrial bubble columns generally operate with an aspect ratio of at least 5, and hence the column length is assumed to equal 38 m (5*diameter).⁵³ The reactor volume would then be approximately 1700 m³. Although this is large, it is not unusual to employ bubble columns with even larger dimensions in industrial processes.⁵⁵ For the Fischer Tropsch gas-to-liquid process, typical column dimensions are a diameter of 5-8 m and height of 20-30 m.⁵⁴ The values found from the calculations are not significantly out of these ranges, which endorses their validity. This ratification is especially valuable due to similarities between the two processes, such as the high reaction temperature and pressure and the use of a heterogeneous catalyst.

In reality, bubble column reactor design is done by careful up scaling of a lab-scale reactor via several formula's.⁵⁴ Since no data on gas hold-up, bubble rise velocities or other process-dependent variables could be found for the Chiyoda™ process, this method could not be applied. Therefore, a rough estimate is provided via the method above. If the model would be built in reality, it is recommended to perform lab-scale bubble column tests to obtain a more accurate scaling. The superficial gas velocity of 5 cm/s is on the low side for the turbulent flow range. A higher velocity could enable the use of a smaller reactor, but this can only be discovered by performing lab scale tests. Therefore, the dimensions based on the largest possible diameter are taken for the calculation of the investment costs.

Hastelloy B-2 (65% Ni, 28% Mo, 6% Fe) coating on Carbon Steel (CS) is chosen as the material of construction for the reactor and associated cooling system.⁵⁶ Hastelloy B-2 has excellent

resistance to corrosion from hydrogen iodide and acetic acid. In other high-pressure processes for the manufacture of acetic acid, such as the BASF process, it is the often-chosen material of construction.⁵⁷ Its physical and chemical properties seem specifically suitable for the bubble column reactor.⁵⁸ Although Hastelloy B-2 is relatively expensive as compared to for example stainless steel, its more resistant nature enable a safer and more resilient process. The recognition that the reactor is arguably the most important piece of equipment merits the high investment costs.

3.2.2 Columns

The dimensions of the columns were found using a combination of manual calculations and the Aspen tray rating functionality. A simple check in Aspen proved that the maximum vapour flow rate scales linearly with the number of columns over which the original inlet is divided. This enabled the use of the sizing equations described by Sinnott et al. (equations 24 and 25).⁵² Here, \hat{u}_v is the maximum allowable vapour velocity (m/s), l_t is the plate spacing (m), D_c is the column diameter (m) and V_w is the maximum vapour rate in kmol/s. ρ_v and ρ_l are the vapour and liquid density (kmol/m³), respectively, and are obtained from Aspen. The diameters of all columns were calculated using these equations. For A1, C3 and C4, the diameter was additionally calculated using Aspen tray rating, enabling a comparison between the two values.

$$\hat{u}_v = (-0.17l_t^2 + 0.27l_t - 0.047) \left[\frac{\rho_l - \rho_v}{\rho_v} \right]^{1/2} \quad \text{Equation 24}$$

$$D_c = \sqrt{\frac{4V_w}{\pi\rho_v\hat{u}_v}} \quad \text{Equation 25}$$

The results of these calculations are shown in Appendix 6. It is shown that no severe discrepancies between the calculated diameters and the Aspen diameters occur. Therefore, the calculated dimensions are used for the cost analysis. Column C3 proved to be the most problematic due to its large boil-up rate, combined with a low vapour density. As of now, the number of parallel columns with a diameter of 5.7 m is set to 10. However, if the column diameter would need to be decreased even further, a higher number of columns could be installed. This also applies in a lesser extent to the rest of the columns. With the dimensions as specified, a total of 24 column is needed in the reaction section. This number could be reduced further by discarding a part of the off-gas from the steel mill and working with smaller flows.

3.2.3 Heat Exchangers

The three heat exchangers explicitly modelled in the reaction section (RE-104, RE803 and RE-104) were sized via an identical approach as described for the purification section. All shell- and tube side velocities were in the required ranges and the exact specifications are given in Appendices 8, 9 and 10. It was assumed that the condensers and reboilers were part of the corresponding columns and they were thus not explicitly sized. Their cost should be covered by the multiplication factor, as explained in chapter 6. However, heat exchanger HEXHI-1 that originated from the heat integration was specified explicitly to check its size, with the high-pressure steam allocated to the tube-side. Reasonable dimensions and velocities could be found, thus endorsing the usage of reactor-generated steam as utility for the reboiler of RC-604.

In the first three heat exchangers mentioned above, the feed stream was allocated to the tube side and the imported utility stream to the shell side. For RE-104, the cooled stream has a high pressure, is partially vapour and slightly corrosive due to its acetic acid content. These are all reasons to allocate it to the tube side. The imported stream used in RE-802 is LP steam, which is usually allocated to the shell side. Stream RG-801 is highly corrosive due to its acetic acid content and thus allocated to the tube side. Moreover, it partially condenses in RE-803, which is easier controllable in the tube side. This condensation also results in a large decrease in volume over the course of the heat exchanger. Yet, the velocity for the out-stream fluid with a liquid fraction of

95% remained in the range specified for liquid tube-side velocities, based on the specifications calculated from the inlet vapour volume.

3.2.4 Pumps & compressors

The specifications of the pumps and compressor in the reaction section were found through an identical approach as described for the purification section. As the pressure drops from the heat exchangers was negligible compared to the high system pressures, no additional pumps were added. It is assumed that the design pressure of the pumps has a sufficient margin to account for these pressure drops too. The material of construction for RP102 is selected to be stainless steel grade 316, as the liquid flow contains some acetic acid and assumedly also some iodide species. Since the compatibility of carbon steel with both methanol and carbon monoxide is excellent, this was selected as material of construction for both RP701 and RK101.⁵⁹ This pump and compressor contain the methanol- and CO feed stream, respectively. All additional pumps needed to overcome pressure drops from piping were ignored, as the allocation of all equipment is unknown.

4. P&ID's and control

Control is an essential part of a well-working factory. In order to make a factory function smoothly and safely, chemical engineers develop a piping and instrumentation diagram (P&ID) before the process is started. In such diagrams, a zoomed-in version of the process flow diagram (PFD) is shown with more detail on how the equipment inside the process is operated, controlled and regulated. Because P&ID's are so detailed, the PFD is split up in parts and so multiple P&ID's combine to form the entire process. There are four main quantities that can be controlled in a process or piece of equipment: flow, pressure, temperature and level. Other quantities that can be controlled (e.g. composition) are used less often. Below, the P&ID's of both sections are discussed and the main approaches when constructing the P&ID's are considered. The complete collection of the blue print P&ID's of the process is given in appendices 13 to 34.

4.1 Purification section

The purification section has been subdivided into the cleanup and purification section. The cleanup section consists of the P&ID's C1 to C4 and the purification section of P1 to P9. These contain equipment for various uses and functions and therefore all are shortly discussed. The P&ID's itself can all be found in the Appendices 13 to 25.

4.1.1 *Electrostatic precipitator & LO-CAT process (Page C1 & C2)*

The gas stream that enters the process goes through a heat exchanger (CE-101) before it enters the electrostatic precipitator (CU-101) as the gas stream needs to be heated from 25 °C to 90 °C. A temperature control system has been placed on the stream from the heat exchanger consisting of a temperature transmitter followed by a temperature indicator controller. This controls the valve on the hot stream and therefore also the temperature of the stream leaving the heat exchanger. The hot gas then enters the ESP which has a voltage indicator installed. The fly ash is removed and the gas stream leaves the ESP to go through a heat exchanger (CE-102) to be cooled down again to 25 °C. This cooler uses a comparable temperature control system as the heater. Subsequently a compressor (CK-101) compensates for the pressure drop over the heat exchangers and the ESP combined. The pressure control system on the compressor ensures a constant set pressure to be fed to the Absorber (CC-101).

The liquid in-flow of the absorber is controlled by a pump (CP-201) that compares the liquid flow to a set value and adjusts its power when required. The LO-CAT absorber has mild operating conditions of 20 – 60 °C (set at 25 °C) at 1 bar and therefore a level controller is enough to ensure proper functioning. The level controller ensures the liquid level remains below a set level to prevent liquid flowing through the gas outlet by controlling a valve on the liquid outlet stream. This liquid flows to the oxidizer (CV-201). The sulfur composition is measured and the oxidizing air-flow is adjusted to this value by a compressor (CK-201). Sulfur slurry leaves the oxidizer at the bottom and is further processed to sulfur. If liquid level in the oxidizer is too high, a level controller ensures that more liquid leaves with the slurry to prevent the liquid flowing through the vapor outflow. A liquid stream leaves the oxidizer halfway that contains the solution to be fed to the absorber. A composition control system on this liquid outlet ensures correct concentrations of chemicals and is able to add more chemicals to the oxidizer when required. The air leaving the oxidizer is led to a cleanup section before disposal. The H₂S concentration of the gas flow leaving the absorber at the top is measured by a composition indicator in order to check proper functioning.

4.1.2 *Limestone wet scrubber process (Page C3 & C4)*

The process gas enters the wet scrubber (CC-301) at the bottom. The scrubber is equipped with a level controller and a temperature transmitter. The temperature transmitter is connected to a computer control system that regulates the composition and flow of the liquid fed to the wet scrubber by adjusting the amount of limestone and fresh water flows. This system can also cool down the scrubber temperature when it might rise due to some malfunction upstream by

increasing the fresh water flow. The liquid flow from the wet scrubber enters the separator tank (CS-401) that separates the heavy solid slurry from the reusable water limestone mixture. A pump (CP-401) ensures a constant combined liquid flow to the mixer (CM-301) by controlling the flow from the separator tank. To prevent overloading and clogging of the separator tank, a level controller ensures more liquid leaves the tank at the bottom to either flush the outlet from solids or lower the tank's liquid level. The thick slurry enters the oxidizer/dewatering tank which is not worked out in detail.

4.1.3 Dryer (P2)

The gas flow that leaves the cleaning section must be dried before it is able to be purified in the COSORB™ process. The gas flow first enters the dryers. Two desiccant dryers are used to keep the flow continuous, as described in chapter 2. Because of this, a well-coordinated control system has to be implemented on the dryers. A composition transmitter keeps track on the water composition of the outgoing gas flow. If this becomes too high, it means that the dryer is saturated with water and thus has to be regenerated. This is done by linking the earlier mentioned composition transmitter to a control unit (FY) that sends a signal to two flow indicator controllers. These systems control the valves that are open and closed, before and after the dryer columns. By alternating between closing and opening a valve the inlet gas flow can be redirected to the other column. The saturated column is now being regenerated using a hot nitrogen flow.

The regeneration of the saturated column is controlled by a composition-, pressure- and temperature transmitter. These are connected to a FY, which sends a signal to a flow - and temperature indicator controller. The flow controller is connected to a motor which manages the pressure, generated by PK-201, that is to be used for regeneration. The temperature controller is connected to heat exchanger, PE-102, that manages the incoming temperature of the nitrogen flow. The pressure and temperature are higher at the start of the regeneration as the nitrogen flow out is deviated more from the reference values of the transmitters. As the flow reaches the reference values, the mass flow and temperature are decreased more.

Filters PS-203 to PS-208 are controlled by composition transmitters, which are in turn connected to a FY. This sends a signal to Composition Indicator Controllers, which controls the valves. When the concentration of the gas flow after the filter becomes too high, the open valve closes and vice versa. PE-201, PE-205 and PE-206 are controlled by a temperature transmitter and a temperature indicator controller. These intend to keep the temperature at a reference value. PK-204 is controlled by a pressure transmitter and pressure indicator controller. The aim is to keep the pressure inside PC-101 at 3 bar. PK-205 and PK-206 are controlled in the manner as PK-204. The difference is the reference value, as these compressors are intended to overcome the pressure drops over the heat exchangers; PE-205 and PE-206

4.1.4 Absorber + flash drum (P1 + P5)

Absorption column PC-101 is controlled on pressure, level and temperature. The pressure is controlled as mentioned in the previous paragraph. The level is controlled by a level transmitter connected to a level indicator controller, that sends a signal to a valve. The temperature is controlled by the cold ethanol flow of which the temperature in turn is controlled by its own heat exchangers. The pressure of the incoming toluene is controlled by a flow transmitter, this sends a signal to a flow indicator controller. This manages the motor that controls pump; PP-101. The temperature of the incoming toluene flow is controlled by the earlier mentioned cold ethanol flow.

Vessel PV-101 is controlled by a level transmitter. It sends a signal to a flow indicator controller. This controls the fresh toluene stream. When the level becomes too low, more fresh toluene is added to the system. If the level is on the maximum allowable level again, the toluene flow valve is closed. PP-102 controlled by a pressure transmitter followed by a pressure indicator controller. This controls the motor to the pump. The pump is intended to overcome the height from the heat

exchanger PE-601 to vessel PV-101. Vessel PV-501 is controlled on pressure and level. It is not necessary to control the temperature, as this is fully determined by the incoming toluene flow. This flow is already controlled by heat exchangers PE-205, PE-206, PE-101 and PE-103. PK-203 is used to suck the evaporating gasses away from the vessel. PP-501 controls the level, whereas pump PP-502 is used to overcome the pressure drop on the heat exchanger.

4.1.5 Solvent recovery + heatex (P3 + P4)

The evaporating toluene is recovered in the solvent recovery unit. The gas inflow is cooled by the cold ethanol flow, which in turn is controlled by a heat exchanger. PP-301 manages the pressure drop over the heat exchangers for the ethanol flow. PK-301 is used to suck away all the gasses that did not condensate in PV-301. The gasses from the vessel are also pushed through the filters PS-301 to PS-304. The level inside the vessel should not be too low and is controlled by a valve. The feed gas entering the heat exchangers PE-401 to PE-408 is cooled by the cold lean gas flow. The heat exchange is controlled by the temperature of the feed gas flow. Compressors PK-402 and PK-401 respectively push and suck the gas flows through the heat exchangers.

4.1.6 Heat exchanger & stripping column (Page P6 & P7)

The toluene stream containing the catalyst-CO complex in toluene is pre-heated in a heat exchanger (PE-601) before it enters the stripping column (PC-701). The heat exchange is controlled by a temperature control system that uses a bypass flow on the hot toluene stream coming from the bottom of the stripper. The flow of the CO containing toluene stream is regulated by a pump (PP-501) that also compensates the heat exchanger pressure drop. The stripper itself is equipped with a liquid level controller attached to a pump (PP-601). Additionally, the stripper temperature is controlled by a hot toluene purge on the bottom of a flash drum (PV-701). The liquid level on the flash drum itself is subsequently controlled by a level controller on the recycle flow to the stripper. The cold flow of condenser (PE-701) is regulated by a pressure control system on the stripper outlet gas flow to ensure the set condenser ratio. The reboiler (PF-701) has a temperature control system on the outlet flow to the stripper that is regulated by a valve on hot flow to the reboiler itself. This ensures the set reboiler ratio is met.

4.1.7 Solvent recovery & heat exchanger (Page P8 & P9)

The purified CO gas stream enters a heat exchanger (PE-809) to be pre-cooled with the cold recovered toluene that flows from the bottom of a flash drum (PV-801). Subsequently the CO gas enters a series of coolers (PE-801 to 808) that cool down the gas to -50 °. This leads to condensation of the evaporated toluene in the flash drum. The liquid toluene level in this flash drum is regulated by the level control system on the bottom outlet. A pump (PP-801) on the cooling liquid compensates for the pressure drop over the heat exchangers by a pressure control system on the outflow of the heat exchangers. A compressor (PK-801) is regulated by a pressure control system on its discharge flow and has to blow the CO gas through the activated carbon filters (PS-801 to 804). These filters remove the remaining toluene from the CO gas. Two sets of two filters each make sure that the process can continue whenever the filters have to be cleaned or replaced. The outlet toluene content is measured after the first filter and if this reaches a set value the control system switches the valves and thereby directing the incoming gas flow to the other set of filters. The second filter for each set makes sure the toluene not caught in the first filter will not exit with the CO gas.

4.2 Reaction section

The overall reaction process is described in nine P&ID's which include a reactor, two absorbers, five distillation columns and an incinerator. The P&ID's are discussed below and all diagrams are presented in the appendices. The heat integration described in section 2.2.7 is also included in the P&ID's.

4.2.1 Reactor (RR-101)

The CO that enters the reactor must first undergo a pressure increase from 1 to 60 bars. In order to obtain this high pressure, a multistage compressor is used, which consists of four distinct compressors. Each compressor is followed by a cooler to avoid the temperature becoming too large. The pressure is controlled by a pressure transmitter (PT) installed directly after a compressor. The PT measures the pressure and signals the compressor via a pressure indicator controller (PIC) when the pressure is too high or too low. The compressor is then able to change its outlet flow adequately. A same type of control loop is used for the coolers: a temperature transmitter (TT) is placed directly after the cooler which measures the temperature and signals the cooler via a temperature indicator controller (TIC) when the temperature is too high or too low. In between the compressors and coolers, there is a HPSD (high pressure safety diaphragm).

The reactor has besides the inlet stream of pressurized CO and an inlet of a recycle stream, also an inlet for methanol. The methanol is released from the absorbers which is premixed there. The temperature in the reactor is measured and via a TT and TIC a stream of reactor mixture is guided through a cooler to control the temperature in the reactor. The reactor has two outlets: an outlet on top of the reactor for off-gases and an outlet for the reaction products. A level transmitter (LT) is fitted on the reactor and via a level indicator controller (LIC), a signal is sent to a pump which adapts its throughput accordingly. In this way, a steady fluid level is established in the reactor. Finally, filters are placed on both outlets which ensure that no catalyst escapes the reactor vessel. The filters are equipped with DPT (differential pressure transmitter) controllers which measure the pressure drop over the filters in order to know when the filters are clogged.

4.2.2 Absorbers (RA-701, RA-802)

The high-pressure absorber (RA-701) and low-pressure absorber (RA-802) have similar functions. Methanol (the inlet of the two absorbers) is pumped from its storage through a pump. A flow transmitter (FT) is equipped after the pump, which measures the flow speed and sends a signal via a flow indicator controller (FIC) to the pump. The methanol feed is split and roughly 80 % is fed to RA-701, the remainder to RA-802. The methanol feed to RA-701 is brought to 60 bars by means of a pump which is controlled similarly as described above. The inlet of methanol is at the top of the column and the reactor off-gas enters at the bottom. The pressure inside the column is regulated by a PT and PIC, which informs a pressure control valve (PCV) to open when the pressure increases too much. Before entering the absorption column, the off-gas feed from the reactor is maintained at 60 bar by a compressor. The level of fluid inside the column is maintained by a LT and LIC which open or close a level control valve (LCV) on an outlet at the bottom. RA-802 is operated similarly with respect to their pressure and level control with the exception of the pressure being only 1 bar here. The 1/5 initial methanol feed has its inlet at the head of the column and, before entering the column, is cooled from 27 °C to 10 °C. More downstream, gaseous products from distillations columns are mixed and cooled to 10 °C. This is the bottom inlet for RA-802.

4.2.3 Distillation columns (RC-201, RC-302, RC-503, RC-604 and RC-905)

RC-302, RC-604 and RC-905

Although dehydration column RC-302 and finishing columns RC-604 and RC-905 all have different functions and sizes, their control systems are the same, since they are all distillation columns. The temperature is measured after the condenser and via a TT, TIC and TCV on the cooling water stream the temperature of the gas is regulated. The liquid level in the condenser separating vessel is controlled via a LT, a LIC and a LCV on the liquid stream that is recharged to the column. The bottom liquid stream is partly reboiled and charged back to the column as vapour. The steam needed for heating the liquid is regulated with DTP, a differential pressure transmitter. This device measures the pressure drop over the column and calculates how much steam is needed in the reboiler. The DTP sends a signal to a PIC and a PCV opens or closes the steam inlet. The column

is equipped with a LT, LIC and the liquid level is controlled by opening or closing a LCV at the product outlet.

RC-201 and RC-503

RC-201 and RC-503 are slightly more complicated than the previous columns. The product stream originating from the reactor undergoes its first purification step in flush column RC-201. At the top of RC-201, the cooling is regulated similarly to the other columns. The difference is that the condensed liquid is partly redirected to the column and partly collected as top liquid product. The vessel is equipped with a LT, a LIC and a LCV on the liquid top product stream which opens when the vessel is sufficiently full. On the previous columns, the LCV was on the recharge stream. The heat integration involving the condenser of RC-201 and the reboiler of RC-503 was also implemented in the P&ID's.

On the second tray from above, a side stream is drawn from the column. This is done by means of a chimney tray, which is schematically depicted in the P&ID. The rate at which liquid is abstracted is regulated by a level control system at the particular tray in combination with a pump at the outlet. The liquid condensate from the top and the side stream are stored in a vessel. A predefined amount of this liquid is removed from the process and can be enlarged by a LCV when the liquid level in the vessel becomes too high. The bulk, however, is recycled back to the reactor. The bottom stream is partly reboiled and charged back to the column. The other part is the acetic acid-rich product stream. The control engineering here is the same as for the previous columns. Because RC-503 also has a side-stream withdrawn, its control systems are exactly the same as for RC-201.

4.2.4 Incinerator

The incinerator is the last stop for the waste streams. Propionic acid from the last finishing column, waste gases from the absorbers and fuel, air and ammonia are combined and burned. Ammonia is used in the incinerator to avoid the formation of nitrogen oxides (NO_x) in the flue gas. Three separate control systems are used in the incinerator. A PT in combination with a PIC is used to indicate the pressure and control a PCV on the smokestack to prevent the incinerator from blowing up and ensure total combustion. The composition inside the incinerator is inspected on the presence of NO_x using a composition transmitter (AT) and a composition indicator controller (AIC). A signal is sent to a composition control valve (ACV) which can open to larger extent when too much NO_x is present inside. The last monitor is a FT, FIC and FCV on the air inlet which controls the amount of air coming in.

5 Process safety

A HAZOP analysis was performed on the most important units in the complete process, under the assumption that all other parts are similar to one of the treated units. Per part of the equipment, the main risks were identified using various combinations of keywords with deviations. If the probability of the actual occurrence of an identified hazard was considerable, safeguards and/or actions were included. The results of the HAZOP study are included in the P&ID's shown in appendices 36, 37 and 39 to 42 and the full table is shown in appendices 35 and 38. Only the P&ID's of the units that were discussed during the HAZOP analysis were adapted, but the safety measures should be included in all of the similar equipment. Some of the main conclusions and adaptations based on the HAZOP table will be discussed below.

5.1 General Safety Measures

Since most materials used in this process are not considered benign, one of the most important goals of the HAZOP analysis is the prevention of loss of containment (LOC). LOC occurs when a fluid that is supposed to be contained in a column, vessel, pipeline or other piece of equipment escapes from that location. LOC incidents are common process incidents, including both small releases of relatively non-hazardous substances and catastrophic events where large amounts of toxic materials might be released. The risk of a certain LOC incident is commonly defined as the product of its frequency and the severity of its consequences. By evaluating all hazards using this definition, appropriate process design for minimization of the potential for LOC can be ensured and safe operating practices can be provided.⁶⁰

An adequate fire-safety strategy should be developed, including evacuation plans, fire drills and maps indicating the locations of fire extinguishers. Eye-wash stations, fire blankets, sand buckets, emergency showers and breathing apparatuses should be available throughout the plant. All parts of the site must be kept well-ventilated and appropriately trained first-aiders must be present at all times. Everyone should wear appropriate personal protective equipment in the plant at all times. This equipment should include but not be limited to safety goggles, gloves and a protective suit. The exact type of protective equipment must be selected according to the concentration and amount of dangerous substance at the specific workplace, and might include respiratory protection and/or face shields.

5.2 Purification

As carbon monoxide is one of the feedstocks for the acetic acid production, it will be present at high concentration in some of the gaseous streams. CO is considered a toxic gas, so its LOC should be prevented at all times.⁶¹ CO meters should be installed throughout the plant and evacuation plans are to be well-known amongst workers. Other hazardous materials are present in gaseous streams as well, such as toluene. This substance is highly flammable and toxic. Toluene originating fires can be extinguished using water spray, alcohol resistant foam, dry chemical or carbon dioxide. In case of a significant toluene spill, the exposure of workers should be minimized. Full-face respirators must be available and symptoms of exposure must be well-known and reported immediately.⁶²

As already mentioned, after completing the hazard and operability analysis, some sections of the P&ID were updated. The absorber (page P1) and the stripper (page P7) were chosen as the most important P&ID's of the purification step and both the updated schemes are shortly discussed below. The HAZOP and updated P&ID sheets itself can be found in the appendices.

5.2.1 HAZOP analysis Absorber

To prevent hazardous situations from occurring the absorber PC-101 was equipped with safety alarms. A temperature alarm high was fitted to the column, this alerts the operators that somewhere at the inlets of the column the cooling system is not working properly. In case of clogging or failure of the valve of the liquid outlet, the level in the column could rise. A level alarm

high system does alert operators that toluene levels are becoming too high, thus preventing the toluene from flowing back to the compressors on the gas feed. The pressure could become too high if somewhere on the gas outlet clogging occurs or the temperature inside the column is too high due to failure of coolers. In case of emergency a pressure safety valve opens, which depressurizes the column. Besides high pressures, the pressure could also become too low. This is probably due to a leakage inside the column. Therefore, the column is also equipped with pressure alarms. Flow alarms indicate whether the inlet flows are too low, as this makes the process less efficient. In case that occurs, the alarms will alert the operators to take action. A detailed overview of the HAZOP is found in Appendix 37.

5.2.2 HAZOP analysis Stripper

For the stripper (PC-701) several safety measurements were added to the P&ID for a variety of malfunctions. Deviations in level from the failure of level controllers were covered by both high and low-level alarms. A flow alarm low was also installed on the top gas outlet from the absorber as this would signify failure of CO being released by the toluene or a gas leakage. As the temperature in the stripper is close to the boiling point of toluene, the temperature also needs a safety measure to ensure a low toluene concentration in the gas outlet. Therefore, a temperature alarm high is installed in case for example the condenser fails. Finally, the stripper has a safeguard installed for high pressures. This consists of an alarm and a control valve that can reduce pressure in the stripper by leading the gas to a gas barrel. This barrel has enough volume to cope with sudden rigorous high pressures but if the problem persists the main gas flow has to be shut down. The flash drum (PV-701) is equipped with a flow alarm low on the top gas outlet and a level alarm low for comparable situations as for the stripper. The detailed overview is given in Appendix 36.

5.3 Reaction section

The main hazards in the reaction section include LOC of acetic acid-rich streams and of the reactor contents. The acetic acid containing streams should be kept away from sources of ignition, as it is a flammable fluid. Water spray, alcohol-resistant foam, dry chemical or carbon dioxide can be used to extinguish acetic acid-originating fires. Furthermore, containers or storage vessels should be kept at low temperatures in well-ventilated areas. Acetic acid causes severe burns and eye damage if contacted with the skin. Inhalation or ingestion may cause permanent damage to the respiratory and digestive tissue. Instructions on the proper handling of this chemical should be taken up in the operator training and symptoms of exposure should be reported immediately.⁶³

The reactor contains hydrogen iodide (HI) at low concentrations, originating from the toxic methyl iodide promoter. As HI is a highly corrosive and hazardous substance, the reactor material of construction is Hastelloy-B 2 to prevent corrosion of its walls. LOC from the reactor should result in immediate evacuation of the entire plant. It is assumed that the hydrogen- and methyl iodide are only present in the reactor and the first absorption column at significant concentrations, and their concentrations downstream in the plant are negligible. This assumption should be checked during start-up operation of the plant, as substantial loss of both hydrogen- and methyl iodide to downstream units should be prevented.^{64,65}

Methanol is a highly flammable fluid which is toxic if swallowed, in contact with the skin or inhaled. Its storage tank should be kept away from sources of ignition and all methanol streams must be handled with care. Upon LOC of methanol-rich fluids, appropriate safety measures include wearing the correct safety gear such as eye, body and respiratory protection. Further leakage or spillage should be prevented if safe to do so. Methanol-originating fires can be extinguished using identical methods as for acetic acid-originating fires. Symptoms of methanol exposure include headache, dizziness and drowsiness. These and other symptoms should be well-known amongst workers and reported to the responsible entity immediately if experienced.⁶⁶

A mixture of waste streams is led to the incinerator to utilize their fuel value. These streams contain mainly carbon monoxide, but also some acetic acid and traces of methanol. Careful ignition in this incinerator is important, since these three substances are highly flammable. The incinerator must be equipped with an afterburner and scrubber, and surplus non-recyclable solutions must be offered to a licensed disposal company.⁶¹ Appropriate residence times, chimney heights and temperatures should be selected for the incinerator to minimize emissions and eliminate pathogens. Air pollution control equipment might need to be installed to meet all environmental regulations and guidelines. The siting of the incinerator should also be taken into account, as this can significantly affect the air quality for workers and the community.⁶⁷

The HAZOP table designed for the reaction section is given in Appendix 38. The most important pieces of equipment were analysed during the HAZOP analysis. For example, one distillation column has been analysed as the other four columns are operated similarly. This does not alter the fact that the HAZOP measures should be installed on all columns. The adapted P&ID's with HAZOP of the reactor, absorber RA-701, distillation column RC-201 and the incinerator are presented in Appendices 39-42. In general, the equipment was examined on what could happen to its temperature, pressure, level or in- and outflows when some other device malfunctions. Besides a variety of alarms, some specific safety equipment was installed as well. Some examples hereof are elaborated upon below.

The reactor has been equipped with a pressure safety valve that opens when the pressure becomes critically high. The toxic gasses that would be liberated are instead collected in an emergency collecting vessel. The high-pressure absorber (RA-701) has an additional level safety valve, which opens when the liquid level becomes too high. This safety valve opens a tube on the methanol feed so that methanol is temporarily collected in a vessel instead of being fed to the absorber. For flash column RC-201 the same procedure as for the reactor is used. When the PSV opens, the feed stream of RC201 should be closed. Via a positive feedback system, this would also lead to the opening of the safety valves on the reactor and on the methanol feed, which would ensure a safe temporarily shut down of the factory. Finally, the incinerator is equipped with a temperature safety valve, which closes the fuel supply when the temperature in the incinerator increases too much. This will prevent the incinerator from exploding.

6 Capital cost estimation

The Aspen Plus Economic Analyzer V8.7.1 was used for the estimation of the equipment costs, with pricing based from the first quarter of 2014. A list of the investment costs per piece of equipment is shown in Appendix 43. In literature, data on the corrosion rates for various acetic acid-containing vapour- and liquid streams were found.⁶⁸ From these data, the material of construction used in the equipment was selected. In general, stainless steel (SS) type 316 can be used as long as acetic acid is not present at high concentrations in the vapour phase or at extreme temperatures. Vapours of acetic acid at higher temperatures are not extremely aggressive in the absence of condensation. However, dripping of liquid on a hot metal surface can produce excessive attack.⁶⁸ Toluene, methanol and all the components in the gas stream do not cause corrosion in SS-316 at the concentrations as in the plant.

6.1 Purification section

One of the major benefits of the COSORB™ process is the non-corrosive character of the solvent and absorption compound¹⁵. This enables the process to use less expensive materials in the equipment and piping. Moreover, the fact that the process occurs at such low pressures and moderate temperatures further reduces costs. Some of the major compounds used in the system are toluene, ethanol and the feed gas with the know gas concentration.

Toluene is not corrosive to carbon steel and shows excellent compatibility⁵⁹. For this reason, all the piping, heat exchangers, pumps and columns that only contacts toluene or CO gas are made from carbon steel. The feed gas however contains methane, this shows poor compatibility with carbon steel. Therefore, the piping and equipment that comes into contact with the feed gas should be coated with 3 mm SS 304. This shows excellent compatibility with all the gasses. The following equipment should be coated with SS 304: PS-201 to PS-206, PK-204 to PK-206, PE-205 shell side and PE-206 shell side, PE-101 shell side, PC-101, PE-301 tube side, PK-301, PE-309 shell side, filters PS-301 to PS-304, PE-401 to PE-408 shell side, PK-401 and all the piping between the equipment.

For the cooling of the purification section cold ethanol is used. This shows slight corrosion with carbon steel.⁵⁹ Therefore, also for the ethanol stream a 3 mm SS 304 coating should be used. The following heat exchangers should be coated; The tube sides of PE-101, PE-103, PE-301 and PE-801.

The use of SS 304 results in higher investment costs, as the equipment costs are higher. By using a coating layer of SS 304 longer equipment lifetime is achieved, so over time maintenance is expected to be lower. The choice of the material of construction of the equipment in combination with the sizing enabled a more detailed estimation of the costs, this was done by using the economic analyzer of Aspen. Corrosion was neglected in the cost analysis as it is very low for this system.

6.2 Reaction section

As already described previously, the reactor contains a highly corrosive mixture of chemicals. Therefore, Hastelloy-B 2 is used to coat the inside of the bubble column and the attached cooling system.⁶⁸ The corrosion rate in the presence of catalyst is approximately 0.2 mm/year, thus leading to the need for a 3 mm thick coating layer to enable continuous usage for 15 years. To ensure process safety and continuous operation, this coating layer will be made 5 mm thick. A packed column without packing is used to model the reactor in the economic analyser, as no bubble column is available and this was the recommended approach for estimating reactor costing according to Sinnott et al.⁵² The packing costs calculated were thus subtracted from the total equipment costs, since the bubble column reactor should simply be an empty column. The fluid volume was set to 80%, but this should be checked in the lab-scale design experiments.

The gaseous inlet to the high-pressure absorber contains 15 wt% acetic acid at 180°C and 60 bar. All the acetic acid dissolves in the methanol liquid stream, which has a final AA concentration of 8 wt%. These concentrations are sufficiently low to justify the use of SS 316 as coating material with CS as main MOC. However, before actually building the absorbers, a careful evaluation of the stability of SS-316 in these environments must be completed. The corrosion rate of SS-316 in similar conditions is <0.03mm/year, thus a cladding thickness of 0.5 mm is chosen.⁶⁸ The liquid inlet to the low-pressure absorber contains 85 wt% acetic acid at 10°C and 1 bar. All acetic acid remains in the liquid phase, thus enabling the use of type 316 stainless coating. The corrosion rate is negligible, so a thickness of 0.5 mm is chosen.

The most corrosive stream exiting the flush column is the liquid product exiting the reboiler. This contains 95 wt% acetic acid at a temperature of 285°C and a pressure of 40 bar. No data on streams resembling these conditions could be found. However, since acetic acid evaporates and condenses again, it is assumed that the stainless steel will erode too fast. Therefore, a Hastelloy-B cladding of 2 mm thickness is applied. The presence of iodide species in this column will accelerate corrosion, so an erosion rate of Hastelloy of 0.13 mm/year is taken. It is advisable to carefully assess the corrosion behaviour of SS-316 in the conditions as in RC201 to check if this assumption is correct. If stainless steel erosion is not a severe issue, no Hastelloy coating might be needed, which would significantly reduce the costs of the flush column.

In the dehydration column, acetic acid evaporation and condensation also takes place, albeit at lower temperatures due to the lower pressure of 3 bar. An identical coating as for the flush column is chosen, namely Hastelloy B with a thickness of 2 mm. A similar choice is made for all of the finishing columns. In these distillations, acetic acid condenses and evaporates at 1 bar and 180°C throughout the columns. Therefore, Hastelloy coating is needed to prevent excessive corrosion of the material from the condensing liquid. From data on an acetic acid vaporizer, a corrosion rate of 0.08 mm/y is assumed for this coating. This leads to a thickness of 1.5 mm. Again, careful testing of the Hastelloy corrosion rates under the applied circumstances is advisable to check if this thickness is indeed sufficient.

The shell- and tube side materials of construction for the three heat exchangers in the purification section are chosen similarly. Since RE802 only contains ethanol and methanol at relatively low temperatures, stainless steel cladding of type 304 should be sufficiently resistant to corrosion. As the heat exchanger does not operate at high pressure, the default stainless steels A 285C and A 214 can be used as main MOC.⁶⁹ RE803 condenses acetic acid, thus leading to the need for a Hastelloy coating in the shell side. The main MOC of the shell is again A 285C, and the tube side consists of SS304. The flow through RE104 does not contain acetic acid at high concentrations, so SS304 can be used as tube-side cladding material. Shell-side, again SS304 can be used since the cooling liquid is ethanol. A-179 is chosen as main MOC, since the heat exchanger must operate at high pressure.⁷⁰ The TEMA conventions are used in the Aspen Process economic analyser, with specifications as in the 'CostEvaluation' excel file.

6.3 Total costs

6.3.1 Profits and production costs

The profit per hour can be calculated based on the costs of all chemicals, utilities and labour and the profit from the acetic acid sales. An overview of this calculation is shown in Table 11. All chemical costs are an estimation based on data found from literature, as cited in the table. The costs for the LO-CAT system were calculated from literature data³⁹, where it was stated that the total costs were \$0.20 per pound of sulphur removed. This amount was recalculated to €/kg sulphur and the total mass of sulphur removed was calculated based on a sulphur content of 300 ppm in the inlet gas. The costs for utilities are calculated based on the total energy used in the

plant, taking into account the heat integration. An overview of all utilities can be found in Appendices 45 to 47.

The costs for labour and maintenance was estimated as described in Sinnott et al.⁵² It was found that approximately 5 shift positions are needed for a fluid handling continuous process. Since our plant is extremely large, we split it into 10 sites, each needing 5 shift positions, so 50 shift positions for the entire plant were estimated. The salary costs for one shift position was valued at \$50000 per year⁵², which was corrected for inflation and calculated to euro's. A factor of 25% was added to account for supervision and management costs. Another factor of 50% was added to account for salary overhead costs such as company benefits and training. The yearly maintenance costs were taken to equal 3% of the total initial investment costs.⁵² Both these values were calculated from a price per year to a price per hour based on a 24/7 operation year-round.

Table 11: Evaluation of overall profits and costs

Costs				Profits			
Chemicals	Price/ton (€)	Amount (ton/hr)	Price/hr (€)	Sales	Price/ton (€)	Amount (ton/hr)	Price/hr (€)
Toluene ⁷¹	7.00E+02	7.42E-01	5.19E+02	Acetic acid ⁷²	6.50E+02	5.12E+02	3.33E+05
Methanol ^{73,74}	3.80E+02	3.00E+02	1.14E+05				
Limestone ⁷⁵	2.16E+01	2.00E+02	4.33E+03				
Water ⁷⁶	3.00E-01	4.76E+03	1.43E+03				
LO-CAT system ³⁹	Price/kg (€)	Amount (kg/hr)	Price/hr (€)				
Total	3.80E-01	5.09E+04	1.94E+04				
Utilities ⁷⁷	Price/kwh	kW (= kwh/hr)	Price/hr (€)				
Total	6.14E-02	2.00E+06	1.23E+05				
Workers ⁵²	Number of shifts	Price per shift (€/hr)	Price/hr (€)				
Labour	5.00E+01	9.62E+00	4.81E+02				
Maintenance	-	-	5.96E+03				
Total			2.81E+05				3.33E+05
Profit (€/hr)			5.19E+04				

It should be noted that this calculation is a very rough approximation, as all prices stated are fluctuating and thus difficult to estimate. Additionally, possible profits from the sale of side-products such as gypsum and elemental sulphur were not taken into account. Costs for insurance, interest, taxes, license fees etc. were also ignored. Moreover, the amount of acetic acid produced in this process is unrealistically large, which can lead to a large influence on the global market if the plant would actually be built. Global Acetic Acid market was valued at 12,124.3 kilotons in 2014 and our process generates 4484.7 kilotons per year, thus increasing the production by 37%.⁷⁸ Nevertheless, the market for acetic acid has steadily increased over the past few years and is expected to grow even further. As already mentioned in the introduction, acetic acid is a key building block for the production of numerous chemicals and is thus in high demand. Additionally, the designed process could be considered more 'green' than conventional processes, due to its use of a waste CO feedstream and high degree of heat integration. This sustainable aspect would also increase the price of the product.

6.3.2 Investment costs

The Aspen Economic Analyser gives an estimate for the equipment costs, based on the material- and manpower costs. These numbers include costs for equipment & setting, piping, civil fees, steel, instrumentation, electricity, insulation and paint. The costs are all corrected via an inflation factor of 1.038, obtained from the yearly average inflation in the Netherlands since 2014.⁷⁹ To obtain the total installation costs, installation Lang factors as found from Sinnott et al.⁵² are applied over the equipment & setting costs obtained from the economic analyser. The installation factors used for this calculation can be found in Appendix 44. These factors are used to include all extra costs, such as equipment erection (setting), piping, instrumentation and electrical costs. For distillation columns, also the condenser and reboiler are included.

Some equipment was ignored in the estimation of the investment costs, such as storage vessels, back-up parts and a condenser for the final acetic acid product. The purchasing costs of the cooling ethanol, all packing materials and all catalysts were also ignored. For the Acetica™ process, this choice can be endorsed by literature data, as the catalyst costs for the literature process amount for less than 1% of the total costs for the process.⁸ For the COSORB™ Copper complex and the LO-CAT™ chelating agent, no such data could be found. Some large parts of equipment were also ignored in the investment costs, such as the electrostatic precipitator, bio treatment unit and incinerator. This choice was mainly made because it was very difficult to obtain reliable data on their costs, as none of these parts were modelled in Aspen.

The final estimation was not adjusted for these ignored initial investment costs. Because the setting costs are already included in the value obtained from the economic analyser, the estimated equipment costs will be on the high side. A significant portion of the equipment costs also originates from expensive coatings, such as the Hastelloy used. These costs do not have to be included in the Lang factors. It is also noted that the total amounts as calculated by the economic analyser, without applying Lang factors, are significantly lower. Therefore, it was considered acceptable to ignore all additional costs mentioned above. The overall estimation should give a reliable impression of the order of magnitude of the initial investment needed. All calculated numbers can be found in Appendix 43 and a more elaborate overview is given in the excel file 'CostEvaluation.xls'.

The total investment as found from the analysis described above is approximately €1.8 billion. As described previously, the profit per hour is approximately €52 thousand. By multiplying this with 24*365, the profit per year was calculated to be approximately €454 million. Dividing the initial investment costs by this yearly profit gives a timespan for earning back the investment of 3.96 years. This is well below the maximum value of 5 years, which means that a margin is available for unforeseen costs. For the scenario in which a process on a smaller scale would be built, the initial investment and yearly profit would both go down. However, because not all cost factors scale linearly with the process size, it is improbable that the same result would be obtained for a

scaled-down project. As it is unlikely that €1.8 milliard could be collected as initial investment costs, a thorough cost analysis would have to be performed again for the smaller plant.

7 Conclusion

In this investigation, the aim was to assess a possible process for the synthesis of acetic acid from a steel-mill off-gas stream. To purify the off-gas stream, the LO-CAT™, limestone wet scrubber and COSORB™ processes were used. The Acetica™ Process was chosen for the carbonylation reaction between CO from the off-gas and purchased methanol. Aspen Plus™ was used to model the process and identify equipment specifications. The results of the simulations indicate that the chosen processes could be well suitable for the desired reaction. However, the large number of assumptions included in this evaluation clearly indicate the need for further research. Other limitations of the models are the absence of all catalysts from the Aspen database and the lack of literature data on the reaction kinetics.

The feed stream obtained from the steel mill is extraordinarily large, leading to the need for high initial investment costs, large equipment and a lot of energy. In retrospect, it might have been more realistic to split the stream and build a number of parallel plants to utilise the entire CO-content. This would have made the potential for downscaling the process larger and the actual implementation of the process more conceivable. Nevertheless, the process model proved to be efficient and profitable even at this scale. An overall acetic acid yield of 97% from methanol could be obtained in high purity and the investment costs would be returned after less than 4 years. Notwithstanding the decreased value caused by a 36% growth of its global production, acetic acid is high in demand and the market is still expected to grow substantially in the coming decade.

Despite its exploratory nature, this project offers some insight into opportunities for the use of the Acetica™ process in acetic acid production from steel mill off-gas. An implication hereof is a reduction in the environmental costs of the steel production, since its off-gas stream would be treated more effectively. In the current climate of sustainable development, this is considered highly valuable. Further research should focus on an accurate scaling of the bubble column reactor. Additionally, investigation and experimentation into the reaction kinetics and Acetica™ catalyst stability is highly recommended. This would enable a more exact simulation of the reactor in Aspen, which would ensure the calculation of accurate energy- and investment costs. Moreover, lab-scale tests on the COSORB™ process might enable the calculation of a more reliable estimation for its energy costs.

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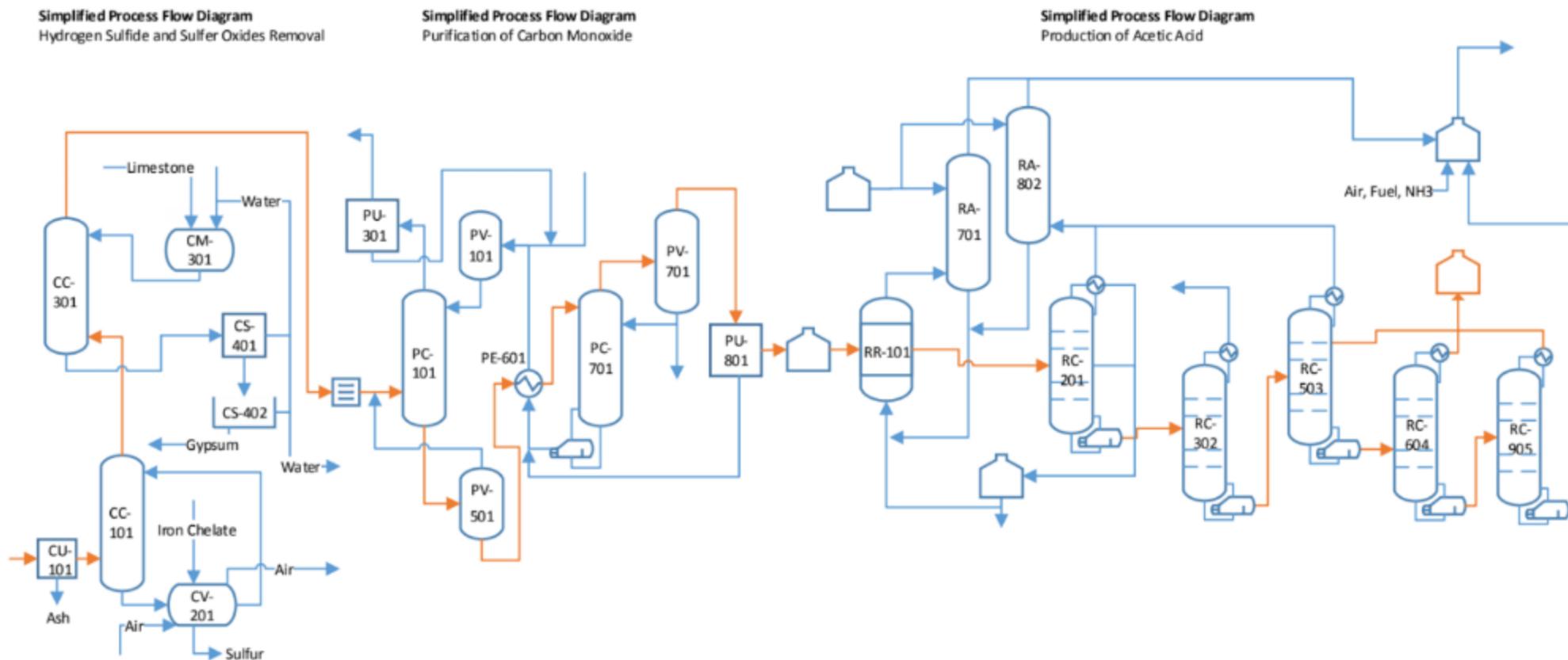
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9 Appendices

Appendices

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1. Process overview



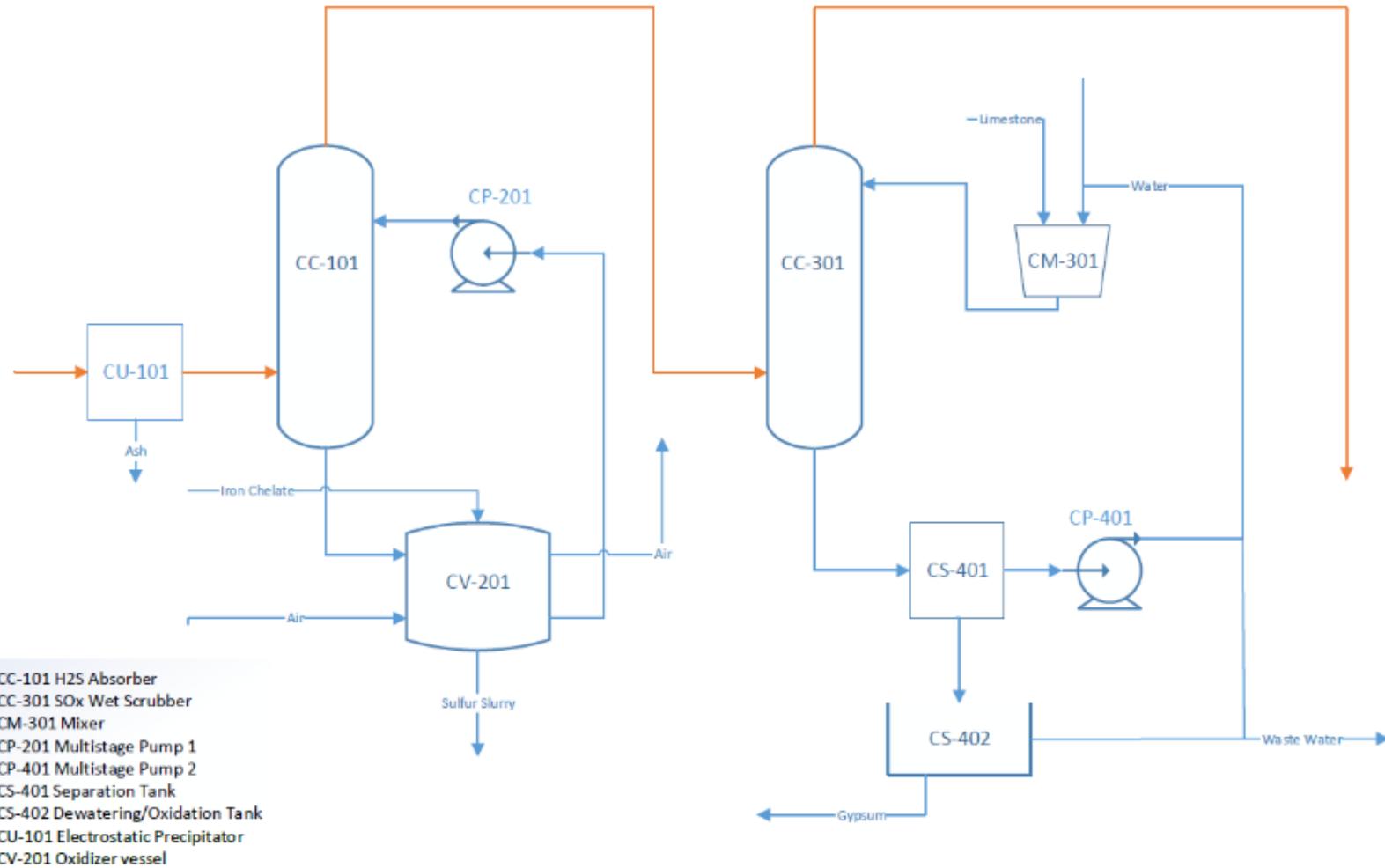
Appendix 1. Process Flow Diagram (PFD) of the whole process, including hydrogen sulfide and sulfur oxides removal, purification of carbon monoxide and production of acetic acid.

2. Process Flow Diagram

2.1 Purification section

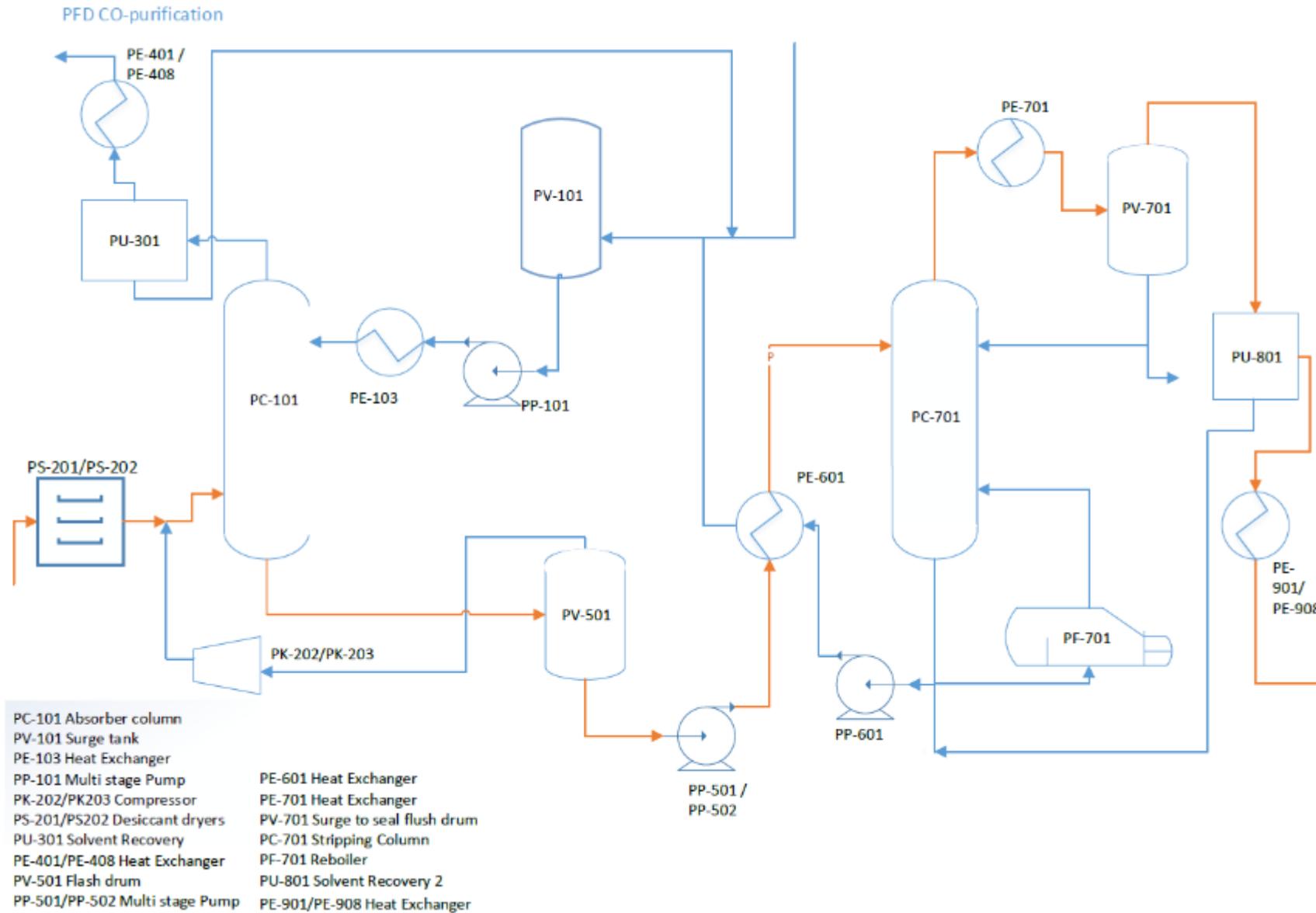
2.1.1 Hydrogen sulfide and sulfur oxides removal

PFD H₂S + SO_x Removal



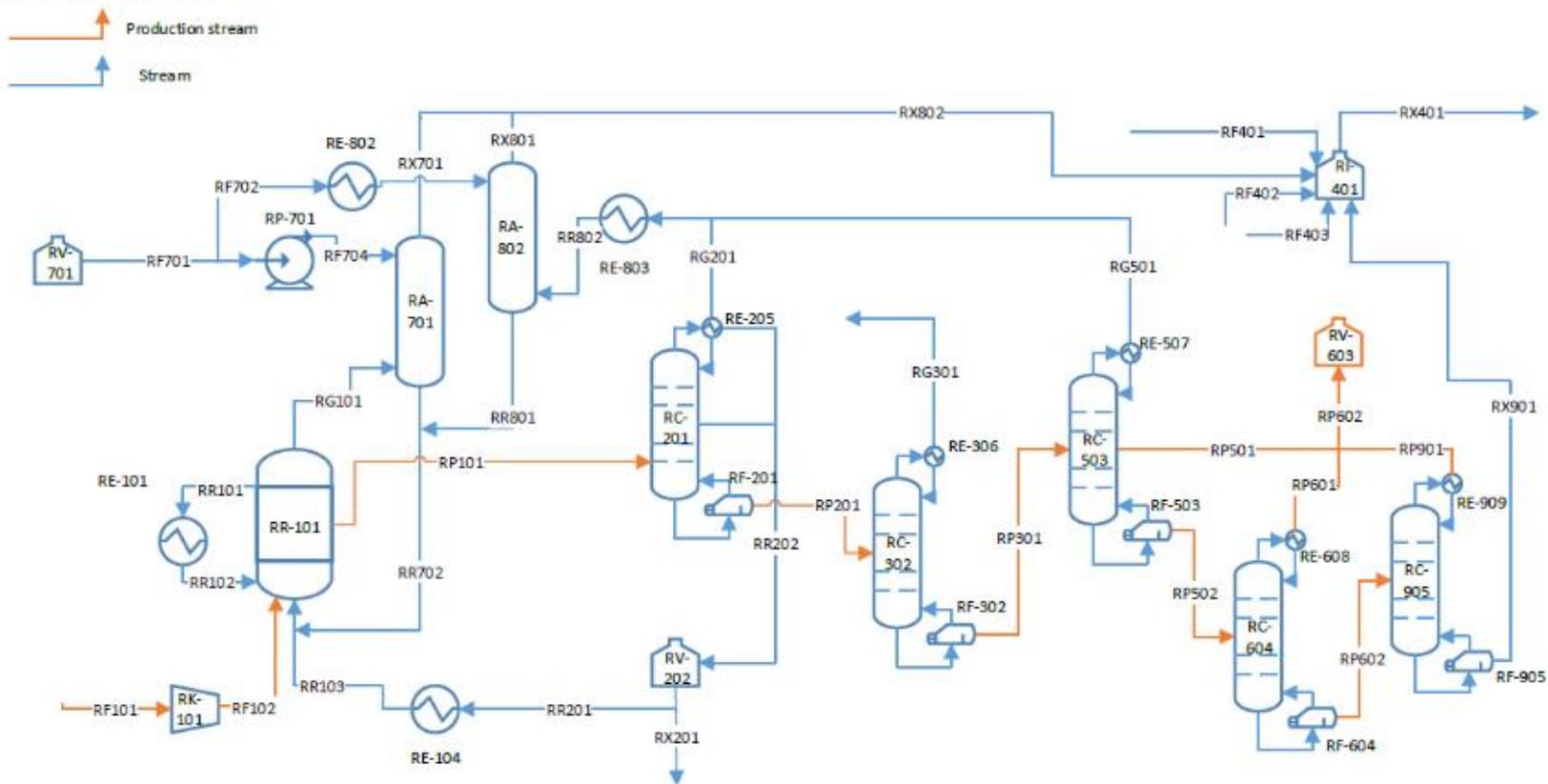
Appendix 2. Process flow diagram: hydrogen sulfide and sulfur oxides removal

2.1.2 Carbon monoxide purification



Appendix 3. Process flow diagram: carbon monoxide purification

Process Flow Diagram
Production of Acetic Acid (AA)



Legend

RA-701 High Pressure Absorber	RV-701: Methanol Drum	RE-101 Heat Exchanger
RA-802 Low Pressure Absorber	RV-202: Collecting Drum	RE-802 Heat Exchanger
RK-101 Multistage Compressor	RV-603: AA Drum	RE-803 Heat Exchanger
RC-201 Flush Column	RP-701 Hydraulic pump	RE-104 Heat Exchanger
RC-302 Dehydration Column	RR-101 Bubble-Column Reactor	RE-205 Condenser RC-201
RC-503 Finishing Column	RF-201 Reboiler RC-201	RE-306 Condenser RC-302
RC-604 Second Finishing Column	RF-302 Reboiler RC-302	RE-507 Condenser RC-503
RC-905 Third Finishing Column	RF-503 Reboiler RC-503	RE-608 Condenser RC-604
RI-401: Incinerator	RF-604 Reboiler RC-604	RE-909 Condenser RC-905
	RF-905 Reboiler RC-905	

Appendix 4. Process Flow Diagram of acetic acid production

Supervisors: J. Winkelman, W. Leusman & K. Zuur

3. Equipment specifications

3.1 Reactor

Appendix 5. Gas flows used for calculation of reactor dimensions.

Gas velocity used (m/s)	0.05	
	Gaseous product	Gaseous inlet
Flow (m ³ /hr)	3.4E+06	8.2E+06
Flow (m ³ /s)	9.3E-01	2.3E+09
Area (m ²)	1.9E+09	4.5E+09
Diameter (m)	4.9E+09	7.6E+09
Length (m)	2.4E+09	3.8E+09
Volume (m ³)	4.5E+09	1.7E+08

3.2 Columns

Appendix 6. Results from column sizing for the reaction section. Diameter values obtained from Aspen tray rating calculations are compared with values determined by hand described in section 3.2.2. In the calculation by hand, the maximum vapor rate and the densities from vapor and liquid are obtained from the Aspen model as well. Finding that the two methods gave similar diameters made it comfortable to use the hand-calculations for the other remainder of columns as seen below.

	RA-701	RA-802	RC-201	RC-302	RC-503	RC-604	RC-905
Feed stage	-	-	2.20E+01	2.30E+01	1.00E+00	2.70E+01	2.70E+01
Side product mass flow (kg/hr)	-	-	7.30E+04	-	1.30E+05	-	-
Side product stage	-	-	2.00E+00	-	1.70E+01	-	-
Reflux ratio	-	-	9.00E+00	1.90E+01	4.50E+00	1.00E+00	1.00E+00
Boil-up ratio	-	-	3.60E+00	1.00E-02	6.00E+00	1.00E+01	1.50E+01
Maximum vapor rate from Aspen (kmol/h)	5.37E+03	6.27E+02	7.19E+04	1.11E+04	3.89E+04	1.08E+04	1.87E+03
Number of columns	1.00E+00	1.00E+00	5.00E+00	3.00E+00	1.00E+01	3.00E+00	1.00E+00
Vapor rate per column (kmol/h)	5.37E+03	6.27E+02	1.44E+04	3.70E+03	3.89E+03	3.60E+03	1.87E+03
Vapor rate per column (kmol/s)	1.49E+00	1.70E-01	3.99E+00	1.03E+00	1.08E+00	1.00E+00	5.20E-01
Density vapor (kmol/cum)	2.35E+00	4.00E-02	1.28E+00	9.00E-02	3.00E-02	3.00E-02	3.00E-02
Density liquid (kmol/cum)	2.20E+01	2.21E+01	1.12E+01	1.62E+01	1.57E+01	1.57E+01	1.53E+01
Tray spacing (m)	7.90E-01						
Maximum allowable vapor velocity (m/s)	1.70E-01	1.36E+00	1.70E-01	7.90E-01	1.33E+00	1.33E+00	1.31E+00
Number of stages	1.70E+01	1.50E+01	3.00E+01	2.30E+01	3.00E+01	3.00E+01	3.00E+01
Diameter (m)	2.17E+00	1.96E+00	4.89E+00	4.27E+00	5.73E+00	5.52E+00	4.01E+00
Aspen tray rating Diameter (m)	3.03E+00	-	-	-	5.05E+00	4.60E+00	-
Column height (m)	1.34E+01	1.19E+01	2.37E+01	1.82E+01	2.37E+01	2.37E+01	2.37E+01

Appendix 7. Results from column sizing for the purification section. Diameter values obtained from Aspen tray rating calculations are compared with values determined by hand. In the calculation by hand, the maximum vapor rate and the densities from vapor and liquid are obtained from the Aspen model.

	CC-101	CC-301	PC-101	PC-701
Feed stage	-	-	-	-
Side product mass flow (kg/hr)	-	-	-	-
Side product stage	-	-	-	-
Reflux ratio	-	-	-	3.20E+01
Boil-up ratio	-	-	-	2.50E+00
Maximum vapor rate from Aspen (kmol/h)	4.79E+04	4.79E+04	4.71E+04	2.10E+04
Number of columns	1.00E+01	1.00E+01	1.50E+01	8.00E+00
Vapor rate per column (kmol/h)	4.79E+03	4.79E+03	3.14E+03	2.62E+03
Vapor rate per column (kmol/s)	1.33E+00	1.33E+00	8.70E-01	7.30E-01
Density vapor (kmol/cum)	4.03E-02	4.03E-02	9.00E-02	1.00E-01
Density liquid (kmol/cum)	4.62E+04	5.10E+05	9.41E+00	8.90E+00
Tray spacing (m)	7.90E-01	7.90E-01	7.90E-01	7.90E-01
Maximum allowable vapor velocity (m/s)	2.02E+00	2.12E+00	6.20E-01	5.60E-01
Number of stages	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Diameter (m)	4.57E+00	4.45E+00	4.56E+00	4.07E+00
Aspen tray rating Diameter (m)				
Column height (m)	1.58E+01	1.58E+01	1.58E+01	1.58E+01

Appendix 8. Utilities used for designing heat exchangers. All calculations can be found in a separate excel file.

Utilities									
Name	Number of heat exchange needed (par)	Stream Tube / Shell	T_Hot_In	T_Hot_Out	T_Cold_In	T_Cold_Out	Q (kW)	U (estimated by aspen) (W/(m2.C))	Exchange area per heat exchange (estimated) (m2)
PE-101	24	Ethanol tube / Gas shell	9.30E+01	2.40E+01	-5.00E+01	-4.00E+01	2.88E+04	4.10E+01	2.93E+02
PE-401	24	Lean tube / Feed shell	1.66E+02	1.16E+02	-5.00E+01	2.50E+01	2.08E+04	9.00E+00	6.00E+02
PE-901	24	Lean tube / Feed shell	1.16E+02	9.40E+01	-5.00E+01	2.50E+01	9.53E+03	7.00E+00	4.92E+02
PE-103	18	Ethanol tube / Toluene shell	2.80E+01	2.30E+01	-4.00E+01	-3.20E+01	2.19E+04	3.03E+02	6.60E+01
PE-301 1st	18	Ethanol tube / Waste gas shell	1.30E+01	-5.00E+01	-8.00E+01	-7.20E+01	2.34E+04	1.48E+02	1.68E+02
PE-601 avg.	14	Toluene tube / Toluene+CO shell	1.05E+02	3.00E+01	2.40E+01	9.00E+01	4.06E+05	6.14E+02	4.59E+03
PE-801	24	Toluene tube / Strip gas shell	6.30E+01	5.40E+01	-5.00E+01	3.90E+01	1.50E+04	2.82E+02	4.00E+01
PE-801 1st	16	Ethanol tube / CO gas shell	5.40E+01	-5.00E+01	-7.20E+01	-5.00E+01	6.03E+04	2.30E+02	3.12E+02
RE-803-2	28	Ethanol / Methanol	3.80E+01	1.00E+01	-8.00E+01	-6.70E+01	9.02E+03	5.41E+02	6.00E+00
RE-802	16	Methanol / Ethanol	2.70E+01	1.00E+01	-3.20E+01	-3.20E+01	7.60E+02	5.16E+02	2.00E+00
RE-803-1	14	Ethanol / Methanol	1.13E+02	3.80E+01	-3.20E+01	1.70E+01	9.00E+04	5.51E+02	1.42E+02
RE-104	1	Steam / Recycle stream	1.97E+02	1.81E+02	1.70E+01	1.90E+01	2.11E+03	5.49E+02	2.30E+01
HEXH11	4	Acetic acid / Steam	6.43E+02	1.80E+02	1.18E+02	1.18E+02	7.69E+04	6.63E+02	1.34E+02
CE-101	12	Steam/feed gas	2.00E+02	1.52E+02	2.50E+01	9.00E+01	2.68E+04	1.00E+01	1.98E+03
CE-102	12	Ethanol/feed gas	9.00E+01	2.50E+01	-3.20E+01	-7.00E+00	2.68E+04	2.40E+01	1.26E+03

Appendix 9. Tube side specifications. All calculations can be found in a separate excel file.

Name	Diameter outside (tube) (mm)	L (tube) (m)	Tube thickness (mm)	Flow tube (l/min)	K1	n1	Number of passes	Orientation	Density tube (kg/m ³)	Viscosity (Pa*s)	Jf tube (friction factor)	STREAM	v (tube side) (m/s)	Pressure drop (tube) (N/m ²)	Pressure drop (bar)
PE-101	16	7.8	2.1	8.3E+04	2.2E-01	2.207	1	square	8.8E+02	2.7E-03	1.8E-03	Ethanol 1 bar	7.0E-01	2.0E+03	2.0E-01
PE-401	25	7.8	2.1	1.0E+07	2.2E-01	2.207	1	square	1.3E+00	2.0E-05	1.3E-03	Lean gas 1 bar	2.1E+01	1.1E+03	1.1E-01
PE-901	25	7.8	2.1	4.8E+06	2.2E-01	2.207	1	square	1.5E+00	1.7E-05	1.3E-03	COPURE 1 bar	1.2E+01	4.3E+02	4.3E-02
PE-103	25	3.7	2.1	8.4E+04	2.2E-01	2.207	1	square	8.7E+02	2.7E-03	1.0E-03	Ethanol 1 bar	1.0E+00	6.1E+02	6.1E-02
PE-301 1st	19	7.8	2.1	8.0E+04	2.2E-01	2.207	1	square	9.1E+02	3.1E-03	1.2E-03	Ethanol 1 bar	1.2E+00	3.3E+03	3.3E-01
PE-601 avg.	16	15.6	2.1	5.2E+05	2.2E-01	2.207	1	square	3.3E+02	5.8E-04	2.0E-03	Toluene 1 bar	9.7E-01	3.3E+03	3.3E-01
PRE-801	16	7.8	2.1	6.9E+03	2.2E-01	2.207	1	square	9.3E+02	5.8E-04	1.8E-03	Toluene 1 bar	4.3E-01	8.0E+02	8.0E-02
PE-801 1st	16	7.8	2.1	8.1E+04	2.2E-01	2.207	1	square	9.0E+02	3.1E-03	1.2E-03	Ethanol 1 bar	9.7E-01	2.7E+03	2.7E-01
RE803-2	50	6.1	2.1	2.0E+04	2.2E-01	2.207	1	square	9.3E+02	3.1E-03	1.2E-03	Ethanol 1 bar	1.1E+00	7.6E+02	7.6E-02
RE802	25	4.9	2.1	1.2E+03	2.2E-01	2.207	1	square	8.0E+02	5.5E-04	1.0E-03	Methanol 1 bar	7.6E-01	4.3E+02	4.3E-02
RE803-1	19	6.1	2.1	5.3E+04	2.2E-01	2.207	1	square	8.6E+02	3.0E-03	1.2E-03	Ethanol 1 bar	9.4E-01	1.5E+03	1.5E-01
RE104	19	6.1	2.1	2.8E+03	2.2E-01	2.207	1	square	6.5E+02	4.3E-04	1.0E-03	Steam 40 bar	4.4E+00	2.1E+04	2.1E+00
(HEXH11)	19	7.8	2.1	1.3E+04	2.2E-01	2.207	1	square	9.5E+02	4.6E-04	1.0E-03	AA	1.1E+00	2.3E+03	2.3E-01
CE-101	25	7.8	2.1	7.4E+06	2.2E-01	2.207	1	square	2.4E+00	5.0E-04	1.3E-03	Steam 5 bar	9.3E+00	4.0E+02	4.0E-02
CE-102	16	15.6	2.1	3.3E+04	1.6E-01	2.263	4	square	8.6E+02	2.8E-03	1.0E-03	Ethanol 1 bar	1.0E+00	4.9E+03	4.9E-01

Appendix 10. Shell side specifications. All calculations can be found in a separate excel file.

Name	Baffle spacing (mm)	Flow shell (l/min)	Shell thickness (mm)	Density shell (kg/m ³)	Viscosity shell side (Pa*s)	Jf shell (friction factor)	STREAM	<u>v (shell side) (m/s)</u> <u>(must be below 1m/s)</u>	Pressure drop (shell) (N/m ²)	Pressure drop (bar)
PE-101	2500	8.2E+06	6.4	2.5E+00	2.0E-05	2.0E-01	Feed gas 3 bar	1.7E+01	7.9E+04	7.9E-01
PE-401	2000	9.7E+06	6.4	2.1E+00	2.0E-05	1.8E-01	Feed gas 3 bar	1.4E+01	6.0E+04	6.0E-01
PE-901	1800	8.6E+06	6.4	2.4E+00	2.0E-05	2.0E-01	Feed gas 3 bar	1.6E+01	8.9E+04	8.9E-01
PE-103	2000	2.0E+05	6.4	8.6E+02	5.8E-04	2.0E-01	Toluene 3 bar	7.7E-01	1.9E+04	1.9E-01
PE-301 1st	2000	6.5E+06	6.4	2.3E+00	2.0E-05	1.5E-01	Lean gas 2 bar	2.7E+01	1.2E+05	1.2E+00
PE-601 avg.	5000	3.3E+06	6.4	5.5E+01	3.9E-04	2.8E-01	Toluene+CO gas 3 bar	2.3E+00	1.1E+05	1.1E+00
PRE-801	3900	9.2E+06	6.4	1.5E+00	1.9E-05	2.6E-01	CO gas 1 bar	3.0E+01	5.0E+04	5.0E-01
PE-801 1st	3500	8.4E+06	6.4	1.6E+00	1.9E-05	2.7E-01	CO gas 1 bar	1.8E+01	5.7E+04	5.7E-01
RE803-2	2500	3.1E+05	6.4	2.7E+01	1.4E-05	2.2E+01	AA	1.5E+00	6.8E+04	6.8E-01
RE802	2000	5.3E+04	7.9	8.6E+02	2.7E-03	2.8E-01	Ethanol 1 bar	1.3E+00	1.7E+04	1.7E-01
RE803-1	2500	5.6E+06	7.9	1.5E+00	1.4E-05	2.2E-01	AA	2.3E+01	5.3E+04	5.3E-01
RE104	2000	5.6E+03	7.9	8.1E+02	2.7E-03	2.8E-01	Ethanol 1 bar	9.2E-01	3.3E+04	3.3E-01
(HEXHI1)	2300	1.4E+06	7.9	2.4E+00	2.2E-05	1.9E-01	Steam 10 bar	2.5E+01	1.1E+05	1.1E+00
CE-101	3500	2.0E+07	7.9	1.0E+00	2.0E-05	2.0E-01	Feed gas 1 bar	2.0E+01	5.9E+04	5.9E-01
CE-102	3500	2.4E+07	7.9	8.5E-01	2.0E-05	2.0E-01	Feed gas 1 bar	4.9E+01	4.6E+05	4.6E+00

Appendix 11. Pump specifications.

Pump	ΔP Heat Exchanger (bar)	Total ΔP (bar)	Flow rate (m ³ /h)	Power (kW)	Head (m)
PP-101	1.9E-01	2.2E+00	3.2E+03	9.3E+02	2.6E+01
PP-102	3.3E-01	3.3E-01	3.1E+04	3.6E+02	1.0E+01
PP-103	2.0E-01	2.0E-01	5.0E+03	3.5E+01	2.3E+00
PP-301	7.6E-02	8.0E-02	1.2E+03	3.2E+00	8.4E-01
PP-502*	1.1E+00*	1.1E+00*	2.0E+05*	7.7E+03*	2.1E+02*
PP-801	2.7E-01	2.7E-01	4.9E+03	4.6E+01	3.0E+00
RP-701	0.0E+00	5.9E+01	3.1E+02	6.3E+02	7.6E+02
RP-102	0.0E+00	2.0E+01	1.4E+02	9.7E+01	2.6E+02

*not realistic

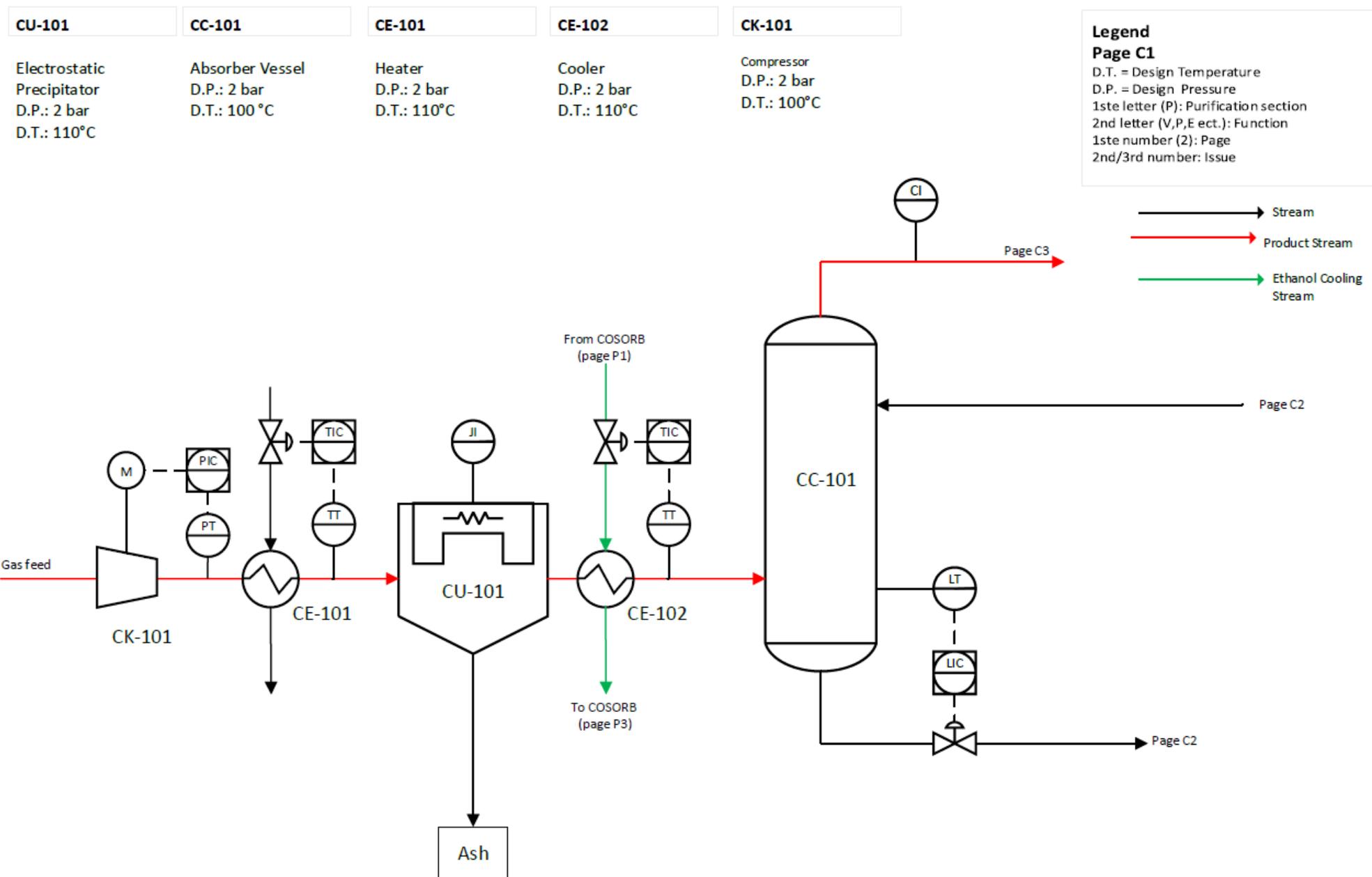
Appendix 12. Compressor specifications.

Compressor	Total ΔP (bar)	Power (kW)	Flow rate (m ³ /h)	Discharge temperature (°C)
CK-101	1.0E+00	3.6E+04	7.5E+05	2.5E+01
PK-202	2.0E+00	3.8E+02	7.8E+03	1.4E+02
PK-204	2.0E+00	5.9E+04	5.8E+05	1.7E+02
PK-205	6.0E-01	1.8E+04	5.8E+05	1.2E+02
PK-206 (=PK-901)	8.9E-01	2.6E+04	5.8E+05	9.4E+01
RK-101/102/103/104	6.1E+01	2.3E+03	1.4E+02	1.8E+02

4. P&ID's and control

4.1 Purification section

4.1.1 *Hydrogen sulfide and sulfur oxides removal*

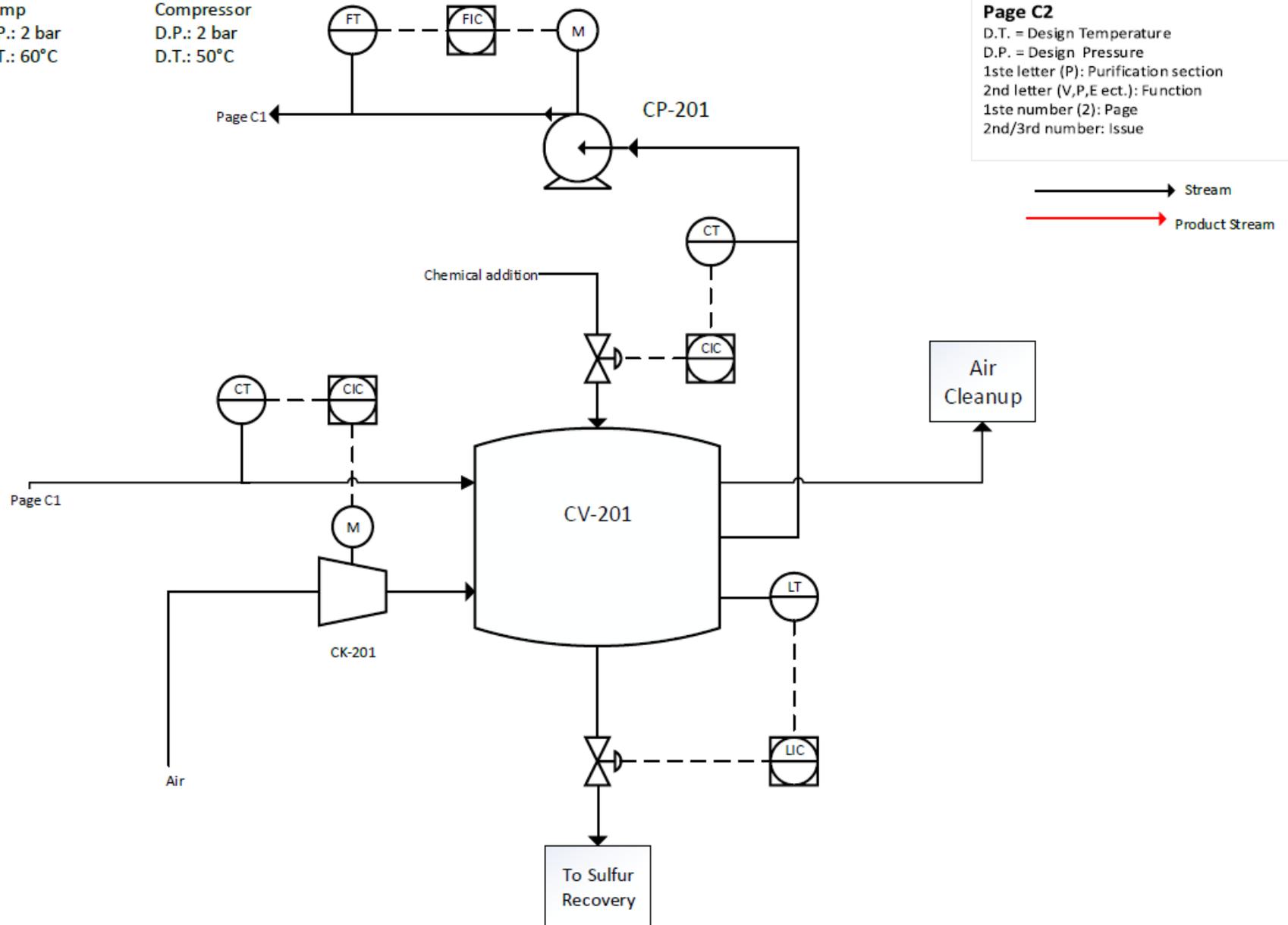


Appendix 13. P&ID Page C1: electrostatic precipitator and absorber vessel. Cooling ethanol from the COSORB process is used to cool down one of the streams.

Supervisors: J. Winkelman, W. Leusman & K. Zuur

CV-201	CP-201	CK-201
Oxidizer Vessel	Pump	Compressor
D.P.: 2 bar	D.P.: 2 bar	D.P.: 2 bar
D.T.: 60 °C	D.T.: 60 °C	D.T.: 50 °C

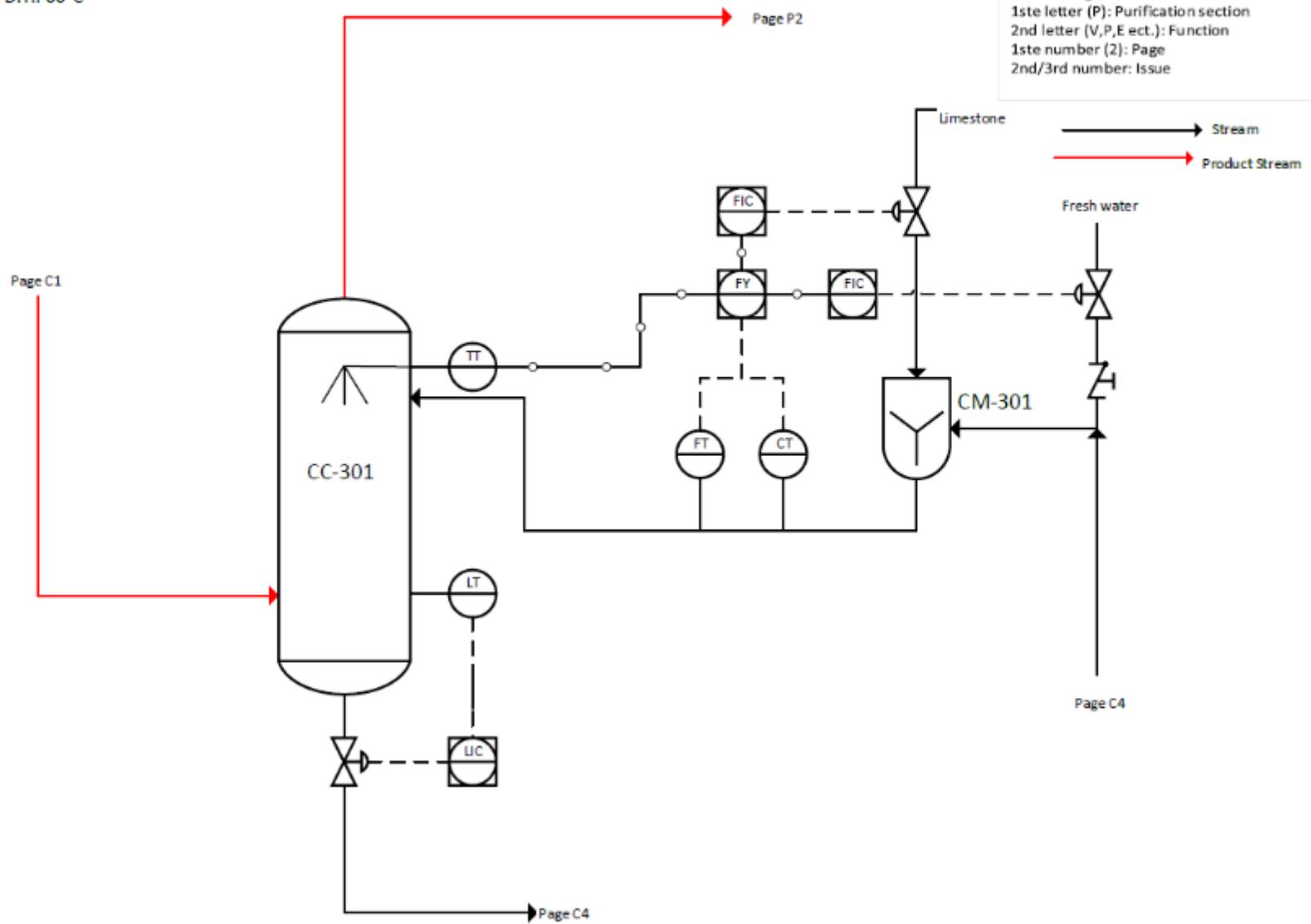
Legend
Page C2
 D.T. = Design Temperature
 D.P. = Design Pressure
 1st letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1st number (2): Page
 2nd/3rd number: Issue



Appendix 14. P&ID Page C2: oxidizer vessel.

CC-301	CM-301
Wet Scrubber	Mixer
D.P.: 2 bar	D.P.: 2 bar
D.T.: 80 °C	D.T.: 60°C

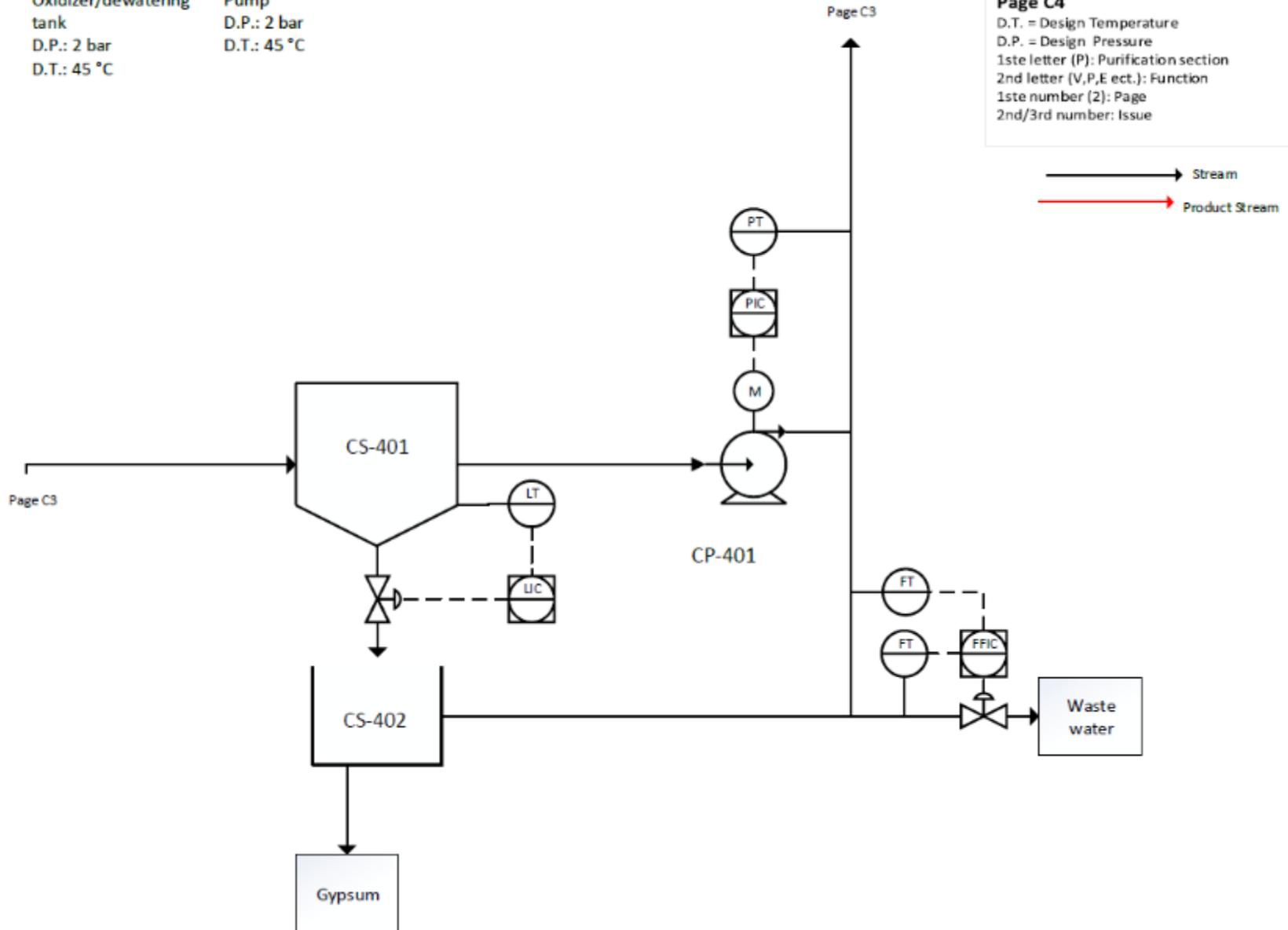
Legend
Page C3
 D.T. = Design Temperature
 D.P. = Design Pressure
 1ste letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1ste number (2): Page
 2nd/3rd number: Issue



Appendix 15. P&ID Page C3: wet scrubber.

CS-401	CS-402	CP-401
Separator tank	Oxidizer/dewatering tank	Pump
D.P.: 2 bar	D.P.: 2 bar	D.P.: 2 bar
D.T.: 45 °C	D.T.: 45 °C	D.T.: 45 °C

Legend
Page C4
D.T. = Design Temperature
D.P. = Design Pressure
1st letter (P): Purification section
2nd letter (V,P,E ect.): Function
1st number (2): Page
2nd/3rd number: Issue



Appendix 16. P&ID Page C4: thickener tank and oxidizer vessel.

4.1.2 Carbon monoxide purification

PC-101
 Column
 (absorption column)
 D.P.: 5 bar
 D.T.: 45 °C

PE-101
 Cooler
 D.P.: 4 bar
 D.T.: 45 °C

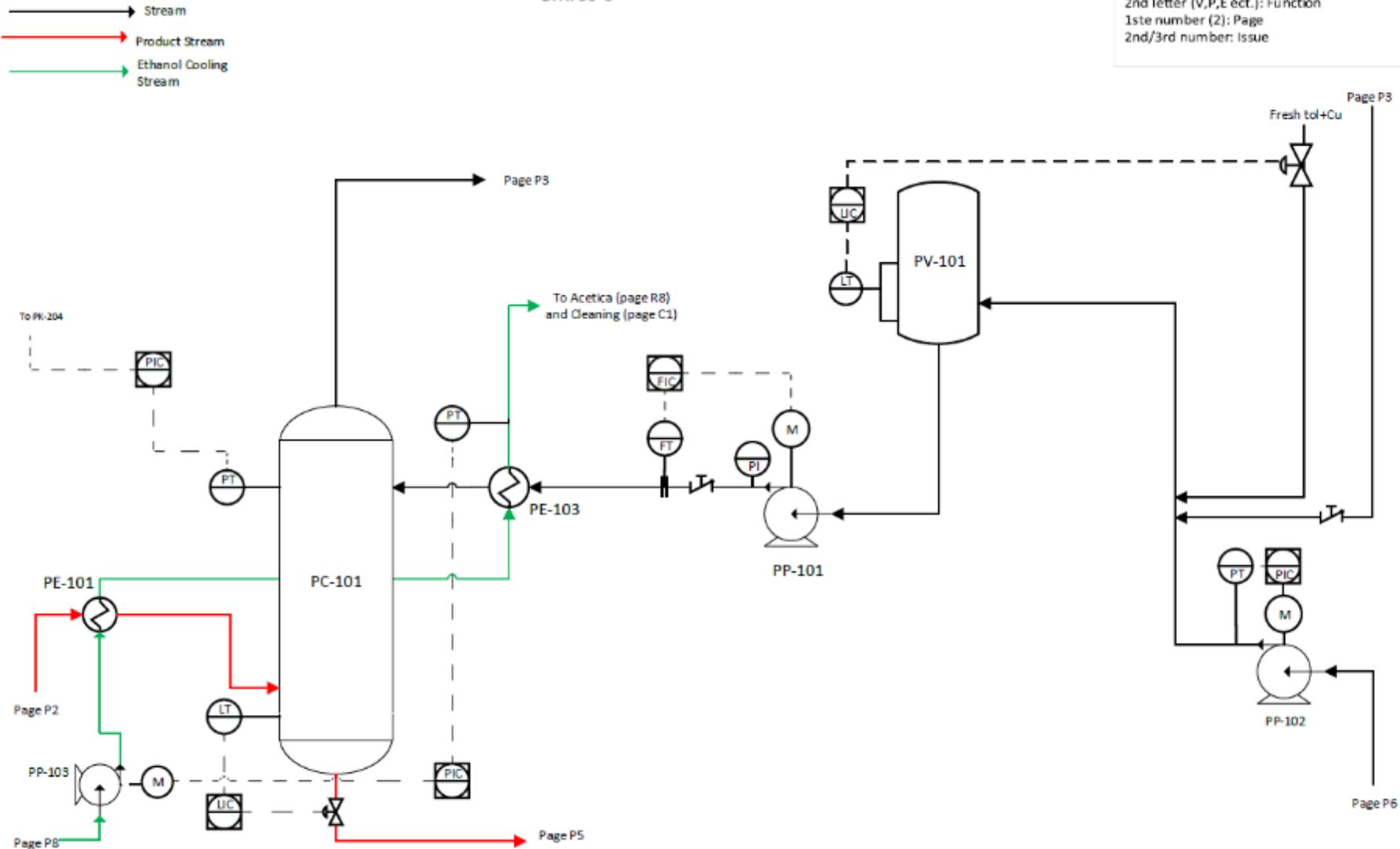
PE-103
 Cooler
 D.P.: 4 bar
 D.T.: 45 °C

**PP-101/
 PP-102**
 Pump
 D.P.: 4 bar
 D.T.: 50 °C

PV-101
 Surge Tank
 D.P.: 4 bar
 D.T.: 50 °C

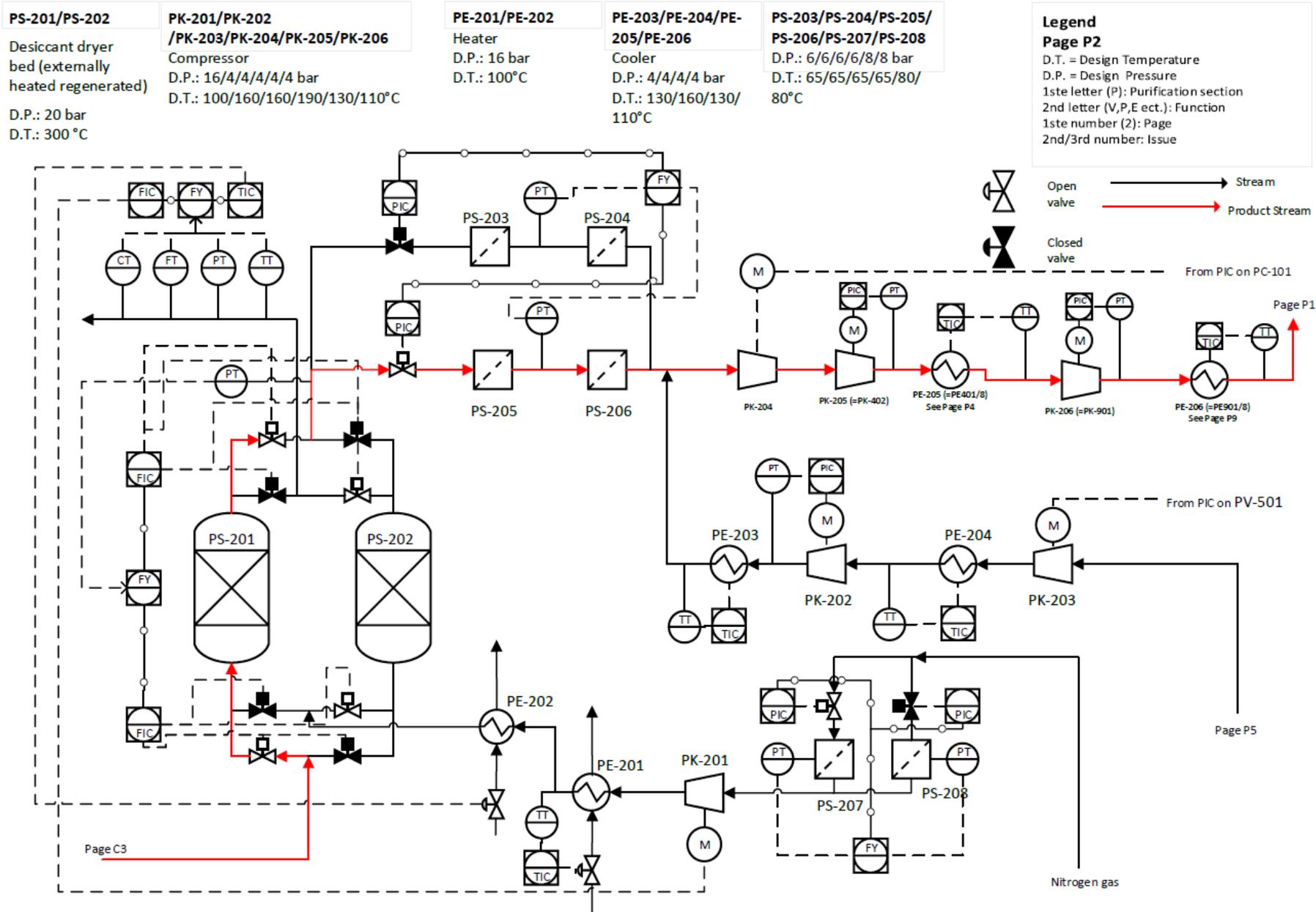
PP-103
 Pump
 D.P.: 2 bar
 D.T.: 45 °C

Legend
Page P1
 D.T. = Design Temperature
 D.P. = Design Pressure
 1ste letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1ste number (2): Page
 2nd/3rd number: Issue



Appendix 17. P&ID Page P1: absorption column. An ethanol stream is used to cool down two streams and a part of the ethanol is subsequently directed to the Acetia process while the other part is led to the Cleaning process.

Supervisors: J. Winkelman, W. Leusman & K. Zuur



Appendix 18. P&ID Page P2: desiccant dryer bed.

**PE-301/PE-302/PE-303/PE-304/PE-305/PE-306/PE-307/
PE-308/PE-309/PE-310**

Cooler D.P.: 3/3/3/3/3/3/3/3/2 bar
D.T.: 40/40/40/40/40/40/40/40/30/30°C

PK-301

Compressor
D.P.: 3 bar
D.T.: 30°C

PV-301

Flash drum
D.P.: 2 bar
D.T.: 30°C

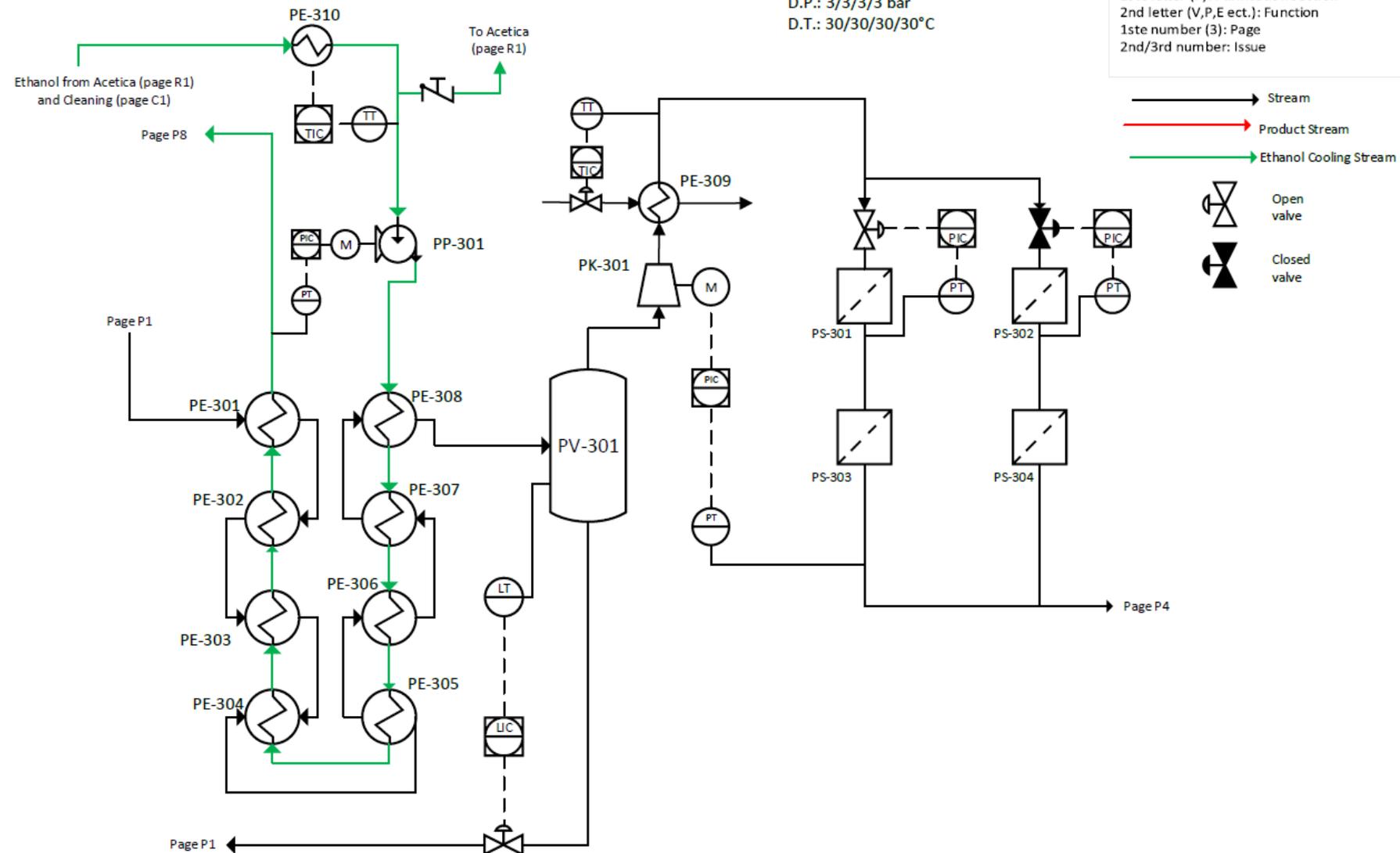
PS-301/PS-302/PS-303/PS-304

Filter (activated carbon)
D.P.: 3/3/3/3 bar
D.T.: 30/30/30/30°C

Legend

Page P3 (PU-301)

D.T. = Design Temperature
D.P. = Design Pressure
1ste letter (P): Purification section
2nd letter (V,P,E ect.): Function
1ste number (3): Page
2nd/3rd number: Issue



Appendix 19. P&ID Page P3: flash drum and filter. An ethanol stream that is warmed up by the Acetia process and Cleaning process is cooled down again. A part of the stream is directed to Acetia again, the rest continues through the COSORB process.

PE-401/PE-402/PE-403/PE-404/PE-405/PE-406/PE-407/PE-408

Heaters (recovery of cold flow)

D.P.: 4/4/4/4/4/4/4/4 bar

D.T.: 180/180/180/180/180/180/180/180°C

PK-401 PK-402

Compressor

Compressor

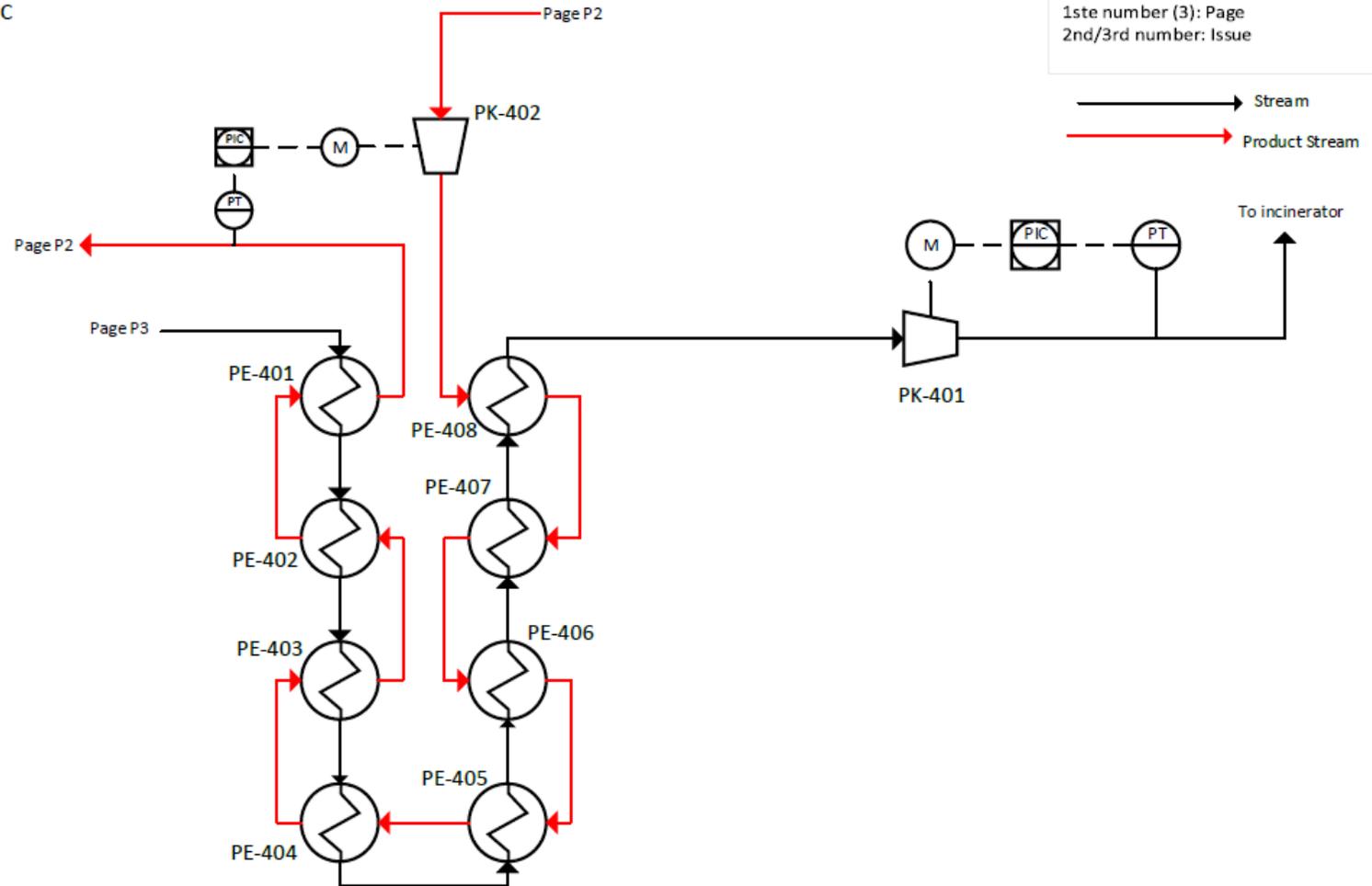
D.P.: 2 bar

D.P.: 4 bar

D.T.: 45°C

D.T.: 180°C

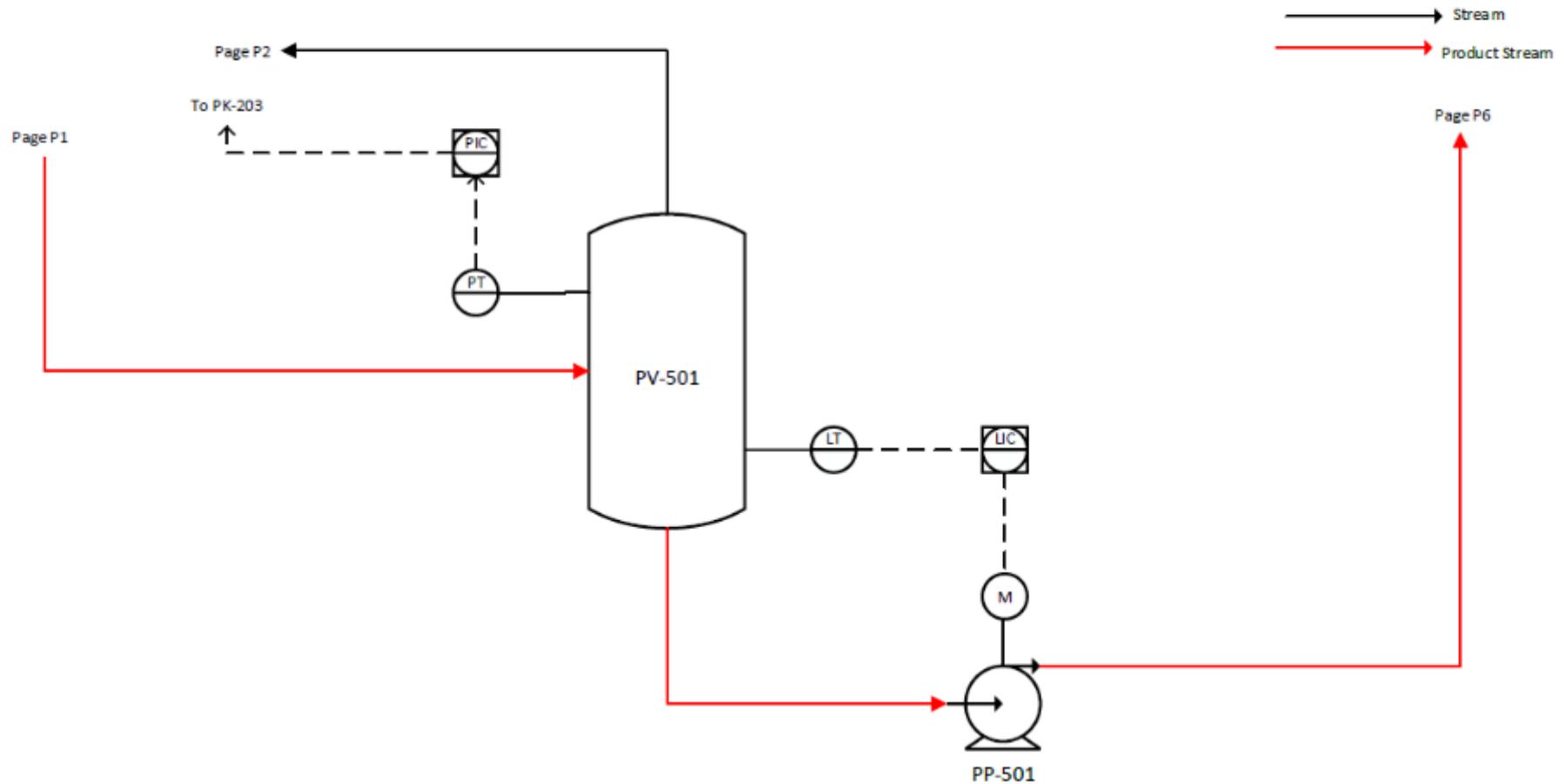
Legend
Page P4
 D.T. = Design Temperature
 D.P. = Design Pressure
 1ste letter (P): Purification section
 2nd letter (D,F,H, ect.): Function
 1ste number (3): Page
 2nd/3rd number: Issue



Appendix 20. P&ID Page P4: heaters.

PV-501	PP-501
Flash drum	Pump
D.P.: 2 bar	D.P.: 3 bar
D.T.: 45 °C	D.T.: 45°C

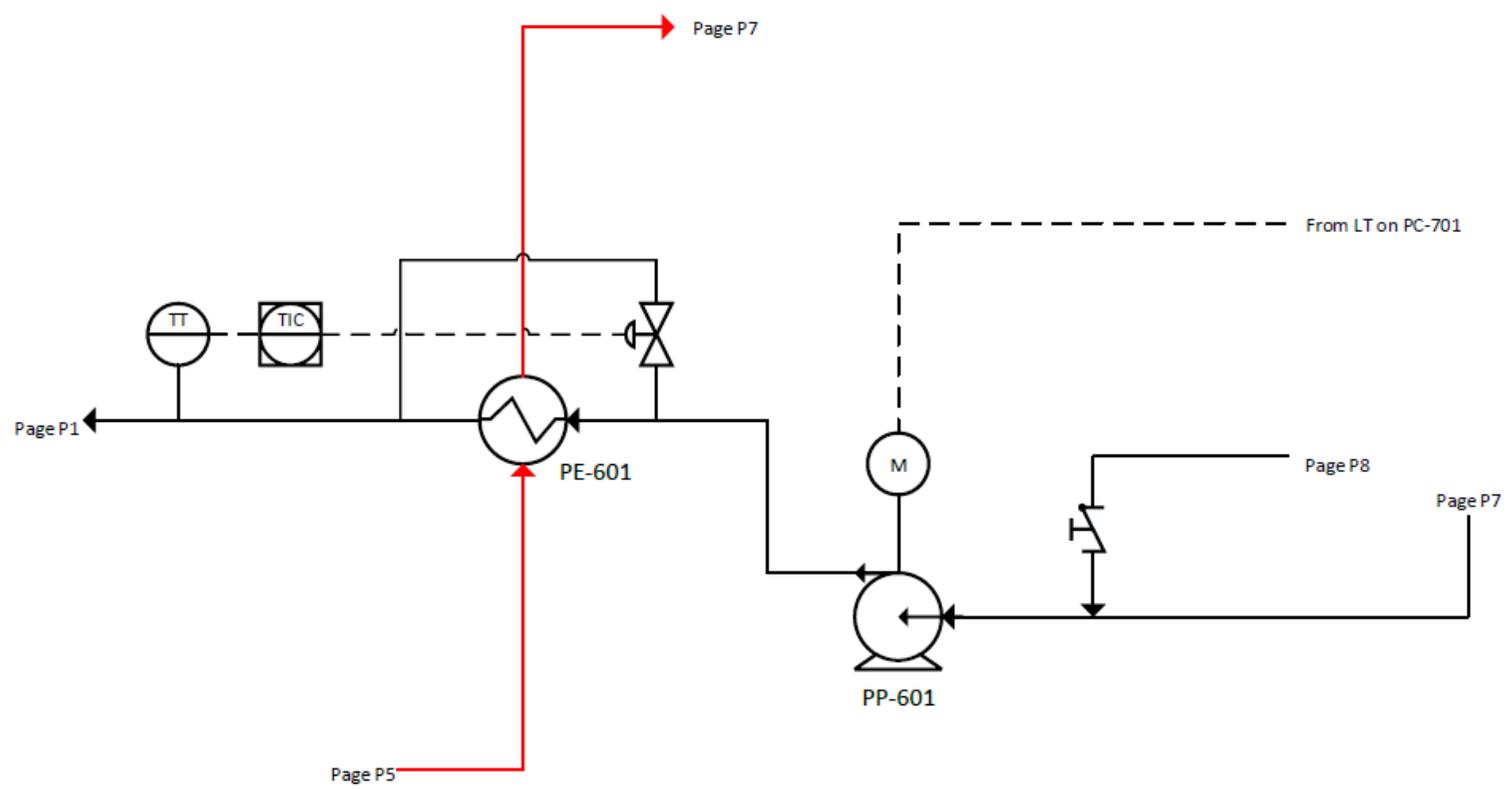
Legend
Page P5
 D.T. = Design Temperature
 D.P. = Design Pressure
 1st letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1st number (3): Page
 2nd/3rd number: Issue



Appendix 21. P&ID Page P5: flash drum.

PE-601	PP-601
Heat exchanger	Pump
D.P.: 3 bar	D.P.: 2 bar
D.T.: 120°C	D.T.: 120°C

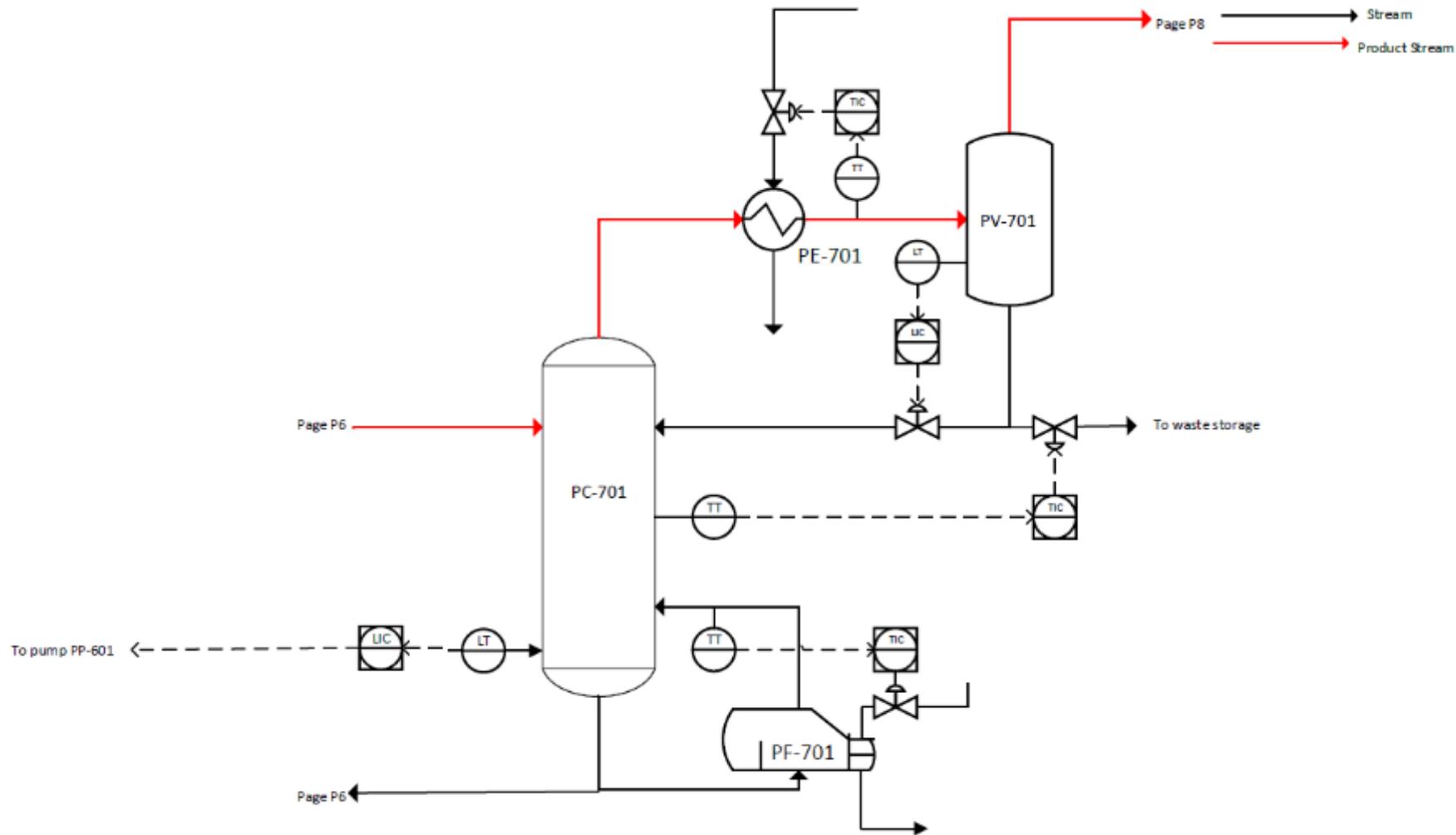
Legend
Page P6
 D.T. = Design Temperature
 D.P. = Design Pressure
 1st letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1st number (2): Page
 2nd/3rd number: Issue



Appendix 22. P&ID Page P6: heat exchanger and pump.

PC-701	PV-701	PE-701	PF-701
Column (Stripper column)	Flash drum	Condenser	Reboiler
D.P.: 2 bar	D.P.: 2 bar	D.P.: 3 bar	D.P.: 2 bar
D.T.: 130 °C	D.T.: 65 °C	D.T.: 130°C	D.T.: 130°C

Legend
Page P7
 D.T. = Design Temperature
 D.P. = Design Pressure
 1ste letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1ste number (2): Page
 2nd/3rd number: Issue



Appendix 23. P&ID Page P7: stripper column.

PE-801/PE-802/PE-803/PE-804/PE-805/PE-806/PE-807/PE-808/PE-809
Cooler
D.P.: 2/2/2/2/2/2/2/2/2 bar
D.T.: 75/75/75/75/75/75/75/75/80°C

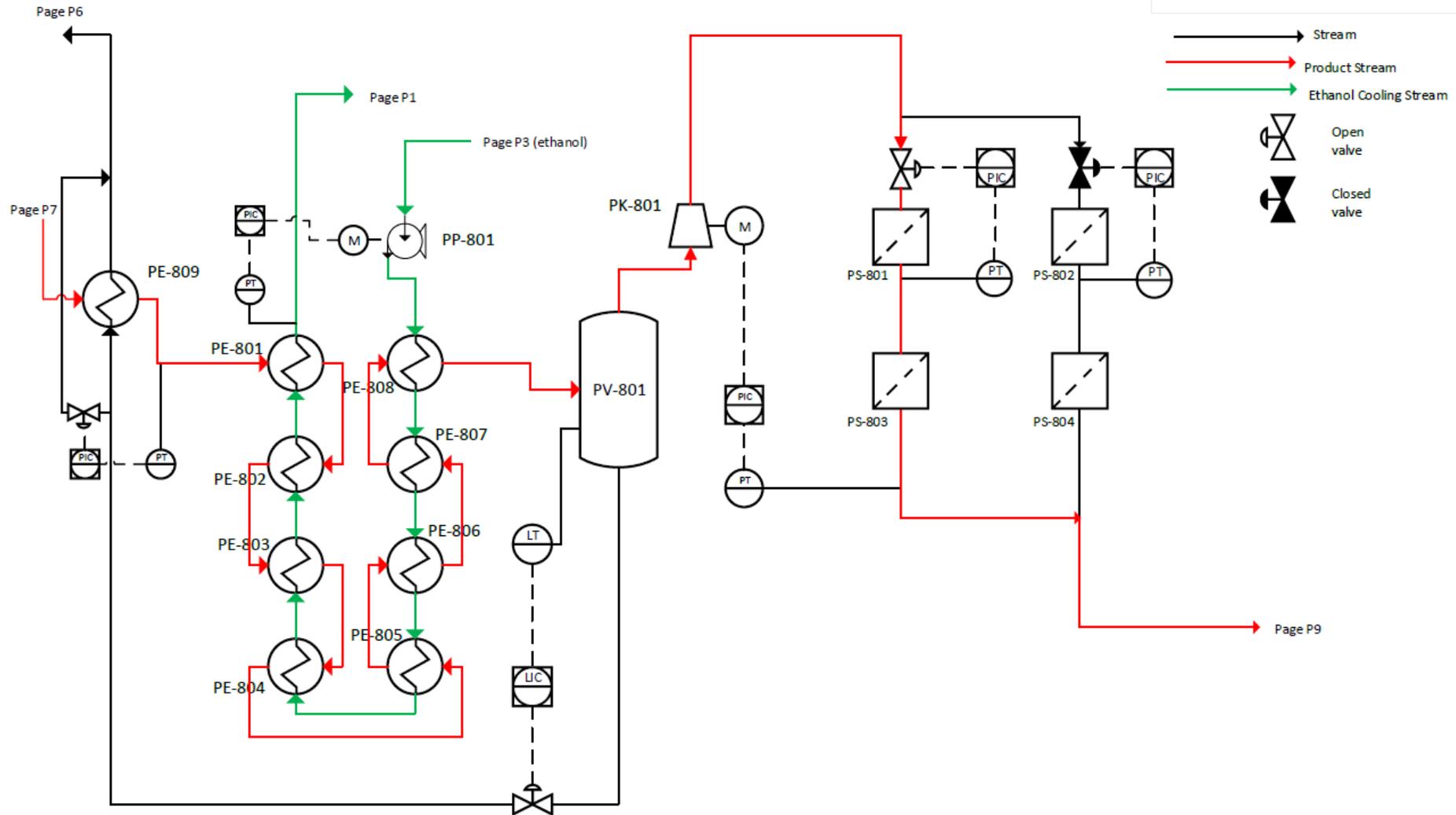
PK-801
Compressor
D.P.: 2 bar
D.T.: 45°C

PV-801
Flash drum
D.P.: 2 bar
D.T.: 45°C

PS-801/PS-802/PS-803/PS-804
Filter (activated carbon)
D.P.: 4/4/4/4 bar
D.T.: 45/45/45/45°C

PP-801
Pump
D.P.: 2 bar
D.T.: 45°C

Legend
Page P8 (PU-801)
D.T. = Design Temperature
D.P. = Design Pressure
1st letter (P): Purification section
2nd letter (V,P,E ect.): Function
1st number (3): Page
2nd/3rd number: Issue



Appendix 24. P&ID Page P8: flash drum and filter.

PE-901/PE-902/PE-903/PE-904/PE-905/PE-906/PE-907/PE-908

Heaters (recovery of cold flow)

D.P.: 4/4/4/4/4/4/4/4 bar

D.T.: 140/140/140/140/140/140/140/140°C

PK-901/PK-902

Compressor

D.P.: 3/2 bar

D.T.: 110/45°C

Legend

Page P9

D.T. = Design Temperature

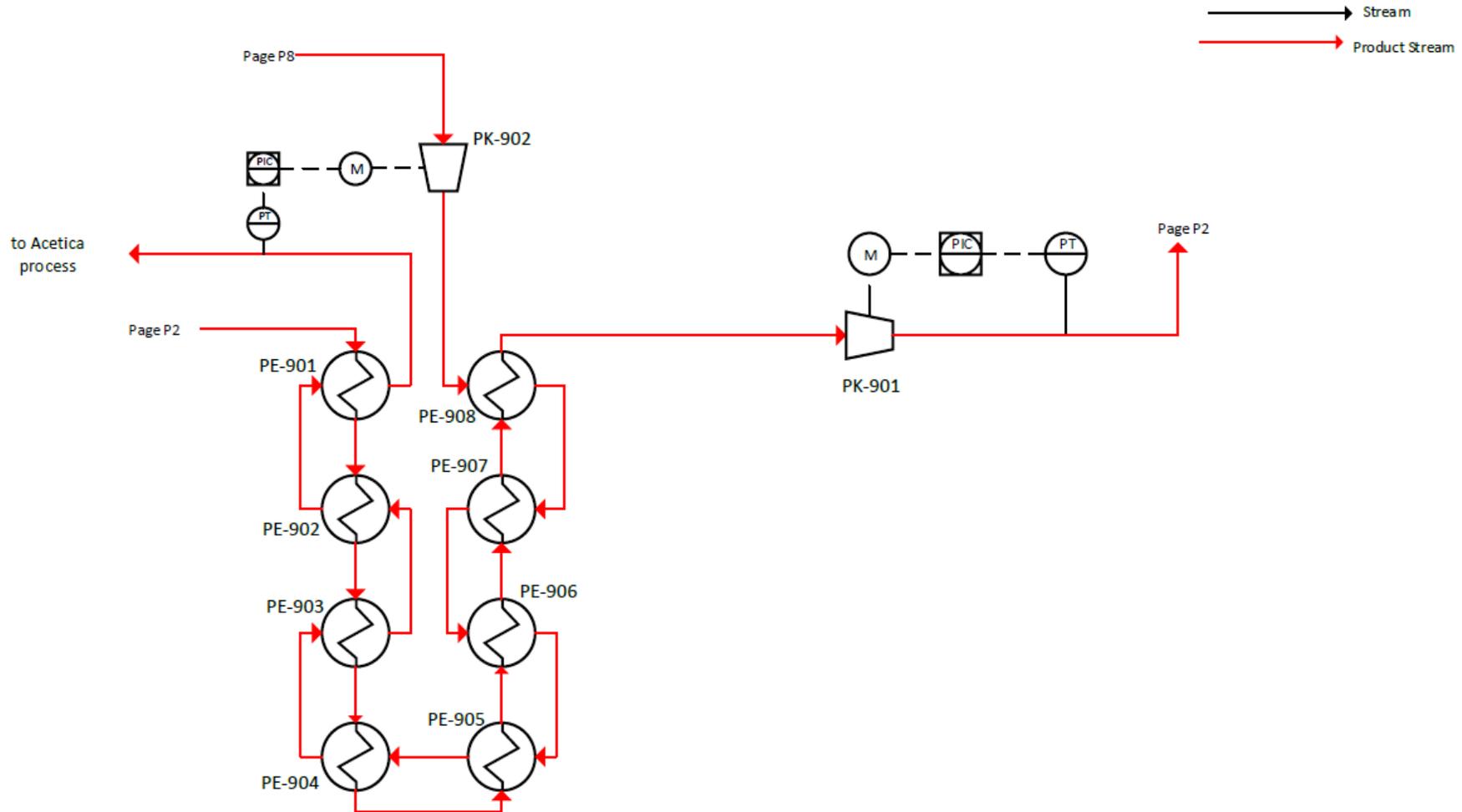
D.P. = Design Pressure

1ste letter (P): Purification section

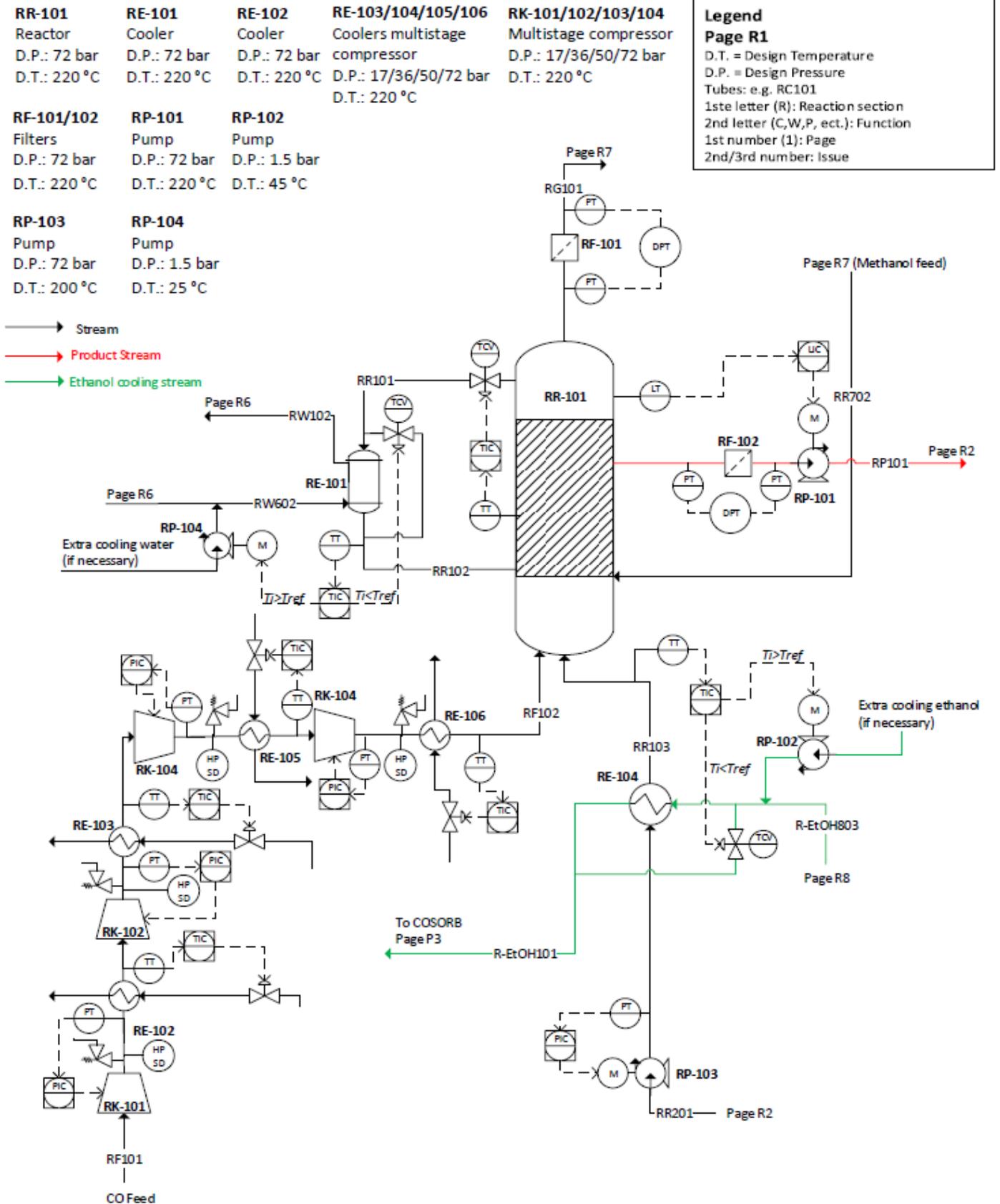
2nd letter (V,P,E ect.): Function

1ste number (2): Page

2nd/3rd number: Issue



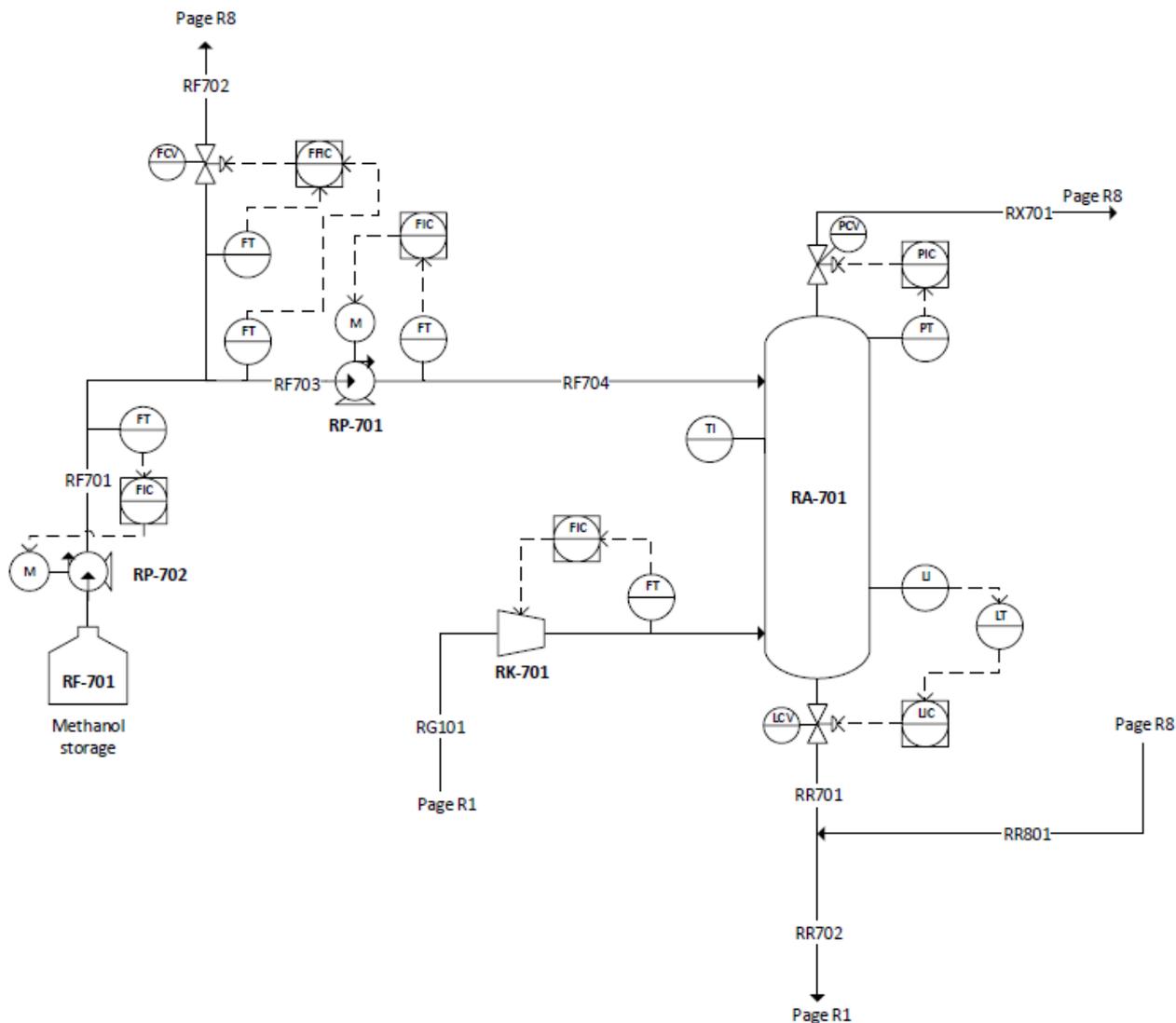
Appendix 25. P&ID Page P9: heaters and compressor.



Appendix 26. P&ID Page R1: reactor and multistage compressor. An ethanol stream originating from the COSORB process (that first cools down two flows on page R8) cools down the recycle stream before entering the reactor. After this, the warm ethanol stream is returned to the COSORB process where it is cooled down again. The cooler of the reactor is connected with the reboiler of RC-604. The water that returns from the reboiler is turned into steam when cooling down the reactor. Extra cooling water can be called upon when needed, the same holds for a by-pass that can be opened when reactor mixture is cooled down sufficiently.

RA-701 High Pressure Absorber D.P.: 72 bar D.T.: 100 °C	RF-701 Vessel D.P.: 1 bar D.T.: 25 °C	RP-702 Pump D.P.: 1 bar D.T.: 25 °C	RP-701 Pump D.P.: 72 bar D.T.: 30 °C	RK-701 Compressor D.P.: 72 bar D.T.: 100 °C
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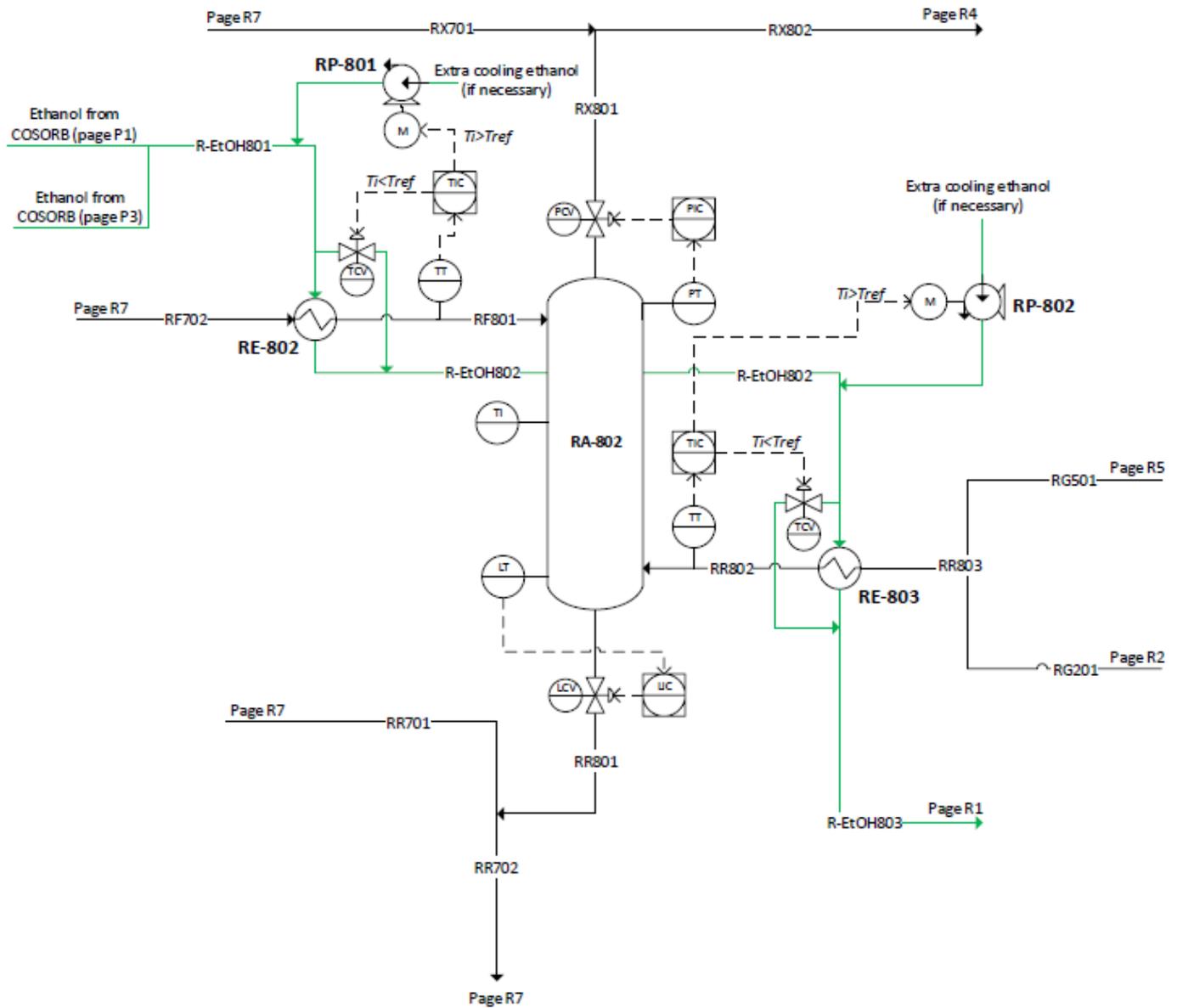
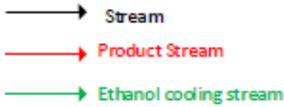
Legend
Page R7
D.T. = Design Temperature
D.P. = Design Pressure
Tubes: e.g. RR701
1ste letter (R): Reaction section
2nd letter (C,W,P, ect.): Function
1st number (7): Page
2nd/3rd number: Issue



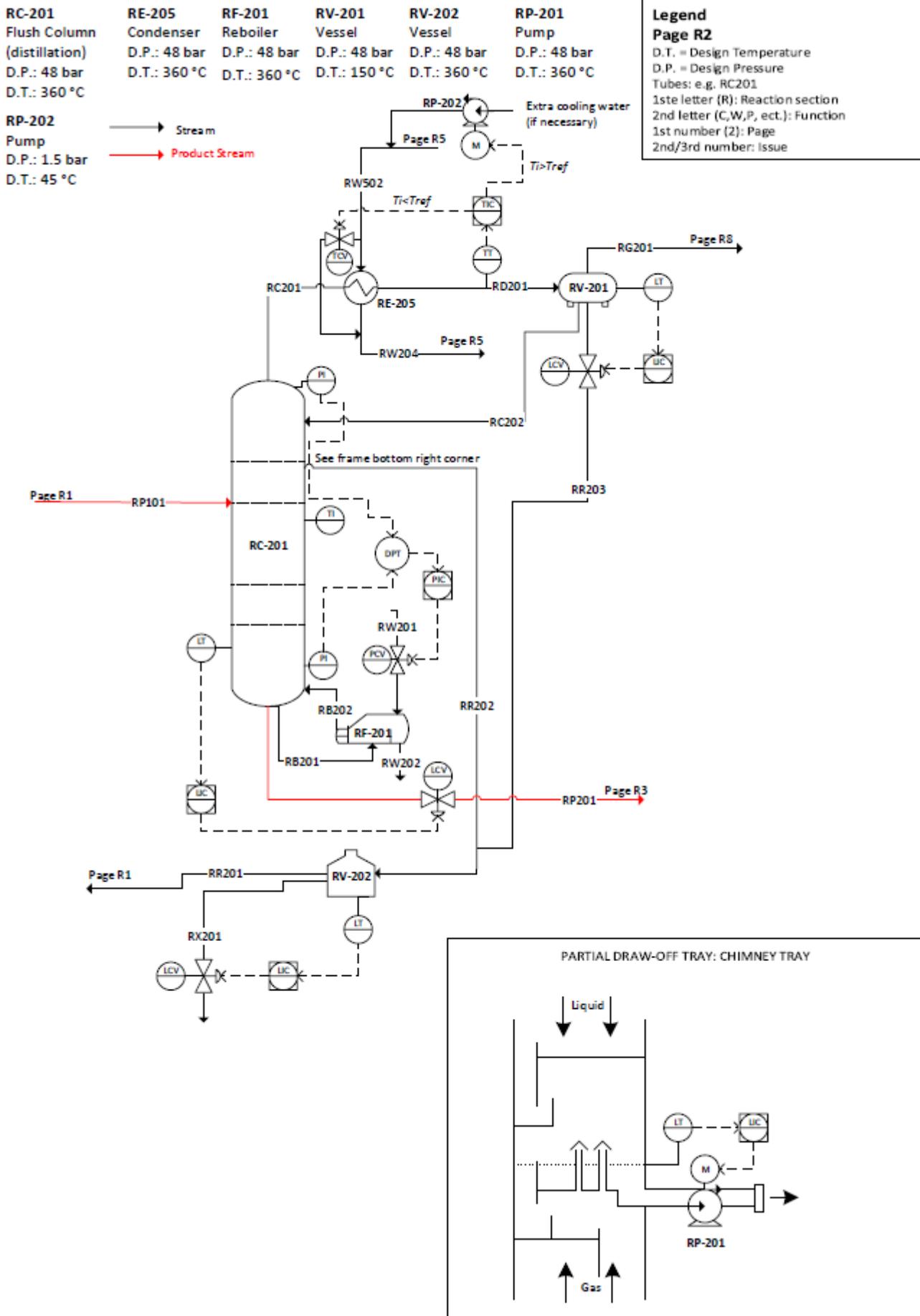
Appendix 27. P&ID Page R7: high pressure absorber and methanol storage.

RA-802 Low Pressure Absorber D.P.: 1.5 bar D.T.: 15 °C	RE-802 Cooler D.P.: 1.5 bar D.T.: 30 °C	RE-803 Cooler D.P.: 1.5 bar D.T.: 45 °C	RP-801 Pump D.P.: 1.5 bar D.T.: 45 °C	RP-802 Pump D.P.: 1.5 bar D.T.: 45 °C
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Legend
Page R8
 D.T. = Design Temperature
 D.P. = Design Pressure
 Tubes: e.g. RX801
 1ste letter (R): Reaction section
 2nd letter (C,W,P, ect.): Function
 1st number (8): Page
 2nd/3rd number: Issue



Appendix 28. P&ID Page R8: low pressure absorber. An ethanol cooling stream originating from the COSORB process is used to cool down the two streams entering the absorber. Because the ethanol stream is predefined and thus cannot be altered by a valve/pump, an extra cooling ethanol reservoir can be used to cool down the stream even more (when $T_i > T_{ref}$). When the stream cools down more than needed ($T_i < T_{ref}$), a control valve opens that establishes a by-pass.



Appendix 29. P&ID Page R2: flush column. The condenser of the column is connected with reboiler of RC-503. Because the stream itself cannot be changed by a valve/pump, an extra cooling stream can be used to cool down the stream even more (when $T_i > T_{ref}$). When the stream cools down more than needed ($T_i < T_{ref}$), a control valve opens that establishes a by-pass.

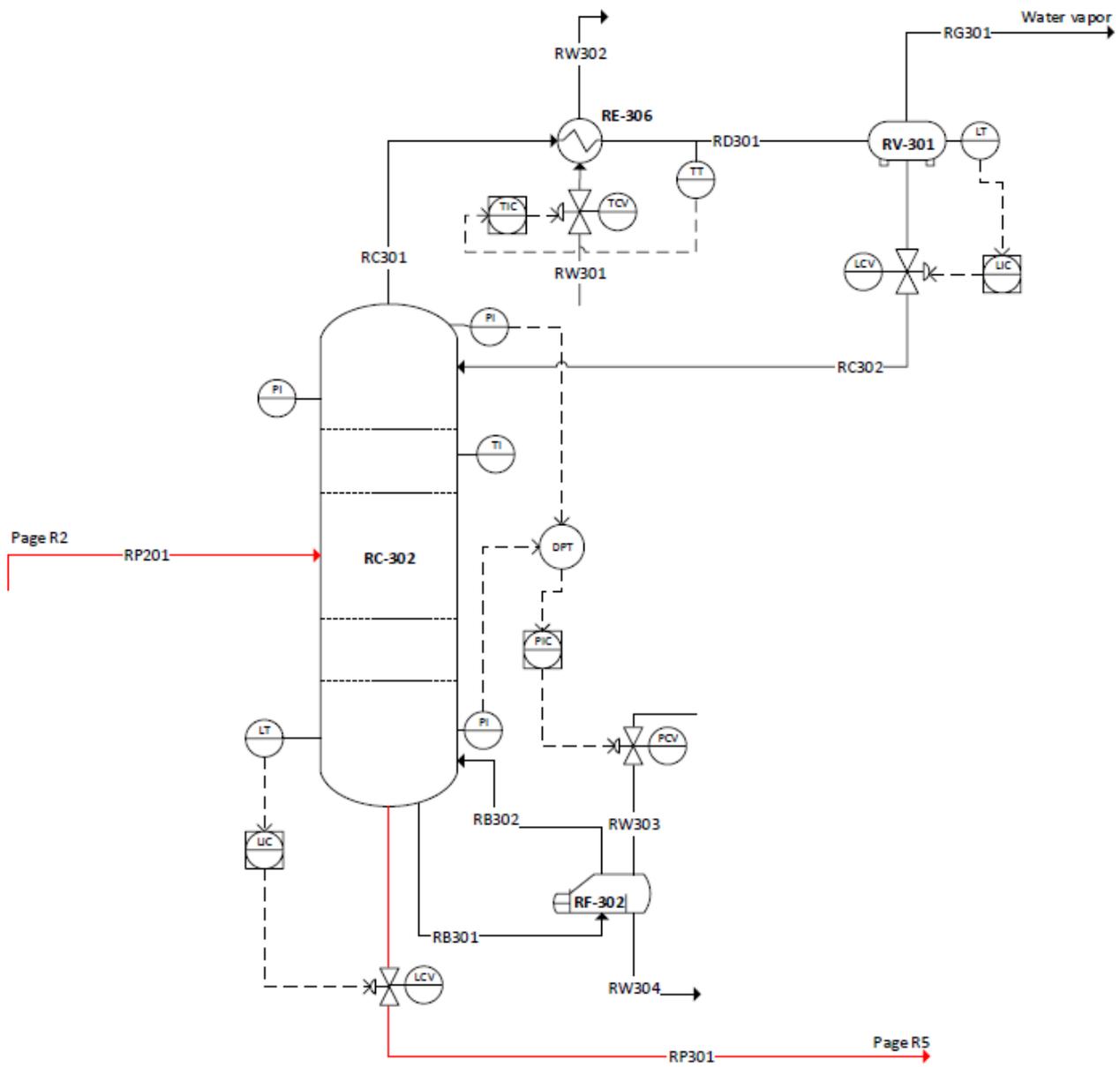
RC-302 Dehydration Column (distillation) D.P.: 4 bar D.T.: 360 °C	RE-306 Condenser D.P.: 4 bar D.T.: 360 °C	RF-302 Reboiler D.P.: 4 bar D.T.: 360 °C	RV-301 Vessel D.P.: 4 bar D.T.: 150 °C
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Legend

Page R3

D.T. = Design Temperature
 D.P. = Design Pressure
 Tubes: e.g. RG301
 1st letter (R): Reaction section
 2nd letter (C,W,P, ect.): Function
 1st number (3): Page
 2nd/3rd number: Issue

→ Stream
 → Product Stream



Appendix 30. P&ID Page R2: dehydration column.

RC-503
Finishing Column
(distillation)
D.P.: 4 bar
D.T.: 180 °C

RE-507
Condenser
D.P.: 4 bar
D.T.: 180 °C

RF-503
Reboiler
D.P.: 4 bar
D.T.: 180 °C

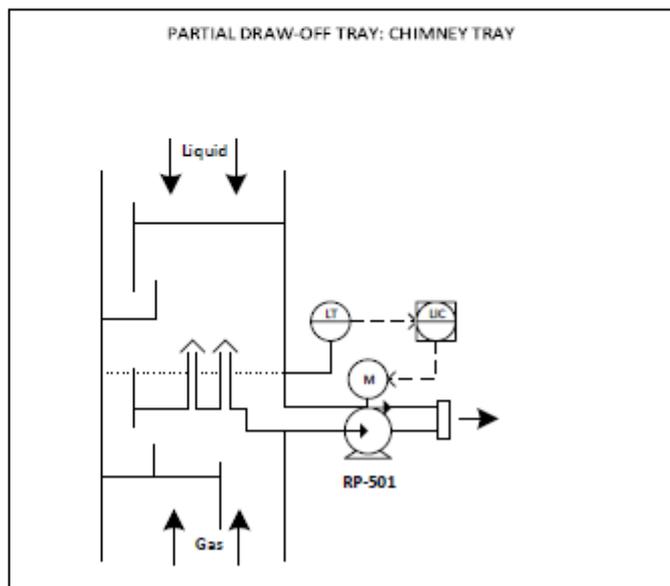
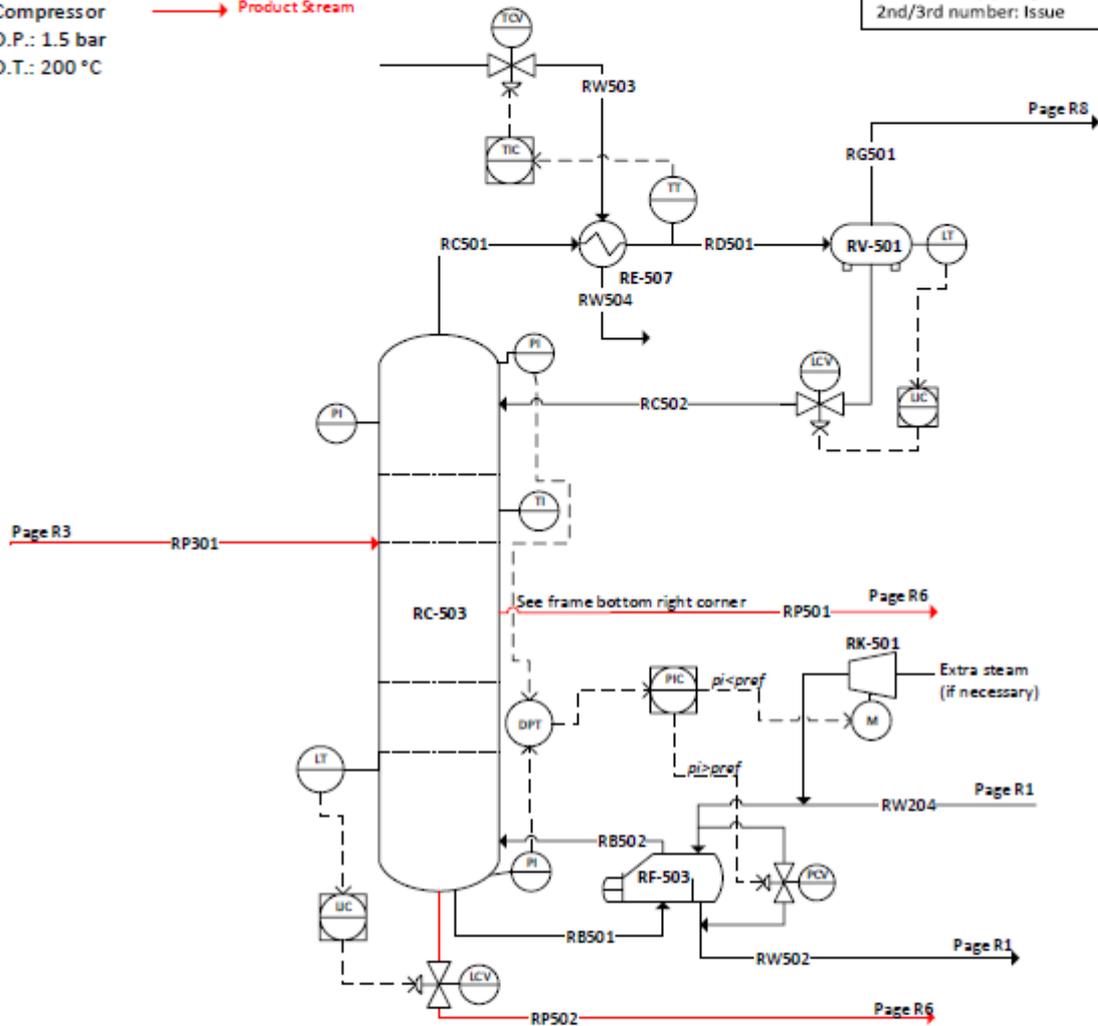
RV-501
Vessel
D.P.: 4 bar
D.T.: 150 °C

RP-501
Pump
D.P.: 4 bar
D.T.: 150 °C

Legend
Page R5
D.T. = Design Temperature
D.P. = Design Pressure
Tubes: e.g. RG501
1st letter (R): Reaction section
2nd letter (C,W,P, ect.): Function
1st number (5): Page
2nd/3rd number: Issue

RK-501
Compressor
D.P.: 1.5 bar
D.T.: 200 °C

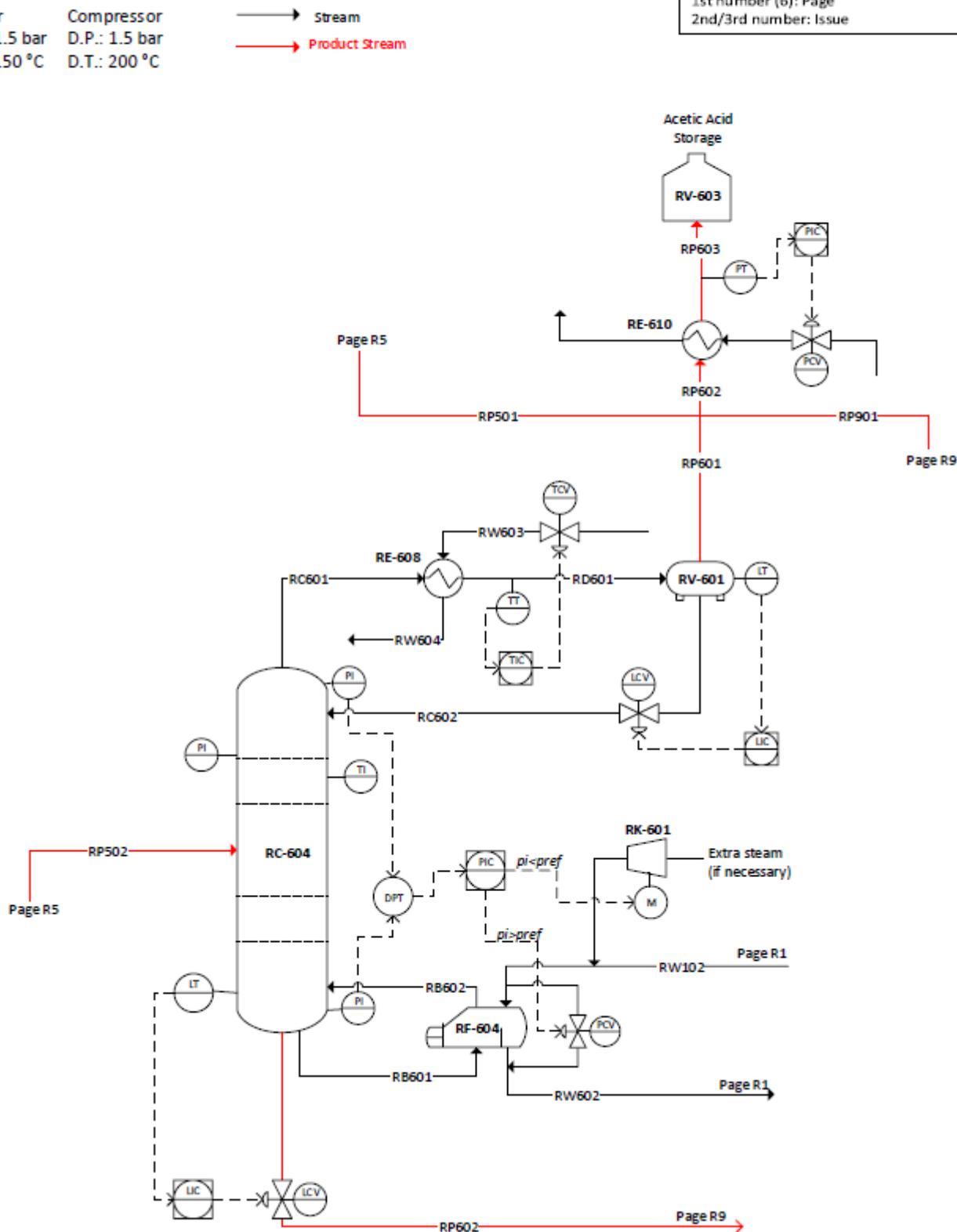
→ Stream
→ Product Stream



Appendix 31. P&ID Page R5: finishing column. The reboiler of the column is connected with the condenser of RC-201. When there is not enough steam ($T_i < T_{ref}$), more steam can be added and when there is too much ($T_i > T_{ref}$), a by-pass can be opened.

RC-604 Second finishing column (distillation) D.P.: 1.5 bar D.T.: 150 °C	RE-608 Condenser D.P.: 1.5 bar D.T.: 150 °C	RF-604 Reboiler D.P.: 1.5 bar D.T.: 150 °C	RV-601 Vessel D.P.: 1.5 bar D.T.: 150 °C	RV-603 Vessel D.P.: 1 bar D.T.: 25 °C
RE-610 Cooler D.P.: 1.5 bar D.T.: 150 °C	RK-601 Compressor D.P.: 1.5 bar D.T.: 200 °C			

Legend
Page R6
 D.T. = Design Temperature
 D.P. = Design Pressure
 Tubes: e.g. RP601
 1ste letter (R): Reaction section
 2nd letter (C,W,P, ect.): Function
 1st number (6): Page
 2nd/3rd number: Issue

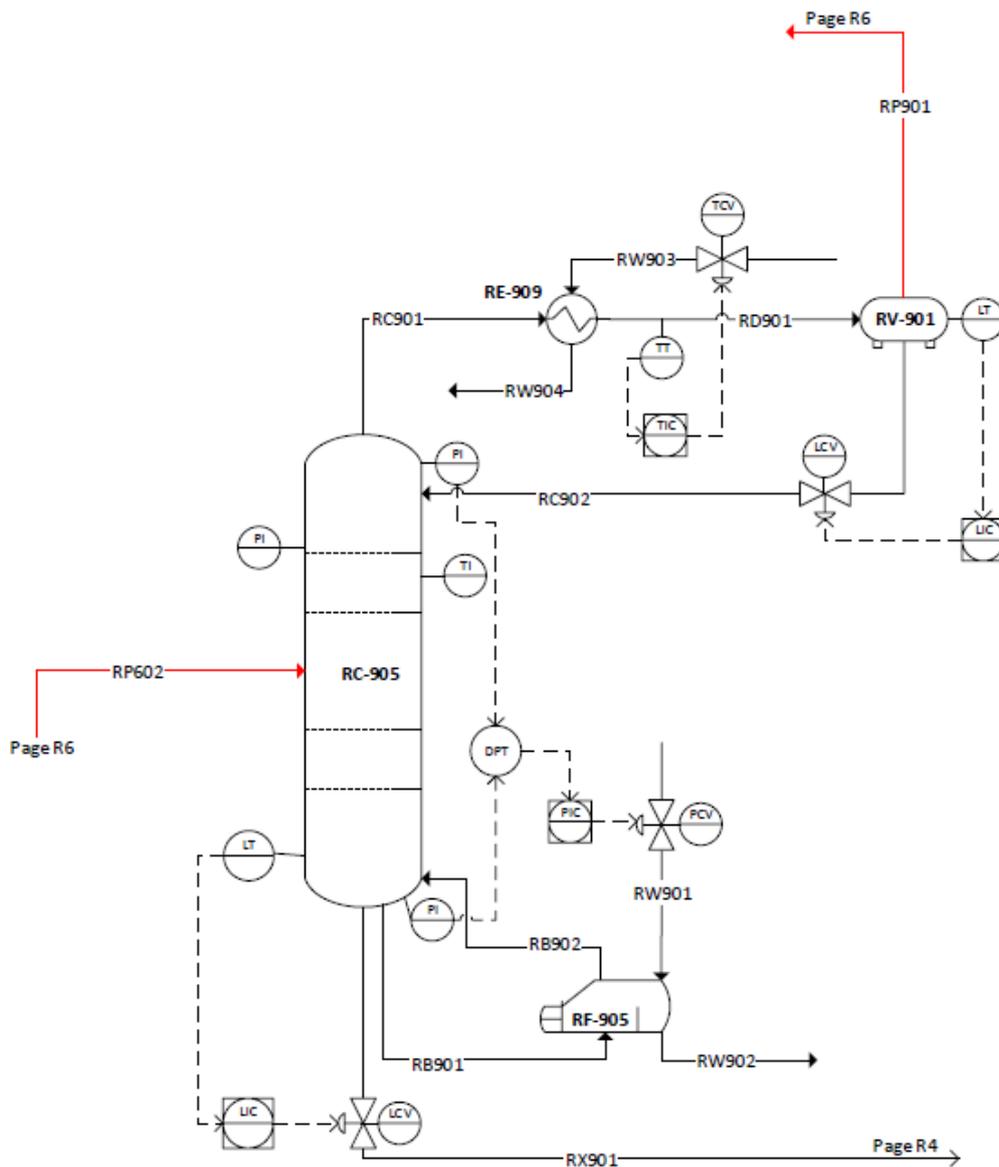


Appendix 32. P&ID Page R6: second finishing column. The reboiler of the column is connected with the cooler of the reactor. Lower pressure steam generated by heat from the reactor is used in this reboiler. When there is not enough steam ($T_i < T_{ref}$), more steam can be added and when there is too much ($T_i > T_{ref}$), a by-pass can be opened.

RC-905 Third finishing column (distillation) D.P.: 1.5 bar D.T.: 150 °C	RE-909 Condenser D.P.: 1.5 bar D.T.: 150 °C	RF-905 Reboiler D.P.: 1.5 bar D.T.: 150 °C	RV-901 Vessel D.P.: 1.5 bar D.T.: 150 °C
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Legend
Page R9
D.T. = Design Temperature
D.P. = Design Pressure
Tubes: e.g. RP901
1st letter (R): Reaction section
2nd letter (C,W,P, ect.): Function
1st number (9): Page
2nd/3rd number: Issue

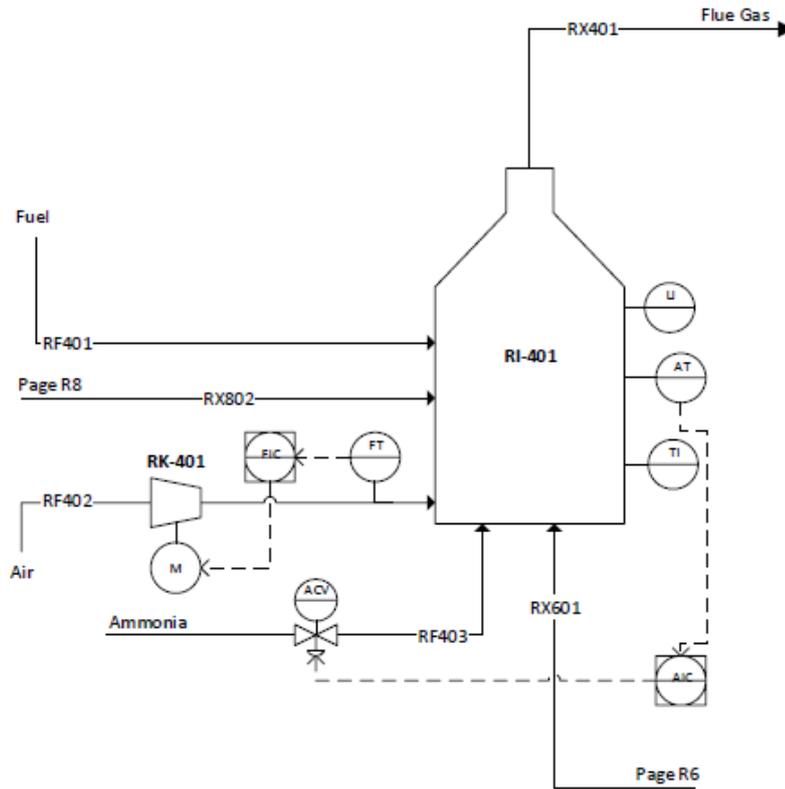


Appendix 33. P&ID Page R9: third finishing column.

RI-401	RK-401
Incinerator	Compressor
D.P.: 10 bar	D.P.: 1.5 bar
D.T.: 500 °C	D.T.: 45 °C

 Stream
 Product Stream

Legend
Page R4
 D.T. = Design Temperature
 D.P. = Design Pressure
 Tubes: e.g. RX401
 1ste letter (R): Reaction section
 2nd letter (C,W,P, ect.): Function
 1st number (4): Page
 2nd/3rd number: Issue



Appendix 34. P&ID Page R4: incinerator.

5. Process safety: hazard and operability (HAZOP) analysis

5.1 Purification section

5.1.1 Explanatory table

Appendix 35. HAZOP table for the purification section. Only the P&ID's from page P1 and page P7 are adapted according to the HAZOP-table, because these two pages contain most of the important equipment used in this section.

Unit	Deviation	Word	Cause	Consequence	Safeguard	Action
PS-201/202	air gas flow	low	failure of compressor	regeneration of column too slow	flow alarm low	none
PS-201/202	air temperature	low	heat exchanger fails	regeneration of column too slow	temperature alarm low	consider installment of spare heat exchanger
PS-201/202	pressure	high	clogging of outlet gas stream or drying bed	explosion risk	pressure alarm high and PSV	include pressure alarm on unit and PSV
PS-203~208	pressure	high	clogging of filter	filter can break under high pre	pressure alarm high and PSV	include pressure alarm on unit and PSV
PC-101	gas flow	none/low	leakage of inlet pipe, failure of PK-205/206	no/low inlet stream	flow alarm low	shut down entire process, educate operators about steps to take action
PC-101	liquid flow	low	failure PP-101, clogging in liquid outlet	less efficient CO absorption, yield loss	flow alarm low	instruct operators on how to act in case of alarm
PC-101	pressure	low	failure of PK-202/203/204	less efficient CO absorption, yield loss	flow alarm low	consider spare compressors, shut down process to replace compressors
PC-101	pressure	low	leakage of column	CO released, dangerous for staff	Pressure alarm low	Shut down entire process, educate operators about steps to take action
PC-101	pressure	high	failure of gas outlet valve	explosion risk	pressure alarm high and PSV	instruct operators to turn off compressors in case of pressure alarm, shut down process
PC-101	temperature	high	failure of PE-101/103/310, failure of pumps in ethanol cooling stream or failure of PE-205 (or PK-401) or failure PE-206 (or PK-902)	less efficient CO absorption, yield loss	temperature alarm high	consider installment of spare heat exchanger, shut down process
PC-101	level	high	clogging of liquid outlet	column capacity reached	level alarm high	ensure level alarm high
PV-101	level	high	clogging of outlet	vessel capacity reached	level alarm high	none
PV-501	Level	high	failure of PP-501/502	liquid to compressor in gas outlet	level alarm high	ensure level alarm high, educate operators about steps to take action, shut down process

PV-501	pressure	high	failure of PK-202/203	gas recycle stops	pressure alarm high and PSV	consider spare compressors, shut down stream to replace compressors
PC-701	gas flow out	low	failure of PF-701	less efficient CO desorption	flow alarm low	instruct operators to turn off compressors in case of pressure alarm, shut down process
PC-701	temperature	high	failure of PE-701, clogging in condenser liquid feedback	large amount of toluene loss	temperature alarm high	consider extra duty in solvent recovery, shut down process
PC-701	level	low	leakage in outlet liquid flow, failure of PE-701, clogging in condenser liquid feedback	large amount of toluene loss	level alarm low	Shut down entire process, educate operators about steps to take action
PC-701	level	high	clogging in liquid flow out or failure of PP-601	no more extraction of CO in absorber	level alarm high	Shut down entire process, educate operators about steps to take action
PC-701	pressure	high	clogging of gas flow out	explosion risk	pressure alarm high and PSV	Shut down entire process, educate operators about steps to take action
PV-701	gas flow out	high	failure of PE-701	large amount of toluene loss	flow alarm high	consider extra duty in solvent recovery, shut down process
PV-701	level	low	leakage of toluene	large amount of toluene loss	level alarm low	Shut down entire process, educate operators about steps to take action
PV-801	gas flow out	low	failure of PK-801	no CO to reactor, no Acetic acid production	flow alarm low	Shut down entire process, educate operators about steps to take action
PV-801	temperature	high	failure of PE-801/809 or PE-310 or PP-801	large amount of toluene loss	temperature high	Shut down entire process, educate operators about steps to take action
PV-801	level	low	leakage of toluene	large amount of toluene loss	level alarm low	Shut down entire process, educate operators about steps to take action
PV-801	level	high	clogging of outlet flow liquid	toluene liquid with CO gas	level alarm high	Shut down entire process, educate operators about steps to take action
PV-301	gas flow out	low	failure of PK-301	no cooling possible in PE-401/9(=PE-205), so less cooling of feed gas and less efficient CO absorption	flow alarm low	Consider spare compressors, shut down process to replace compressors
PV-301	temperature	high	failure of PE-301/309 or PE-310 or PP-301	large amount of toluene loss	temperature high	Shut down entire process, educate operators about steps to take action
PV-301	level	low	leakage of toluene	large amount of toluene loss	level alarm low	Shut down entire process, educate operators about steps to take action
PV-301	level	high	clogging of outlet flow liquid	toluene liquid with lean gas	level alarm high	Shut down entire process, educate operators about steps to take action
CU-101	current	low	power failure	no solid particles removal	alarm (low)	fix power supply

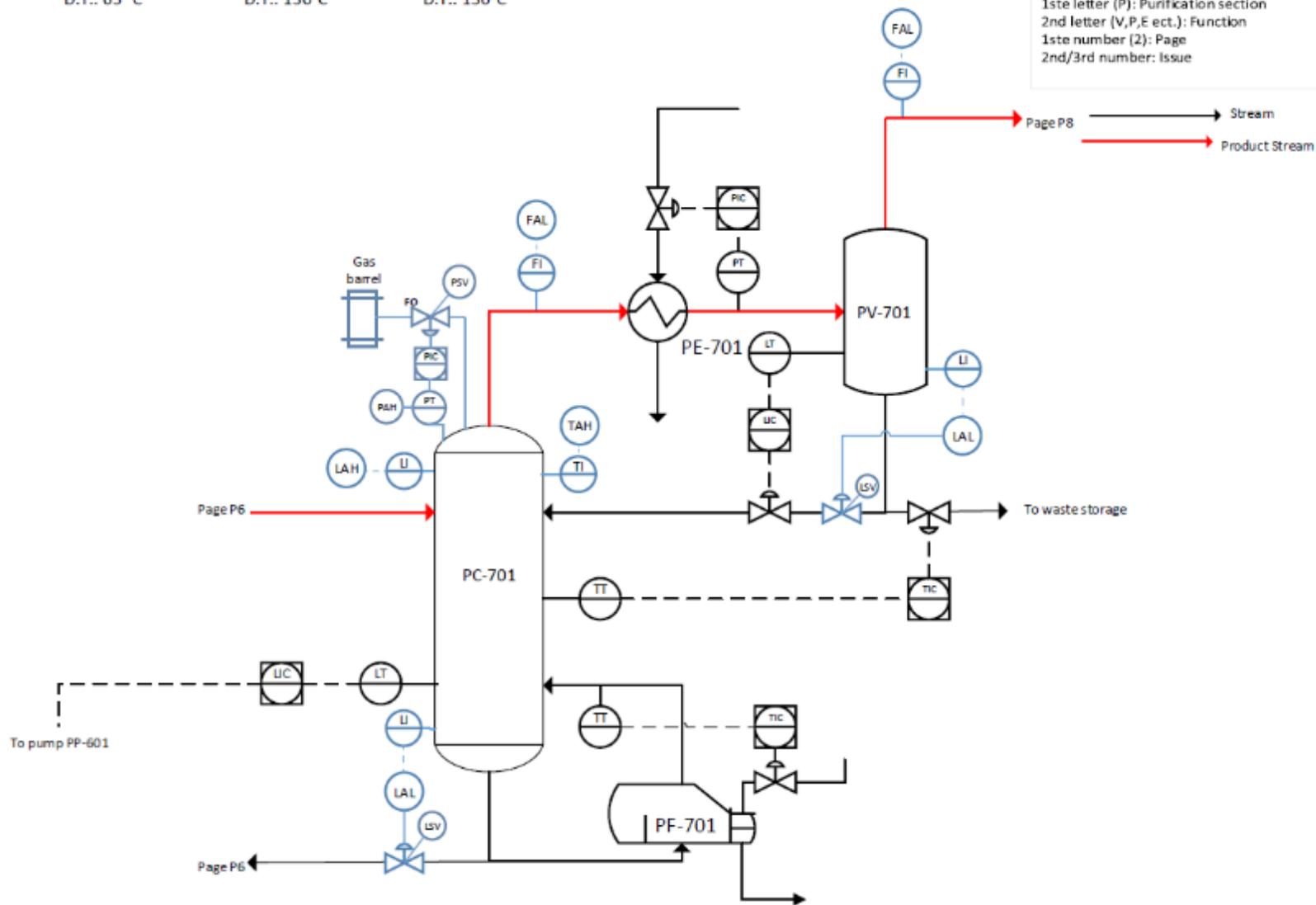
CU-101	current	high	disturbance in power supply, short circuit	dangerous operation	alarm (high)	fix power supply
CC-101	gas flow	none	clogging of inlet pipe; failure of C-U1; shutting down of steel plant	no inlet stream	alarm (low)	shut down entire process, educate operators about steps to take
CC-101	gas flow	high	high gas production from steel mill	H2S removal fails	flow indicator	include control system to CP-201 to compensate for higher pressure
CC-101	gas flow	low	clogging of inlet pipe; failure of C-U1; failure in steel plant	disturbed balance between recycle stream and inlet stream	flow alarm (low)	include control system to CP-201 to compensate for lower pressure
CC-101	liquid flow	none	CP-201 fails	H2S removal fails	flow alarm (low)	consider installment of spare pump or ensure easy replacement
CC-101	liquid flow	low	CP-201 fails	H2S removal less efficient	flow alarm (low)	consider installment of spare pump or ensure easy replacement
CC-101	level	high	CP-201 deviates	H2S removal less efficient	level switch low	ensure installment of LSV
CC-101	level	low	recycle stream too high	H2S removal less efficient	liquid level indicator controller	ensure installment of LSV
CC-101	level	none	failure of iron sulfate (aq) stream; failure of CP-201	gas product stream flows through CV-201	liquid indicator controller	ensure installment of LSV
CC-101	pressure	high	inlet gas flow increases, outlet gas valve fails	explosion risk	pressure safety valve	ensure installment of PSV
CC-101	temperature	high	inlet gas flow at higher temperature	possible increase of water content in product stream	none	consider installment of heat exchangers on gas inlet
CC-101	temperature	low	inlet gas flow at lower temperature	none	none	none
CV-201	level	high	high inlet liquid flow	vessel might overflow, possible liquid in gas outlet stream	level control to valve in slurry outlet stream	ensure installment of LSV
CV-201	air flow	none	compressor failure	H2S oxidation fails	flow alarm (low)	consider installment of backup compressor
CV-201	iron sulfate flow	none	pump failure; storage vessel empty	no control of pH, H2S oxidation fails	flow alarm (low)	install level alarm on storage vessel for iron sulfate solution
CV-201	pressure	high	high inlet air flow, CP-201 deviates, clogging of air outlet	liquid inlet flow prohibited	pressure safety valve	install pressure safety valve on CV-201
CC-301	gas flow	high	high gas production from steel mill	removal of SOx fails	flow indicator control system on liquid inlet flow	install flow control system

CC-301	gas flow	low	low gas production from steel mill	less efficient process due to imbalance between liquid and gas flow	flow indicator control system on liquid inlet flow	install flow control system
CC-301	liquid level	high	inlet water stream too high	vessel capacity reached	level alarm high	level transmitter shall have alarm
CC-301	liquid level	low	inlet water stream too low	removal of SOx fails	level alarm low	level transmitter shall have alarm
CC-301	pressure	high	clogging of outlet gas pipe	explosion risk	pressure safety valve	ensure installment of PSV
CM-301	lime flow	high	failure of supply stream	clogging of mixer	none	instruct operators about risks of lime accumulation
CM-301	lime flow	low	lime storage empty	reaction fails	back-up storage	instruct operators to purchase new lime if storage is empty
CS-401	level	high	failure of CP-301	liquid recycle fails	level alarm high	consider installment of spare pump or ensure easy replacement
CS-401	level	high	clogging of solid outlet	solids in liquid outlet	level alarm high	install back-up outlet for solids with safety valve
CS-401	level	low	clogging of liquid inlet	no liquid outlet	level alarm low	none
CS-402	level	high	clogging of liquid outlet	overflow of vessel	level alarm high	instruct operator on required actions

5.1.2 Stripper column (PC-701, page P7)

PC-701	PV-701	PE-701	PF-701
Column (Stripper column)	Flash drum	Condenser	Reboiler
D.P.: 2 bar	D.P.: 2 bar	D.P.: 3 bar	D.P.: 2 bar
D.T.: 130 °C	D.T.: 65 °C	D.T.: 130°C	D.T.: 130°C

Legend
Page P7
 D.T. = Design Temperature
 D.P. = Design Pressure
 1ste letter (P): Purification section
 2nd letter (V,P,E ect.): Function
 1ste number (2): Page
 2nd/3rd number: Issue



Appendix 36. P&ID Page P7 (stripper column), adapted according to the HAZOP table.

Supervisors: J. Winkelman, W. Leusman & K. Zuur

5.1.3 Absorption column (PC-101, page P1)

PC-101

Column
(absorption column)
D.P.: 5 bar
D.T.: 45 °C

PE-101

Cooler
D.P.: 4 bar
D.T.: 45 °C

PE-103

Cooler
D.P.: 4 bar
D.T.: 45 °C

PP-101/

PP-102
Pump
D.P.: 4 bar
D.T.: 50 °C

PV-101

Surge Tank
D.P.: 4 bar
D.T.: 50 °C

PP-103

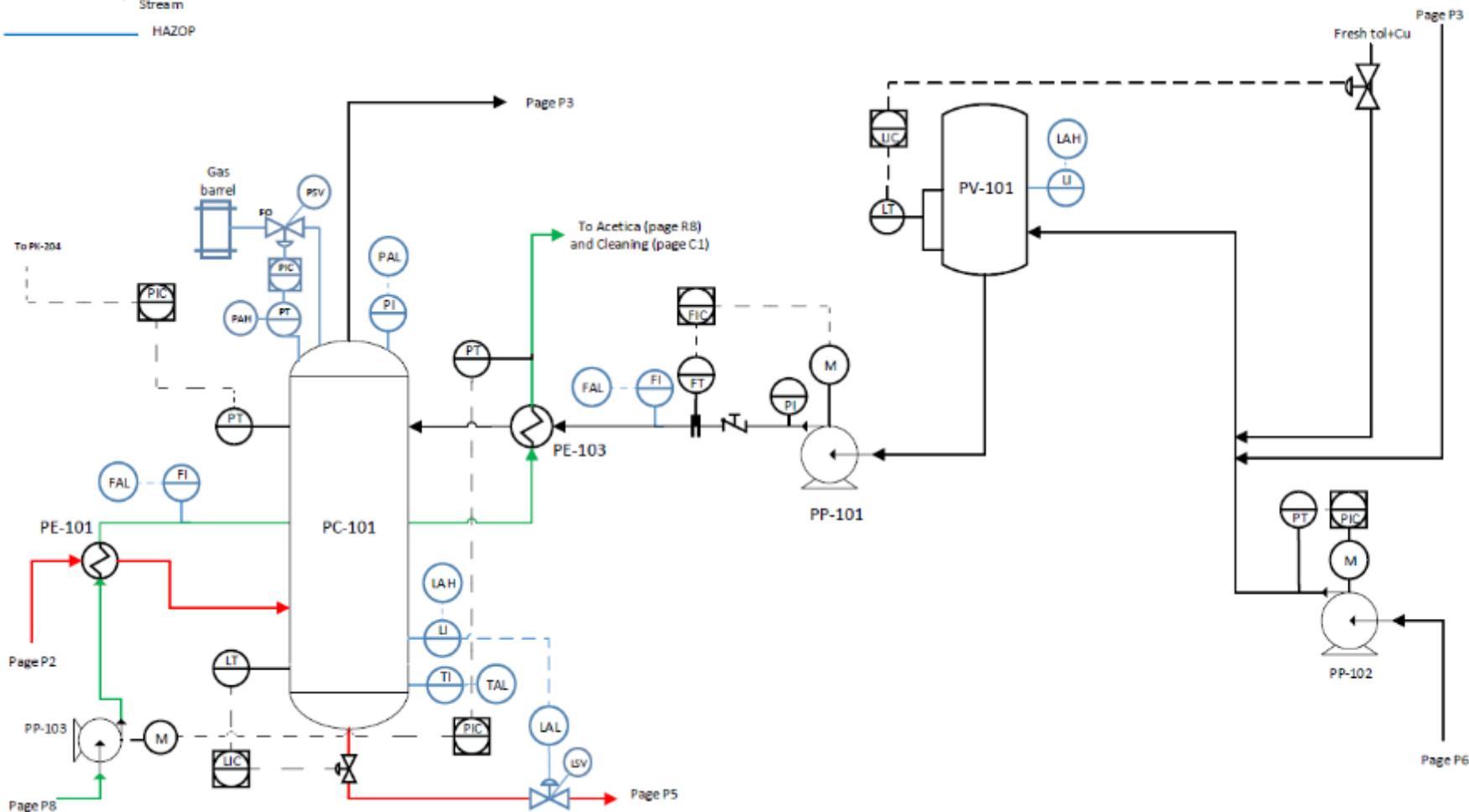
Pump
D.P.: 2 bar
D.T.: 45 °C

Legend

Page P1

D.T. = Design Temperature
D.P. = Design Pressure
1st letter (P): Purification section
2nd letter (V,P,E ect.): Function
1st number (2): Page
2nd/3rd number: Issue

-  Stream
-  Product Stream
-  Ethanol Cooling Stream
-  HAZOP



Appendix 37. P&ID Page P1 (absorption column), adapted according to the HAZOP table.

5.2.1 Explanatory table

Appendix 38. HAZOP table for the reaction section. The P&ID's from RR-101, RA-701, RC-201 and RI-401 are adapted according to the HAZOP-table.

Unit	Deviation	Word	Cause	Consequence	Safeguard	Action
RR-101	flow RR702	low	failure of RA-701	loss of containment, not enough methanol feed	flow alarm (low)	consider installment of backup absorber or ensure easy repairs
RR-101	flow RR702	low	failure of RA-802	loss of containment, not enough methanol feed	flow alarm (low)	consider installment of backup absorber or ensure easy repairs
RR-101	flow RR702	low	clogging/leakage of pipe RR702 or RF701	loss of containment, not enough methanol feed	flow alarm (low)	consider installment of extra pipeline connecting the methanol feed directly to the reactor
RR-101	flow RR702	none	breakage/clogging of pipe RR702	no methanol feed	flow alarm (low)	shut down entire process, educate operators about steps to take
RR-101	flow RR702	none	failure of both absorption columns	no methanol feed	flow alarm (low)	consider installment of extra pipeline connecting the methanol feed directly to the reactor
RR-101	flow RR101/102	none	clogging of pipe	temperature rises sharply	temperature alarm high	installment of backup piping and heat exchanger
RR-101	flow RR103	low	clogging of pipe	no hazardous consequences for unit	flow alarm (low)	increase capacity of RV-202 or decrease RX-201 stream
RR-101	level	low	decreased inlet liquid streams	RP-101 might become a gaseous stream	flow alarm (low)	no additional action required
RR-101	level	high	failure of RP-101	RG-101 might contain liquid	level alarm high	consider adding another outlet flow with a valve that opens when the level alarm goes off
RR-101	level	low	reactor leaks	danger for operator safety, loss of containment	level alarm low	include evacuation plans in operator training
RR-101	pressure	high	failure of RG-101	explosion risk	pressure safety valve	install pressure safety valve that leads gas outlet back to RA-701 or to a containment tank
RR-101	pressure	low	gas inlet fails	reaction fails	flow alarm (low)	no additional action required
RR-101	temperature	high	cooling system fails	explosion risk, heat accumulation	temperature alarm high	installment of backup piping and heat exchanger
RR-101	temperature	high	reaction too fast	explosion risk, heat accumulation	temperature alarm high	bypass CO inlet to incinerator
RR-101	temperature	low	cooling inlet too cold	reaction slows down	temperature control system	none
RA-701	flow RF-701	high	clogging of RF-702	no hazardous consequences for unit	none	none
RA-701	flow RF-701	low	pump failure	no more methanol feed	flow alarm low	consider installment of backup pump

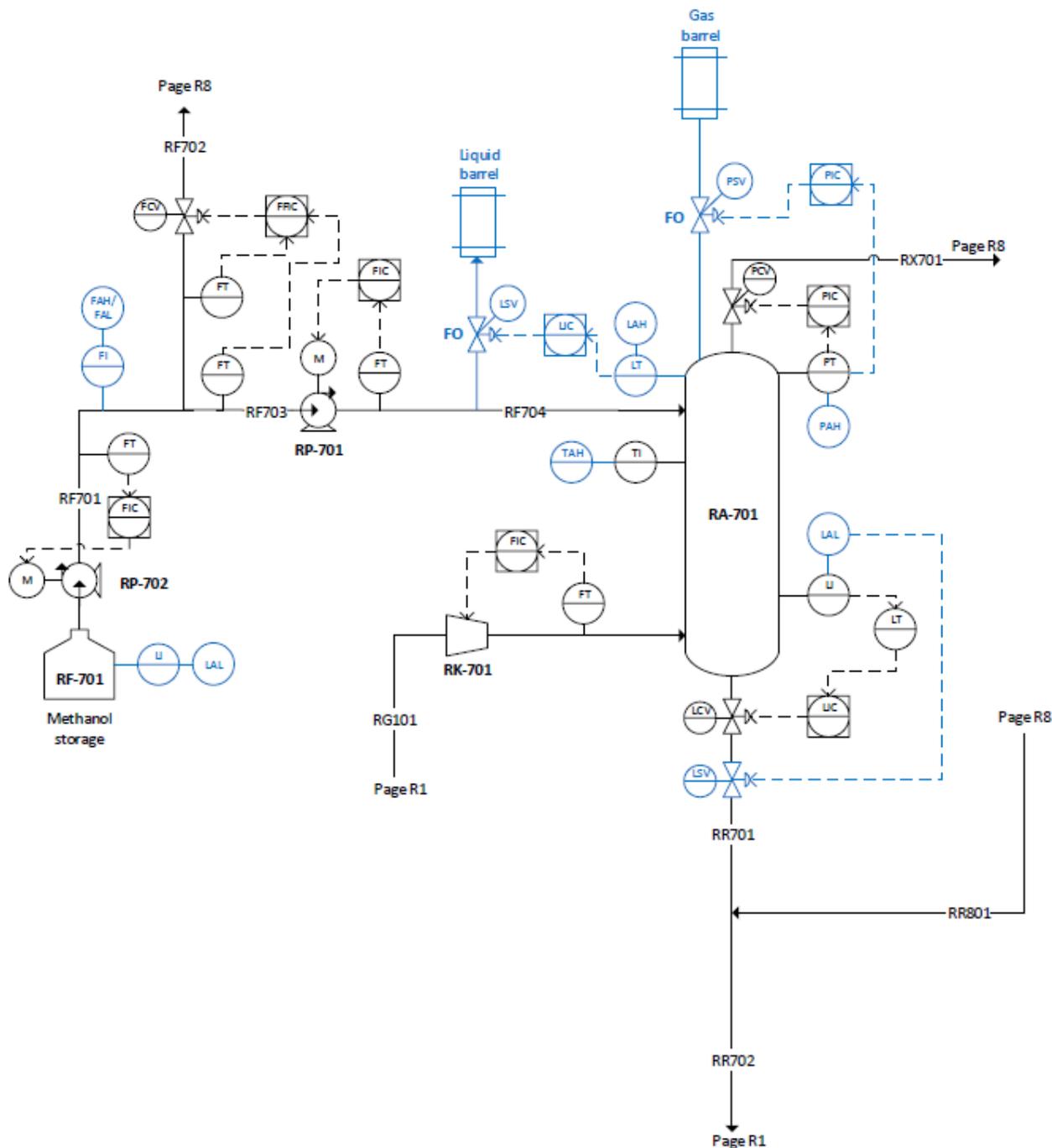
RA-701	flow RF-701	low	storage vessel empty	no more methanol feed	level alarm low on storage vessel	install level alarm on storage vessel
RA-701	level	low	liquid outlet stream too large	no efficient absorption	level control system	none
RA-701	level	high	clogging of RR702	methanol in stream RX701 which goes to incinerator	level alarm high	consider installment of LSV that is opened by the level alarm high
RA-701	temperature	high	reactor temperature too high	no hazardous consequences for unit	none	none
RA-701	pressure	high	clogging of outlet gas pipe	explosion risk	pressure alarm high	consider installment of PSV
RA-701	pressure	low	low inlet gas stream	no efficient absorption	regulated in reactor	none
RF-701	level	low	methanol stock not refilled	No methanol feed for the process	level alarm low	none
RC-201	level	high	clogging of RP-201	risk of liquid in gas outlet streams	level alarm high on bottom tray	installment of level alarm system connecting to a safety valve
RC-201	level	low	low inlet liquid flow, condenser failure	no distillation possible	level alarm low	none
RC-201	temperature	low	failure of RF-201	no efficient distillation	temperature alarm low	consider installment of spare reboiler
RC-201	temperature	high	failure of RE-205	loss of acetic acid to vapor outlet, dangerous operation, pressure increase,	temperature alarm high on RC202	consider control system regulating a lower duty for the reboiler. Ensure easy replacement for condenser
RC-201	pressure	high	clogging of RC-201	explosion risk	pressure alarm high	consider a pressure safety valve which closes the feed stream RP101
RC-201	pressure	low	failure of RF-201	inefficient distillation	none	none, will be noticed via temperature alarm low
RC-201	pressure	low	Failure of RP-201	risk of implosion	pressure alarm low	none
RC-201	pressure	high	Clogging of any outlet	risk of explosion	pressure alarm high	none
RC-201	flow RR202	low	draw-off of liquid product fails	impure bottom product	flow alarm low	none
RI-401	temperature	high	combustion goes too fast	pressure and temperature too high, explosion risk	temperature alarm high	consider installment of PSV to close fuel supply and stop combustion
RI-401	level	high	too much liquid in the incinerator	combustion not sufficient	level alarm high	none

RI-401	composition	none	too less an ammonia flow into the incinerator	too much NOx in the flue gas	composition alarm	none
RI-401	pressure	high	combustion goes too fast	pressure and temperature too high, explosion risk	pressure alarm high	none

5.2.3 Absorber (RA-701, page R7)

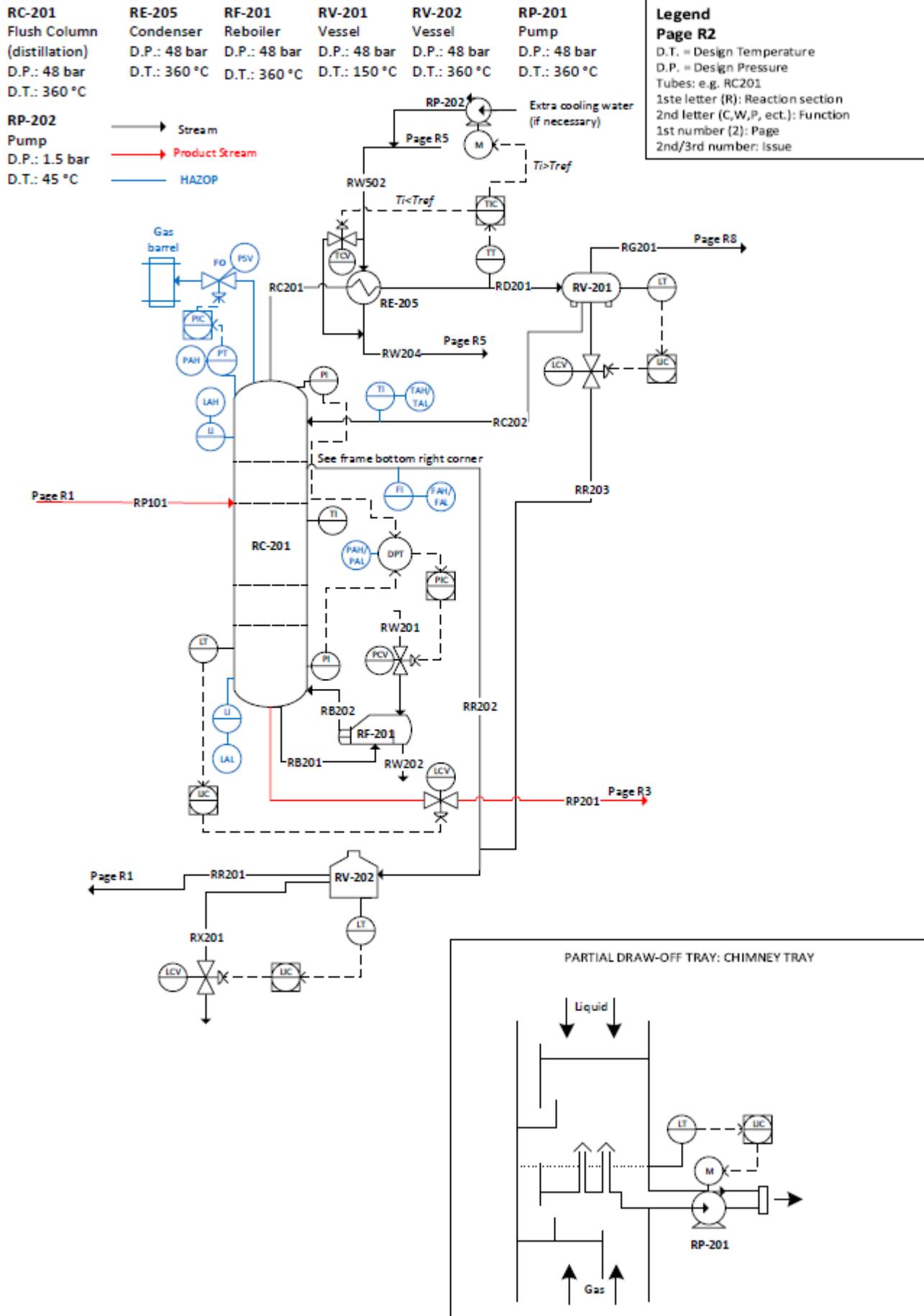
RA-701 High Pressure Absorber D.P.: 72 bar D.T.: 100 °C	RF-701 Vessel D.P.: 1 bar D.T.: 25 °C	RP-702 Pump D.P.: 1 bar D.T.: 25 °C	RP-701 Pump D.P.: 72 bar D.T.: 30 °C	RK-701 Compressor D.P.: 72 bar D.T.: 100 °C
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Legend Page R7 D.T. = Design Temperature D.P. = Design Pressure Tubes: e.g. RR701 1ste letter (R): Reaction section 2nd letter (C,W,P, ect.): Function 1st number (7): Page 2nd/3rd number: Issue



Appendix 40. P&ID Page R7 (high pressure absorber), adapted according to the HAZOP table.

5.2.4 Distillation column (RC-201, page R2)



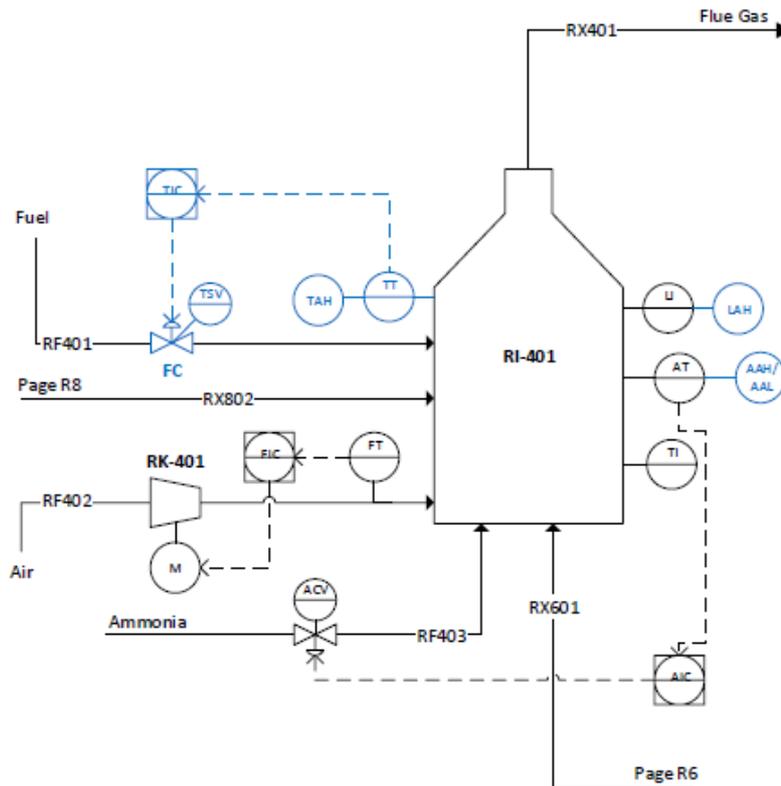
Appendix 41. P&ID Page R2 (flush column), adapted according to the HAZOP table.

5.2.5 Incinerator (RI-401)

RI-401	RK-401
Incinerator	Compressor
D.P.: 10 bar	D.P.: 1.5 bar
D.T.: 500 °C	D.T.: 45 °C



Legend
Page R4
D.T. = Design Temperature
D.P. = Design Pressure
Tubes: e.g. RX401
1st letter (R): Reaction section
2nd letter (C,W,P, ect.): Function
1st number (4): Page
2nd/3rd number: Issue



Appendix 42. P&ID Page R4 (incinerator), adapted according to the HAZOP table.

6. Capital cost estimation

6.1 Equipment investment costs

Appendix 43. Equipment investment costs.

Equipment Investment Costs				
Columns				
Equipment number	Equipment setting costs (€)	and	Multiplied by Lang factor of 4 (€)	Corrected for inflation (€)
CC101	7.33E+06		2.93E+07	3.04E+07
CC301	3.73E+06		1.49E+07	1.55E+07
PC101	1.05E+07		4.20E+07	4.36E+07
PC701	6.05E+06		2.42E+07	2.51E+07
RR101	3.97E+07		1.59E+08	1.65E+08
RC201	7.09E+07		2.84E+08	2.95E+08
RC302	1.41E+07		5.65E+07	5.87E+07
RC503	7.57E+07		3.03E+08	3.14E+08
RC604	1.89E+07		7.57E+07	7.85E+07
RC905	5.05E+06		2.02E+07	2.10E+07
RA701	9.11E+05		3.65E+06	3.78E+06
RA802	2.21E+05		8.86E+05	9.19E+05
Heat exchangers				
Equipment number	Equipment setting costs (€)	and	Multiplied by Lang factor of 3.5 (€)	Corrected for inflation (€)
CE101	4.65E+06		1.63E+07	1.69E+07
CE102	3.17E+06		1.11E+07	1.15E+07
PE101	1.38E+06		4.84E+06	5.02E+06
PE401	2.71E+06		9.49E+06	9.85E+06
PE901	2.28E+06		8.00E+06	8.30E+06
PE103	5.62E+05		1.97E+06	2.04E+06
PE301	7.29E+05		2.55E+06	2.65E+06
PE601	3.67E+06		1.28E+07	1.33E+07
PE809	3.96E+05		1.39E+06	1.44E+06
PE801	9.97E+05		3.49E+06	3.62E+06
RE802	3.47E+05		1.22E+06	1.26E+06
RE803	3.28E+06		1.15E+07	1.19E+07
RE104	2.36E+04		8.26E+04	8.57E+04
Compressors				
Equipment number	Equipment setting costs (€)	and	Multiplied by Lang factor of 2 (€)	Corrected for inflation (€)
RK101	6.46E+07		1.62E+08	1.68E+08
CK101	5.30E+07		1.33E+08	1.38E+08
PK202	7.42E+05		1.86E+06	1.93E+06
PK204	3.48E+07		8.71E+07	9.04E+07
PK205	4.07E+07		1.02E+08	1.06E+08
PK206	4.21E+07		1.05E+08	1.09E+08
Pumps				
Equipment number	Equipment setting costs (€)	and	Multiplied by Lang factor of 4 (€)	Corrected for inflation (€)

RP102	1.15E+05	4.61E+05	4.78E+05
RP701	7.03E+05	2.81E+06	2.92E+06
PP101	1.31E+06	5.23E+06	5.43E+06
pp102	8.48E+06	3.39E+07	3.52E+07
PP103	2.62E+05	1.05E+06	1.09E+06
PP301	4.14E+04	1.66E+05	1.72E+05
PP801	2.55E+05	1.02E+06	1.06E+06
Total			
			€ 1797991692 ≈ € 1.8 billion

6.2 Installation factors

Appendix 44. The installation factors applied over the equipment & setting costs obtained from the economic analyzer, in order to obtain the total installation costs.

Equipment Type	Installation factor
Compressors	2.5
(Distillation) Columns	4
Heat Exchangers	3.5
Pumps	4

6.3 Duties

Appendix 45. Duties of the heat exchangers.

Equipment	Heat without heat integration	Absolute value	Use of heat	Heat after correction for heat integration	absolute value (kW)
PE-301	-2.34E+04	2.34E+04	Cold ethanol stream used to cool gas from PC-101	0	0
PE-801	-6.03E+04	6.03E+04	Cold ethanol stream used to cool gas from PC-701	0	0
PE-101	-2.88E+04	2.88E+04	Cold ethanol stream used to cool feed gas to PC-101	0	0
PE-103	-2.19E+04	2.19E+04	Cold ethanol stream used to cool toluene liquid to PC-101	0	0
PE-809	-1.50E+04	1.50E+04	Cold toluene from PV-801 used to cool gas from stripper	0	0
PE-901	-9.53E+03	9.53E+03	Cold CO gas from solvent recovery used to cool incoming feed gas to PC-101	0	0
PE-401	-2.08E+04	2.08E+04	Cold lean gas from solvent recovery used to cool incoming feed gas to PC-101	0	0
PE-601	4.06E+05	4.06E+05	Warm toluene used to warm up cold toluene to PC-701	0	0
PE-310	-2.63E+05	2.63E+05	Cooling of the ethanol cooling flow from all heat exchangers in the plant	2.63E+05	2.63E+05
RR101	-2.05E+05	2.05E+05	Generation of LP steam that is used as utility stream in the reboiler of RC604	-1.28E+05	1.28E+05
RE104	-2.11E+03	2.11E+03	Cold Ethanol stream from purification section used	0	0
RC201-Condenser	-3.00E+05	3.00E+05	Combined with the reboiler of RC503	-7.15E+03	7.15E+03
RC302 - Condenser	-7.96E+04	7.96E+04		-7.96E+04	7.96E+04

RC503 - Condenser	-1.79E+05	1.79E+05		-1.79E+05	1.79E+05
RC604 - Condenser	-3.51E+04	3.51E+04		-3.51E+04	3.51E+04
RC905- Condenser	-6.20E+03	6.20E+03		-6.20E+03	6.20E+03
RE802	-7.60E+02	7.60E+02	Cold Ethanol stream from purification section used	0	0
RE803	-9.90E+04	9.90E+04	Cold Ethanol stream from purification section used	9.02E+03	9.02E+03
RC201- Reboiler	3.73E+05	3.73E+05		3.73E+05	3.73E+05
RC302 - Reboiler	1.48E+03	1.48E+03		1.48E+03	1.48E+03
RC503 - Reboiler	2.53E+05	2.53E+05	Combined with condenser of RC201	0	0
RC604 - Reboiler	7.02E+04	7.02E+04	Combined with LP steam generated by reactor cooler	0	0
RC905- Reboiler	1.24E+04	1.24E+04		1.24E+04	1.24E+04
CE-101	2.68E+04	2.68E+04		2.68E+04	2.68E+04
CE-102	-2.68E+04	2.68E+04	Cold ethanol from purification section used to cool feed gas from CU-101	0	0
TOTAL based on absolute values		1.62E+06			

Appendix 46. Literature duties.

From literature	J/cum	cum/min	cum/s	W	kW	
Electrostatic Precipitator					4.27E+02	From literature data
Reboiler heat	1.00E+06	6.02E+03	1.00E+02	1.00E+08	1.00E+05	COSORB stripper
Condenser heat	5.50E+06	6.02E+03	1.00E+02	5.51E+08	5.51E+05	COSORB stripper

Appendix 47. Pump and compressor duties.

Pumps	kW
PP-101	9.31E+02
PP-102	3.64E+02
PP-103	3.50E+01
PP-301	3.00E+00
PP-801	4.60E+01
RP-701	6.33E+02
RP-101	9.70E+01
Compressors	
CK-101	3.59E+04
PK-202	3.78E+02
PK-204	5.86E+04
PK-205	1.76E+04
PK-206 (=PK-901)	2.59E+04
RK-101/102/103/104	8.18E+04

Appendix 48. Mole balance over absorber and solvent recovery PU-301. Note: all mole/mass balances are given in a separate excel file. This balances is explicitly given in the appendix as it is referred to in the report.

Stream	Toluene In (kmol/hr)	Feed gas (kmol/hr)	CO + Toluene (kmol/hr)	Lean gas (kmol/hr)
In/Out	In	In	Out	Out
H2	0.0E+00	7.3E+03	0.0E+00	7.3E+03
N2	3.0E-01	1.7E+04	7.5E+01	1.7E+04
CO	8.6E+01	1.5E+04	1.4E+04	3.8E+02
CO2	3.8E+01	6.8E+03	7.6E+02	6.1E+03
CH4	1.6E+00	2.4E+03	1.6E+02	2.3E+03
Toluene	1.1E+05	0.0E+00	1.1E+05	5.5E+00
Ethanol	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Appendix 49. Mole balance over absorber and solvent recovery PU-301 with expected CuAlCl_4 added and expected equilibrium reached. Note: all mole/mass balances are given in a separate excel file. This balances is explicitly given in the appendix as it is referred to in the report.

Stream	Toluene In (kmol/hr)	Feed gas (kmol/hr)	CO + Toluene (kmol/hr)	Lean gas (kmol/hr)
In/Out	In	In	Out	Out
H2	0.0E+00	7.3E+03	0.0E+00	7.3E+03
N2	3.0E-01	1.7E+04	7.5E+01	1.7E+04
CO	0.0E+00	1.5E+04	0.0E+00	3.8E+02
CO2	3.8E+01	6.8E+03	7.6E+02	6.1E+03
CH4	1.6E+00	2.4E+03	1.6E+02	2.3E+03
Toluene	7.1E+04	0.0E+00	8.5E+04	5.5E+00
Ethanol	0.0E+00	0.0E+00	0.0E+00	0.0E+00
$\text{CuAlCl}_4.\text{tol}_2$	2.0E+04	0.0E+00	6.2E+03	0.0E+00
$\text{CuAlCl}_4.\text{CO.tol}$	8.6E+01	0.0E+00	1.4E+04	0.0E+00

8. Distribution of work by team members

Appendix 50. Below a table of the distribution of the work that has been done on the research project. This is just an approximation, as everyone helped everyone with everything during this project.

Part	Section	Calculated/made by:	Part in report written by:
Introduction	-	-	Sanne
	Purification - Clean-up	-	Vincent
	Purification - COSORB	-	Onno
	Purification - Aspen model	Onno&Vincent	-
Process Overview	Purification - PFD	Onno&Vincent	
	Reaction - report	-	Sanne
	Reaction - Aspen model	Maurits&Sanne	-
	Reaction - PFD	Maurits	-
	Purification - Columns	Maurits&Sanne	Sanne
Equipment specifications	Purification - Heat exchangers	Onno	Onno
	Purification - Pumps	Vincent	Vincent
	Reaction - Reactor	-	Sanne
	Reaction - Columns	Maurits&Sanne	Sanne
	Reaction - Heat exchangers	Onno	Sanne
	Reaction - Pumps	Vincent	Sanne
P&ID's and control	Purification - Clean-up	Vincent	Vincent
	Purification - Absorber	Onno	Onno
	Purification - Stripper	Vincent	Vincent
	Reaction - All	Maurits	Maurits
Process Safety	General process safety	-	Sanne
	HAZOP table	Everyone	Everyone
	Adapted P&ID's Reaction section	Maurits	Maurits
	Adapted P&ID's Purification section	Onno&Vincent	Onno&Vincent
Capital Cost Estimation	Economic Analyzer - Heat exchangers	Onno	-
	Economic Analyzer - Pumps	Vincent	-
	Economic Analyzer - Columns	Sanne&Maurits	-
	Report - Purification	Vincent&Onno	Onno
	Report - Reaction	Sanne	Sanne
	Report - Total Costs	-	Sanne
Conclusion	-	-	Sanne
Appendices	Purification Part	Vincent&Onno	Maurits
	Reactor part	Maurits&Sanne	Maurits
List of abbreviations	-	Onno	-

10 List of abbreviations

Abbreviation	Definition
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ACV	composition control valve
CC-xxx	Cleanup column
CE-xxx	Cleanup heat exchanger
CI/AI	composition indicator
CIC/AIC	composition indicator controller
CK-xxx	Cleanup compressor
CM-xxx	Cleanup mixer
CP-xxx	Cleanup pump
CS-xxx	Cleanup separator
CT/AT	composition transmitter
CU-xxx	Cleanup utility
CV-xxx	Cleanup vessel
D.P.	design pressure
D.T.	design temperature
ESP	electrostatic precipitator
FAH	flow alarm high
FAL	flow alarm low
FC	opens with failure
FFIC	Flow fraction indicator controller
FI	flow indicator
FIC	flow indicator controller
FO	opens with failure
FT	flow transmitter
HAZOP	hazard and operability study
JI	power indicator
LAH	level alarm high
LAL	level alarm low
LCV	level control valve
LI	level indicator
LIC	level indicator controller
LOC	loss of containment
LSV	level safety valve
LT	level transmitter
M	molar (mol/l)
M (P&ID)	motor
MOC	materials of construction
NTA	Nitrilotriacetic acid
PAH	pressure alarm high
PAL	pressure alarm low
PC-xxx	Purification column
PE-xxx	Purification heat exchanger
PF-xxx	Purification reboiler
PI	pressure indicator
PIC	pressure indicator controller

PK-xxx	Purification compressor
PP-xxx	Purification pump
ppm	parts per million
PS-xxx	Purification separator
PSA	pressure swing absorption
PSV	pressure safety valve
PT	pressure transmitter
PU-xxx	Purification utility
PU-xxx	Purification utility
PV-xxx	Purification vessel
PVP	polyvinyl pyridin
RA-xxx	Reaction absorber
RC-xxx	Reaction column
RE-xxx	Reaction heat exchanger
RF-xxx	Reaction reboiler
RI-xxx	Reaction incinerator
RPMIX	product mixture stream of reactor
RR-xxx	Reaction reactor
Rstoic	Stoichiometric reactor
RV-xxx	Reaction vessel
SS 304	stainless steel type 304
SS 316	stainless steel type 316
TAH	temperature alarm high
TAL	temperature alarm low
TI	temperature indicator
TIC	temperature indicator controller
TT	temperature transmitter
vol%	volume percent
wt%	weight percent