ACE Group

MethanolPlant

Brief Process Description

The plant was designed by ICI to operate in two primary modes, methanol production and hydrogen recovery for the ICI complex. Most of the time the plant was operated more in the hydrogen recovery mode with less emphasis on actual methanol production. Hydrogen production required high purge gas from the synthesis loop going to a Hysieve unit, with waste gas returning as fuel to the reformer burner system.

Natural Gas Treatment

Natural gas feed is processed in the normal manner to remove any sulphur from the gas. Firstly the gas is heated in a gas-fired heater to 375 oC the gas then flows through the topside of the hydrotreater where any sulphur compounds are converted to H2S, this gas then passes through the zinc oxide bed where any H2S is removed. Present UK gas is very low in sulphur.

Steam Reforming System

The steam reforming system is based on twin Foster Wheeler terrace fired reformers, with top mounted convection banks and ID fans and stacks. As is typical of this vintage of reformer there was very little effort made in regards to tight efficiency. The plant was originally designed at 380 therms per ton. However, it would not take a considerable amount of investment to reduce this to 350 therms per ton (35 million BTU) and possibly as low as 340 therms for ISBL numbers. Reformed gas exiting from the reformers is then partially cooled by producing 900# saturated steam. This 900# steam is then superheated in stand alone gas fired heaters. The reformed gases are then further cooled, firstly by exchange with BFW followed by finfan coolers prior to compression. (It is interesting to note that, reformed gases are not utilized on this plant for methanol distillation reboilers)

Compression

The compressors were purpose built for this plant and are one off in design. The Make-Up-Gas (MUG) designed and built by Demag of Germany has proven to be a very sturdy design with absolutely no problems and in fact has only been opened on 1 occasion.
The circulator is of an overhung design and again is very reliable in operation. Both machines are driven by steam turbines using 900# steam. The MUG has twin turbines with extraction to 400# steam from the first case and pass out to 50# from the second

case and the circulator direct pass out to 50#.

The MUG compressor is a dual barrel multi-stage machine raising the pressure from around 20barg to some 105barg.

Methanol Synthesis

The methanol synthesis converter originally utilized the old ICI Lozenge-type Quench Converter, this was up-graded during the 1996 to the Casale Arc type converter which provides a better conversion ratio. All in all the synthesis loop on this plant is very simple yet reliable. Methanol is extracted by condensation from the circulating gas stream, letdown in pressure removing some of the dissolved gases. The crude methanol can then either go to a crude methanol storage tank of 600 M3 capacity from where it is pumped to distillation or it can pass directly to the distillation section.

Distillation

The distillation process is based on the typical 2 column system. The first and smaller column removes any dissolved gases and light fractions, where the second column removes water and any higher boiling point fractions producing chemical grade methanol. The product methanol leaves the distillation section running down into 2 shift tanks of 600 M3 capacity each. This is the limit of onsite storage capacity there are no offsite storage tanks associated with this plant.

Utilities

This plant depends entirely on imported utilities with the exception of cooling water which is dedicated to this plant. Main electrical switchgear forming primary distribution will have to be renewed should the plant be moved.

Process Overview

The methanol plant consist of two methanol production units (MeOH-1 and MeOH-2) and are both designed to produce chemical grade methanol using natural gas as feedstock. Both units are able to produces approx. 1250 ton methanol per day. MeoH-1 is currently running and MeoH -2 is “mothballed” since mid 2005.

Today there are different approaches and designs, but the overall philosophy consists of 4 major process-units namely; steam reforming, compression, methanol synthesis and distillation. Steam reforming can take the form of:

Steam Methanol Reforming (SMR)

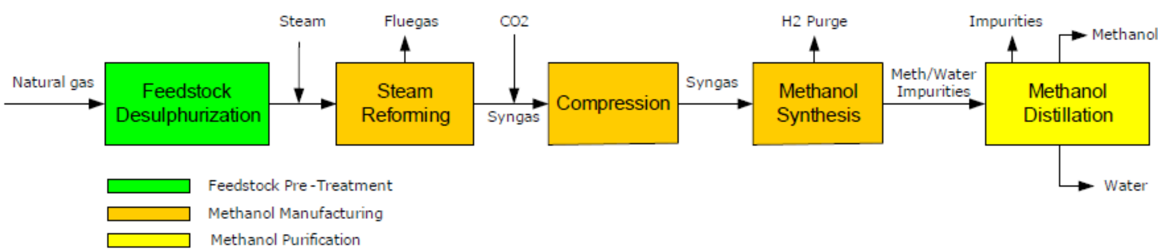
Autothermal Reforming (ATR)

Combined Methanol Reforming

(CMR)

The methanol units use SMR technology based on ICI/Davy design. Many such designs have been built worldwide. The overall SMR design is given below

Typical SMR based “Grey” Methanol Production Block Scheme

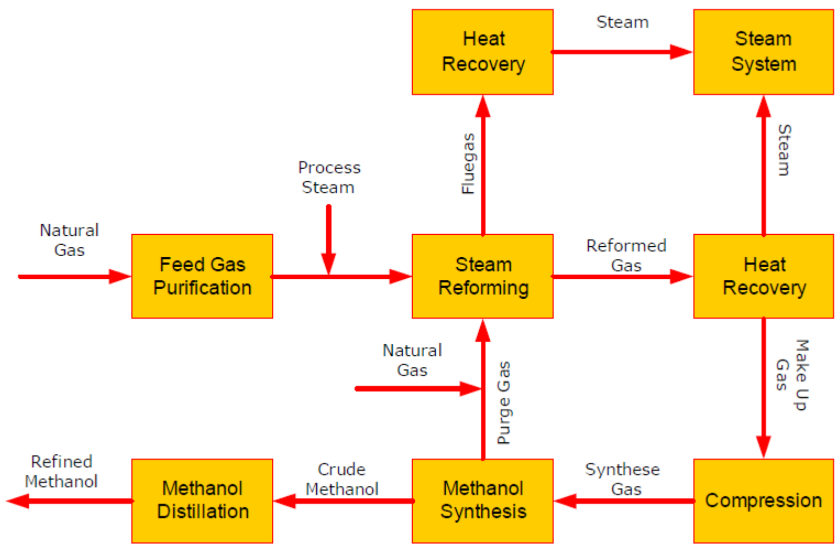


whereby the methanol synthesis unit produces some excess hydrogen, i.e., more than that is needed to balance the methanol production. Hence, some plants will import carbon
dioxide to balance off this hydrogen and make additional methanol. If carbon dioxide is not imported directly into the process then the excess of hydrogen can be exported, preferably in purified form or used as an additional fuel in the reformer section.

Typical SMR based “Grey” Methanol Production Block Scheme

In our case the excess of hydrogen, a mix stream of CO, CO_2, H_2, CH_4 and small traces of nitrogen, is used as fuel for the reformer. The main processing steps are described in next figure and the relation between the process units is shown in next figure

Integrated Methanol Production Scheme



Desulphurization of Natural Gas

Sulfur compounds in the feedstock are harmful for reformer efficiency because they permanently poison the nickel catalyst resulting in deactivation of the Ni catalyst. Sulfur concentration is for this reason reduced to lower then 20 ppb.

Natural gas is heated to approx. 370 °C at a pressure of 26 barg by integrated heaters in the reformer. After addition of a small amount of hydrogen it is possible to remove sulfur compounds and if present chloride from the natural gas.

The desulphurization of natural gas is a two step process using two different catalysts in different vessels. The first vessel contains a Co/Mo catalyst to convert sulfur components to hydrogen sulfide (H_2S). The second vessel contains ZnO to convert the formed H_2S to solid sulfur. The solid sulfur is adsorbed over three beds, from which the last one is a pilot (police) bed to prevent in all cases throughput of sulfur to the reformer unit and protecting the catalyst.

The following reactions occur:

Co/Mo catalyst:	RSH (g) + H_2 (g)	←→	H_2S (g) + RH (g)
ZnO catalyst:	H_2S (g) + ZnO (s)	←→	ZnS (s) + H_2O (g)

MeOH Gas Purification Plant

Steam Reforming

Steam is fed together with natural gas to the reformer where different chemical reactions takes place at high temperature, ranging from 500 °C to 800 °C, over a nickel supported catalyst (Ni/Al_2O_3).

(Syngas reaction)	$2CH_4 + 2H_2O$	←→	$2CO + 6H_2$	(Exothermal)
(Water/gas shift reaction)	$CO + H_2O$	←→	$CO_2 + H_2$	(Endothermal)
(Overall reaction)	$2CH_4 + 3H_2O$	←→	$CO + CO_2 + 7H_2$	

- A high steam to carbon ratio (S/C) of approx. 3 to 1 is needed to prevent carbon formation on the catalyst and into the pores, deactivating the catalyst.
- The syngas reaction requires heat which is provided by burning fuels inside the reforming furnace.
- The reformed gas (a mixture of mainly H2O, CO, CO_2, H_2 and a small amount of CH_4) is cooled from 800°C to approx 25°C. The dry reformed gas is then compressed and routed to the methanol synthesis unit.

- Heat from the reformed gas is used for boiler feedwater, both distillation columns and primary for the production of High Pressure (HP) steam.

This process is well understood and well practiced. The SMR process produces excess hydrogen. If carbon dioxide is locally available the hydrogen can be balanced to optimize carbon efficiency. A key parameter in the production of synthesis in the reformer is the Stoichiometric Number (SN), expressed on a molar/volume basis as:

$SN = (H_2 - CO_2) / (CO_2 + CO)$

In the case of MeOH in "Grey" methanol mode provides a synthesis gas number of minimum 2.05. The excess of hydrogen increases the SN significant. No carbon dioxide

at this moment is available to balance the excess of hydrogen. The hydrogen is used as fuel in the reforming section.

Two reformers (south and north) consist each of two cells (NW, NE, ZW, ZE) and are a proven Foster Wheeler “Terrace Wall” design. Each cell consists of 144 tubes (a total of 576 tubes) of chromium-nickel “Micro” alloy. The furnaces use low NOx burners (PXMR- 20) of John Zink design.

MeOH Reformer Unit

Compression

The syngas from the reformer unit is cooled down and condensate is separated and reused in the process of making HP steam. The dry syngas is compressed (supplier: Creusot Loire, model RC-9B firstandsecondstep) to approx. 95 barg. First step is to compress the gas from 15 to 40 barg. The gas temperature increases, due to this compression step, to 150 °C, which is then cooled down with air coolers to 25-30 °C. The high pressure part of the compressor brings the gas from 40 barg to 95 barg resulting in a gas discharge temperature of 130 °C. Air coolers are used to cool the gas to 30 °C, before it is fed to a second compressor.

The second compressor (supplier: Creusot Loire, model RC 3-2B), so called circulator, is used to recycle over the methanol converter to maintain pressure at approx. 100 barg.

Turbines (Siemens model EHNG 40/32 and Alstohm Rateau model TU 8070 CD 37) uses high and middle pressure steam to generate the power for the compressors.

Circulator in the Compressor housing

Methanol Synthesis

If possible carbon dioxide is added to the dry reformer gas and compressed, prior to entering the converter, to meet optimal conditions (250 °C, 80-100 barg) for the following overall exothermal reactions:

$CO + 2H_2 \leftrightarrow CH_3OH$

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

$CO + H2O \leftrightarrow CO2 + H2$

These reactions use CuO/ZnO catalyst and produce heat that needs to be removed from the methanol converter. The existing methanol converter is an "ICI Quench Cooled Converter" type, characterized by a quench system that relies on cold shot cooling to hold the catalyst bed temperatures in the range in which high methanol yields and selectivity may be obtained.

Heat regenerated from the process is used to heat up the feed stream and to produce low pressure (LP) steam. The synthese gas from the methanol converter is cooled and the condensed methanol and water is separated from the gas. The remaining gas is then cooled further to 35 °C, using air coolers. Liquefied water and methanol is collected in a high pressure separation vessel. The remaining gas is partly recycled back to the suction of the circulator and the main part of the gas is used as fuel for the reformer.

During depressurizing from 80 barg to 3 barg a small amount of flash gas is formed and this is released to the flare for safety reason. The methanol, water and impurities are processed further for separation in the distillation columns

MeOH Methanol Synthesis Reactor

Methanol Purification:

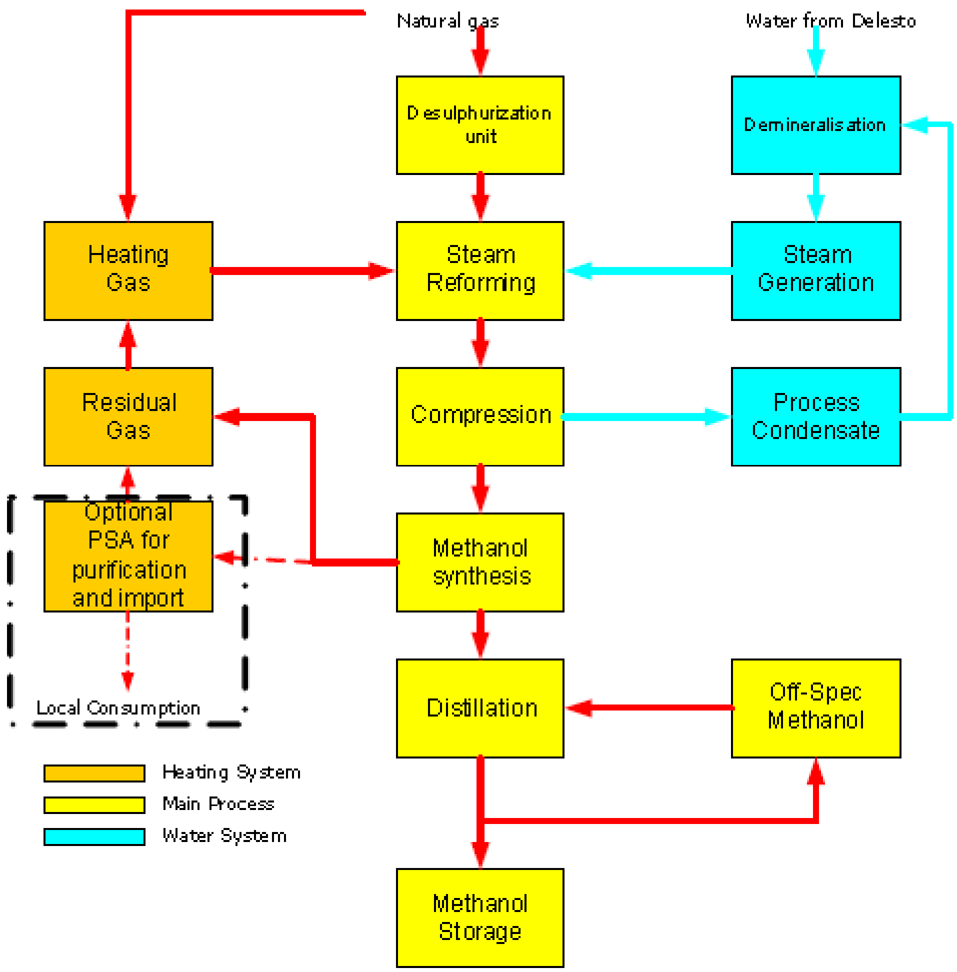
In addition to water (17%) a number of organic impurities (1%), such as methyl esters, simple fatty acids, ketones, benzene, paraffinic hydrocarbons with molecular weights between 70 to 170, ethanol, higher alcohols, DME, are produced at the same time as methanol (80%). These chemicals are separated from the methanol in two distillation columns. Both columns are made of carbon steel and the material is protected by pH control with caustic soda. The first column, so called “topping” column removes the light ends from the feed. These light ends are burned in the flare. The bottom product of the topping column is the feed to the main distillation column. For the main distillation column methanol is the top product and water is the bottom product. Water is collected and disposed as a waste stream. Investigation is started to see whether this water stream can be purified and reused as steam after demineralization. The quality of methanol is process controlled and after measuring it is stored in storage vessels owned by a third party (JPB).

On sieve tray number 12 to 20 (lower section of the column) there is the possibility to withdraw the heavy alkenes, ethanol and higher alcohols from the column and use it as fuel for the reformer.

Methanol Purification
Refining (C302) and Topping (C301) Columns

Configuration

Natural gas is used for process and utility needs. Water is imported from Delesto and together with condensate from the process fed to the demineraliÂ£ation unit and then used for the steam production. The process chemistry produces condensate and this is reused in the process.



Overall Mass Balance

Next Figure illustrates the overall mass balance for MeOH-1 in “Grey” methanol case including air consumed and carbon dioxide co-produced.

MeoH Overall Mass Balance

COMMENTARY ON OTHER PROCESS FACTORS

Impurities

When operating with natural gas as feedstock the desulphurization unit will reduce sulfur to ppb (part per billion) levels in the gas and this allows the catalyst to operate effectively. As the catalyst deactivates, the reformer temperature must be increased requiring additional natural gas.

Failure of the desulphurization unit could irreversibly damage the catalyst such that replacement is necessary. The existing plant has reliable process safeguards in place to prevent this.

Utilities and Other Infrastructure

Power and Steam

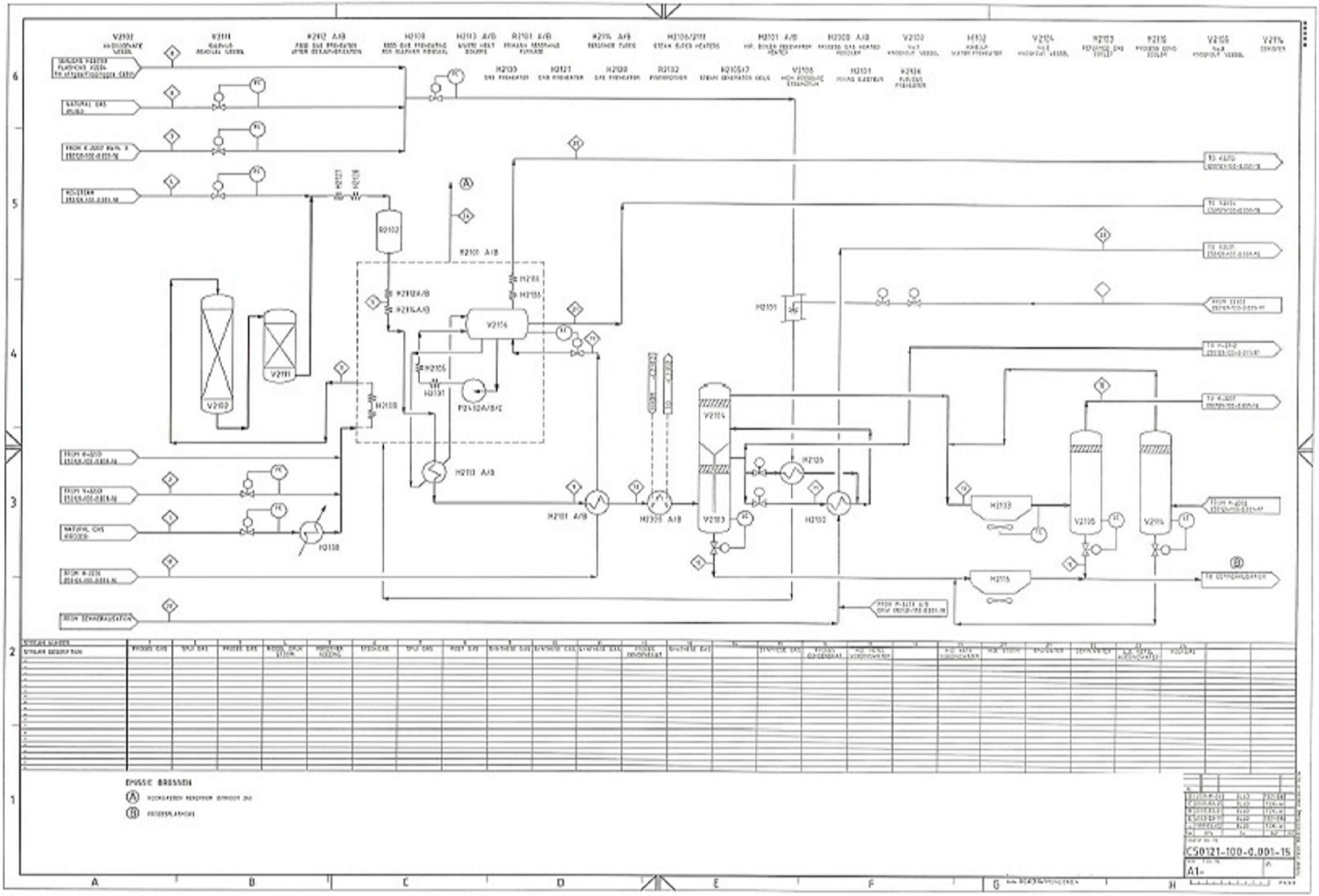
This is mainly supplied to the site by Delesto BV, a 50%-50% joint venture with Essent and AkzoNobel. The company operates a modern natural gas powered cogeneration plant that provides steam and electricity to the various customers at the Chemical Park (CPD).

Delesto supplies steam (700 ton/h), electricity (530 MWe) and other utility products. Most of the electrical power generated is exported to the public network.

Recently building activities have started for the waste to energy plant . The construction of this plant guarantees long standing durable energy delivery. The EON facility is on-stream. At this moment we are purchasing “green” steam from EON with a contract of 240.000 ton/a (191.000 MWh/a).

Water Systems

The existing facility incorporates two demineralization lines with cation and anion resin and bed with combined anion and cation resin. The unit is capable to produce 200 m^3/h water for steam production



V2102
V2111
R2102
H2101 A/B
V2116
H2105
P2412A/B/C
H2108
H2113 A/B
H2101
V2104
V2103
H2125
H2102
H2133
H2115
V2105
V2114
H2130
A
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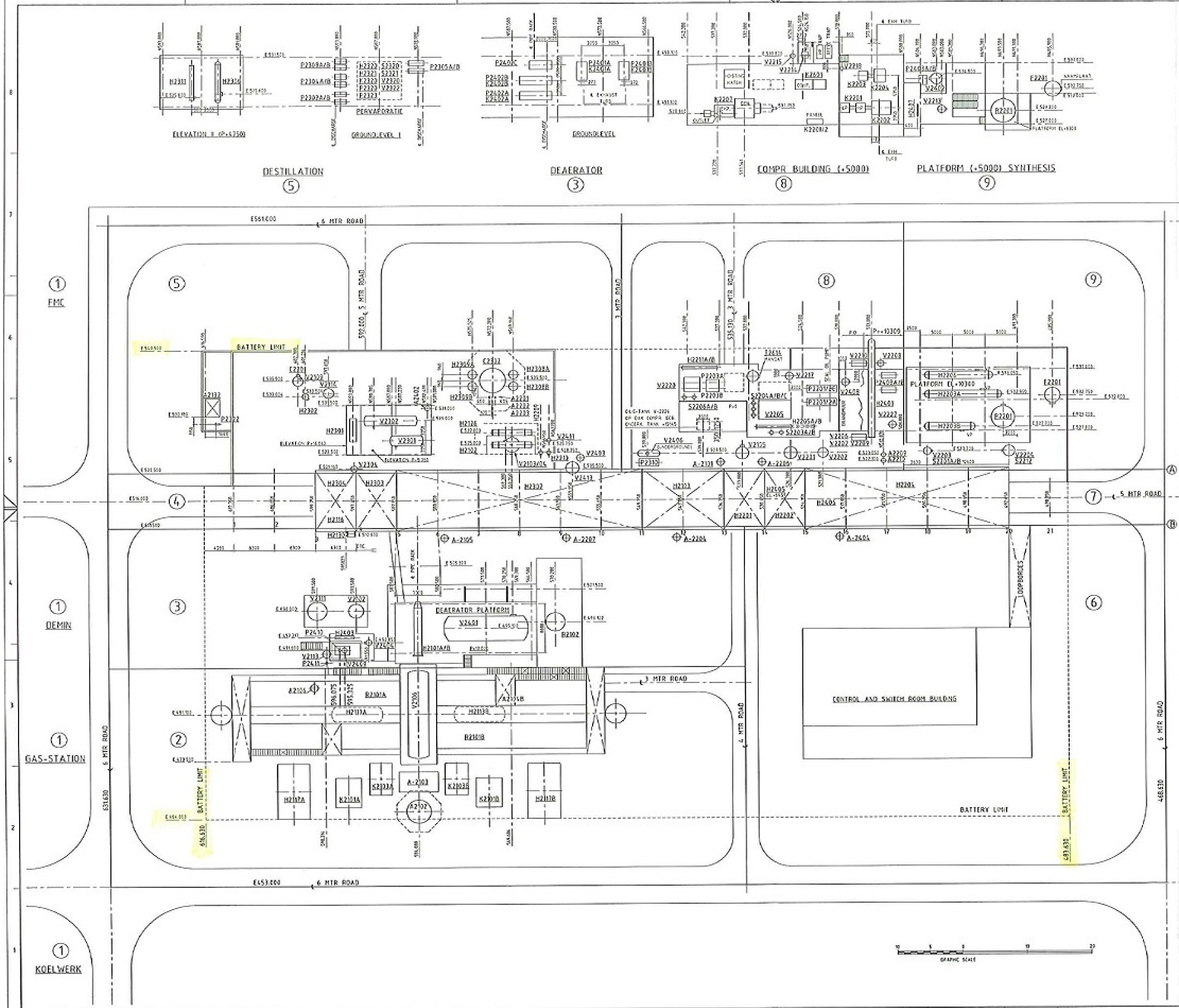

EQUIPMENT - LIST

CODE	DESCRIPTION	ELEVATION	NOTE	CODE	DESCRIPTION	ELEVATION	NOTE
A2101	PROCESS GAS VENT SILENCER			P2201A	OIL-PUMP (LUBE)		
A2102	FLUE GAS STACK			P2201C	OIL-PUMP (LUBE)		
A2103	AIR INTAKE FILTER			P2202A	OIL-PUMP (SEAL)		
A2104	FUSEL OIL BURNER			P2202C	OIL-PUMP (SEAL)		
A2105	NATURAL GAS SILENCER			P2203A	OIL-PUMP		
A2106	SILENCER	P+2100		P2203B	OIL-PUMP		
A2132	COOLING UNIT			P2102A	TOPP.COL.REFLUX PUMP	P+535	S.pmp
A2201	FLARE-STACK D819			P2102B	TOPP.COL.REFLUX PUMP	P+535	S.pmp
A2202	FLARE-STACK D039			P2104A	TOPP. METHANOL PUMP	P+535	S.pmp
A2203	FLARE-STACK D103			P2104B	TOPP. METHANOL PUMP	P+535	S.pmp
A2204	HP. PURGE GAS SILENCER			P2105A	REF. COL. REFLUX PUMP	P+535	
A2205	ANTI-SURGE SILENCER			P2105B	REF. COL. REFLUX PUMP	P+535	S.pmp
A2209	[illegible]	P+7140		P2108A	FOEZELOLIE PUMP	P+535	S.pmp
A2210	[illegible]	P+7140		P2108B	FOEZELOLIE PUMP	P+535	S.pmp
A2402	L.P. STEAM VENT SILENCER			P2111	DRIPTANK METHANOL PUMP		
A2403	HP.STEAM SILENCER			P2122	CIRCULATION PUMP		
A2404	HP.STEAM SILENCER			P2401A	B.F.W. PUMP	P+1050	
				P2401B	B.F.W. PUMP	P+1050	
C2301	TOPPING COLUMN	P+4450		P2402A	BOILER CIRCULATION PUMP	P+715	
C2302	REFINING COLUMN	P+5750		P2402B	BOILER CIRCULATION PUMP	P+715	
				P2402C	BOILER CIRCULATION PUMP	P+715	
F2201	START-UP HEATER [illegible]	P+7650		P2403A	STEAM CONDENSATE PUMP		
				P2403B	STEAM CONDENSATE PUMP		
H2101A	HP. BOILERFEEDWATER HEATER	P+14500		P2408A	CONDENSATE PUMP (K2101)		
H2101B	HP. BOILERFEEDWATER HEATER	P+12200		P2408B	CONDENSATE PUMP (K2101)		
H2102	MAKE-UP WATER PREHEATER	P+12500		P2410	CONDENSATE PUMP FROM V2409		
H2103	REFORMED GAS COOLER	P+14450	yes	P2411	PHOSPHATE DOSING PUMP V2410	P+0	
H2105	STEAM GENERATOR		[illegible]				
H2106	STEAM SUPERHEATER		[illegible]	R2101A	REFORMING FURNACE		
H2107	STEAM GENERATOR		[illegible]	R2101B	REFORMING FURNACE		
H2108	FEED GAS PREHEATER		[illegible]	R2102	PRE-REFORMER		
H2111	STEAM SUPERHEATER		[illegible]	R2201	METHANOL CONVERTER	P+3130	
H2112A	MIXED GAS PREHEATER		[illegible]				
H2112B	MIXED GAS PREHEATER		[illegible]	S2201A	HP.CRUDE METHANOL FILTER		
H2113A	STEAM GENERATOR			S2201B	HP.CRUDE METHANOL FILTER		
H2113B	STEAM GENERATOR			S2203A	LUBE-OIL FILTER		
H2114A	RADIANT COIL		[illegible]	S2203B	LUBE-OIL FILTER		
H2114B	RADIANT COIL		[illegible]	S2204A	SEAL-OIL FILTER		
H2115	HP. STEAM DESUPERHEATER			S2204B	SEAL-OIL FILTER		
H2116	PROCESS COND. COOLER	P+14450	yes	S2204C	SEAL-OIL FILTER		
H2117A	COMBUSTION AIR HEATER			S2206A	OLIE-FILTER		
H2117B	COMBUSTION AIR HEATER			S2206B	OLIE-FILTER		
H2119	SAMPLE COOLER (V2103)			S2212	SCRUBBER		
H2120	STEAM SAMPLE COOLER (V2106)						
H2121	SAMPLE COOLER LP. B.F.W.			T2614	LUCHTKETEL		
H2122	BLOWDOWN SAMPLE COOLER						
H2123	CONDENSATE COOLER		[illegible]	V2102	HYDROGENATE VESSEL	P+1900	
H2126	FUEL GAS PREHEATER		[illegible]	V2103	NR1 K.O.VESSEL ONDER	P+1455	
H2127	MIXED FEED OUTLET DESUPERHEATER		[illegible]	V2104	NR2 K.O.VESSEL BOVEN		
H2128	MIXED FEED PRE-REFORMER			V2105	NR3 K.O.VESSEL	P+1150	
H2130	HEAT EXCHANGER			V2106	STEAMDRUM	P+21600	
H2201	MUG COMPR. INTERCOOLER	P+14450	yes	V2109	PROCESS CONDENSATE SCRUBBER		
H2202	MUG COMPR. INTERCOOLER	P+14450	yes	V2111	DESULPHURISATION VESSEL		
H2203A	LOOP INTERCHANGER	P+1900		V2113	PHOSPHATE DOSING VESSEL	P+0	
H2203B	LOOP INTERCHANGER	P+1900		V2114	DEMISTER-VAT	P+3100	
H2204	LOOP CONDENSER	P+14450	yes	V2201	MUG COMPR.AFTERCOOLER K.O.VESSEL	P+150	
H2205A	LUBE-OIL COOLER			V2202	MUG COMPR.INTERCOOLER K.O.VESSEL	P+200	
H2205B	LUBE-OIL COOLER			V2203	METHANOL SEPARATOR 2	P+1050	
H2206	HP. B.F.W. HEATER			V2204	LET-DOWN VESSEL	P+2150	
H2209	PURGE GAS HEATER HPSL			V2205	MAIN-OIL TANK		
H2210	PURGE GAS HEATER LPSL			V2206	HP.SEAL-OIL OVERHEADTANK		
H2211A	OLIE KOELER			V2207	LP.SEAL-OIL OVERHEADTANK		
H2211B	OLIE KOELER			V2208	RECYCLE SEAL-OIL OVERHEADTANK	P+10000	
H2301	FEED OVERHEADS EXCHANGER	P+14300		V2209	MUG LUBE-OIL OVERHEADTANK		
H2302	TOPP. COL. REBOILER	P+2100		V2210	RECYCLE LUBE-OIL OVERHEADTANK	P+10000	
H2303	TOPP. COL. REFLUX CONDENSER	P+14450		V2211	COLLECTING POT M.U.G. TURBINE		
H2304	SEC. METHANOL CONDENSER	P+14450		V2212	COLLECTING POT RECYCLE		
H2306	REFINED METHANOL COOLER	P+5200		V2213	METHANOL SEPARATOR 1	P+6500	
H2307	REF. COL. REFLUX CONDENSER	P+14450	yes	V2214	OIL SEPARATOR		
H2308A	PROCESS GAS REBOILER	P+2100		V2215	OIL SCRUBBER		
H2308B	PROCESS GAS REBOILER	P+2100		V2217	OIL-GAS SEPARATOR	P+1430	
H2309A	REF. COL. REBOILER	P+2100		V2218	OIL-GAS SEPARATOR		
H2309B	REF. COL. REBOILER	P+2100		V2220	OLIE-TANK		
H2311	BOTTOMS WATER COOLER	P+5150		V2224	OLIE-TANK OP DAK COMPRESSOR	P+15545	[illegible]
H2403	STEAM CONDENSER	P+20910		V2227	MENGCONDENSORFLASHVAT		
H2405	L.P. STEAM DESUPERHEATER			V2301	TOPP.COL.REFLUX DRUM	P+9250	
H2406	H.P. STEAM OUTLET DESUPERHEATER			V2302	REF. COL. REFLUX DRUM	P+10000	
H2407	SURFACE CONDENSER FOR M.U.G.			V2304	SEC. METHANOL SEPARATOR	P+11000	
H2408	CONDENSATE COOLER			V2401	DEAERATOR	P+11000	
				V2402	CONDENSATE VESSEL	P+150	
K2101A	INDUCED DRAUGHT FAN(EXH)			V2404	BLOW DOWN FLASH VESSEL	P+150	
K2101B	INDUCED DRAUGHT FAN(EXH)			V2406	DRIP TANK IN DE GROND	P-1469	
K2103A	FORCED DRAUGHT FAN(CMBUST.)			V2408	NITROGEN BUFFERTANK	P+910	
K2103B	FORCED DRAUGHT FAN(CMBUST.)			V2409	FLASH TANK		
K2201	MAKE-UP GAS COMPRESSOR	P+6560	L.cmpr.	V2410	PHOSPHATE DOSING VESSEL		
K2202	MUG COMPR. TURBINE	P+6560	L.turb.	V2411	FLASH VESSEL	P+850	
K2203	LOOP CIRCULATOR	P+6560	L.cmpr.	V2418	NITROGEN BUFFERTANK		
K2204	CIRCULATOR TURBINE	P+6560	L.turb.				
K2207	EXPANDER (GENERATOR)						
K2401A	B.F.W. PUMP TURBINE	P+1100	L.turb.				
K2401B	B.F.W. PUMP TURBINE	P+1100	L.turb.				
K2402A	BOILER CIRC. PUMP TURBINE						
K2402B	BOILER CIRC. PUMP TURBINE						
K2601	LUCHTCOMPR. MET DROGER						
	WEIGHT				1355,958 kg		

1356 Ton

Ground level
Peil 0 =2650+NAP
NORTH

1. Koelwerk,Gasstation,Dem'in,FMC
2. Reformer
3. Reformer-pompenplaat
4. Koelerbank N.Z.
5. Destillatie.
6. Controlegebouw.
7. Koelerbank Z.Z.
8. Compressie.
9. Synthese.

28
ALGEHELE REVISIE

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