Waste non-recyclable plastic and CO2 as carbon source in large-scale, energy self-sufficient n-butanol production

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Abstract

As a part of the initiative towards integrating sustainability among already existing technological solutions in chemical industry, this report aims at proposing a way of overcoming the standard metrics in order to provide an innovative solution that satisfies industrially relevant demand for n-butanol of 100 000 tonnes/year by designing a highly integrated process in Greece. In particular, n-butanol production from non-recyclable plastic, CO_2 and H_2O combines three sub-processes: Co-electrolysis in solid-oxide electrolysis cell, Plastic thermal pyrolysis and the well established butanol production route: Oxo synthesis. The state of continuous plastic waste growth and the abundance of CO_2 emissions served as the inspiration to be used as alternative carbon sources. Carbon and generalized reaction mass efficiency as the main KPIs for the process equal 28% and 21% respectively. However, detailed process models developed in Aspen Plus enabled effective energy optimization through which it was proven that the process is self-sufficient in terms of energy by including steam cycles. In this way, extensive heating demands were completely satisfied internally in the process by performing Pinch analysis, while the cooling needs were minimized to 22.2MW after steam cycle integration. Thus, no renewable energy is required and additionally 14.7 MW of electricity is exported to the grid. Complementing the study with techno-economic assessment, the process was proven to be viable at the industrial scale. Total profit of 41.5 Mio USD/year is achieved without the introduction of any of gate-fees for treating plastic waste and unwanted CO_2 emissions. This provides the evidence that considering this process on an industrial scale would be of high scientific and societal value, not only in the present, but also in the times to come.

1 Introduction

The scenario of achieving net-zero GHG emissions by 2050 is of high importance for the society as it would stabilize the temperature increase on a global level, but is hard to achieve. It requires for the development of new technologies, but above all, knowing how to integrate the existing ones in the way that would lead to the lowest possible environmental impact. Sustainability practice, Green Chemistry principles and Paris agreement serve as driving force for boosting innovation and finding creative solutions in the pool of alternative feedstock (e.g. waste, CO_2, biomass etc.), renewable energy and less energy-intensive technologies. In this transition towards greener solutions, employing renewable energy plays an important role, as the conventional energy generation technologies are highly reliant on fossil fuels and mitigate the positive impact by increasing the CO_2 emissions. Although complete transformation of the chemical industrial sector is impossible to achieve over night, fast and creative solutions are required with the already existing process infrastructure and readily available feed stock that could replace fossil fuels derivatives. Additional difficulty concerning the transition lies in the technological readiness of the solutions proposed in literature and vast amount of research: much of it not being transferable, robust enough or even possible to implement on a larger scale, thus remaining in the domain of reduced impact.

The idea of using waste material as the carbon source and as renewable feedstock to produce important platform molecules is not new, yet its implementation needs to be followed by incentives as the additional pretreatment and product upgrading steps that increase complexity and induce higher expenses to the production process. Plastic waste is one of the major problems modern society is facing as it is estimated that more than 380 million tonnes of plastics are produced every year and continues to increase at the annual rate of 4% [1]. The rate of plastic production is expected to reach 1100 Mt per year by 2050 and is responsible for 15% of the yearly greenhouse gas emissions [2]. Despite technological advancement, current recycling rates are discouraging: only 23% [3] of the overall amount of plastic produced. Even with current advances in terms of favoring the production of bio-based plastics from second generation biomass (non-edible, waste biomass), the problematic of waste generation remains persistent: its share in the overall plastic balance is expected to increase in the years to come (Figure 1). This is to say that without efficient means of recycling, the carbon cycle of plastic cannot be closed.

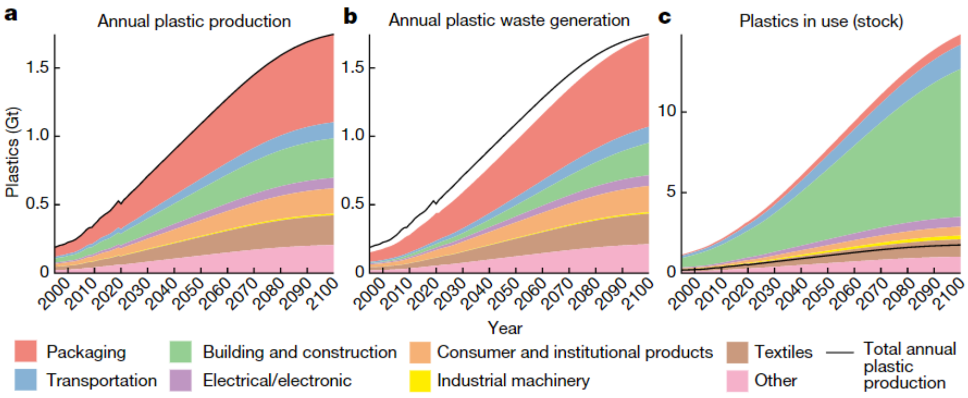


Figure 1: Waste contribution in the overall plastic balance across different sectors [4]

Following current best practice solution, chemical recycling has been considered as the best way to tackle plastic waste problematic, focusing on upgrading the waste to platform molecules, such as propylene in this case that can be further used in Oxo-synthesis to produce n-butanol. By employing such strategy, extensive CO_2 emissions from incineration and other harmful emissions induced by land-filling, as well as micro plastic production are avoided. In addition, by providing alternative source of carbon for n-butanol synthesis, the dependency on fossil fuel is successfully reduced.

Butanol is a commodity chemical used mainly in coating and varnishes applications (see Figure 2), but due to its chemical structure (short alkyl chain and hydroxyl group) it can be used as a standalone solvent, or mixed with other solvents to improve their properties. Furthermore, it is an important intermediate in industry and can even find its application as fuel in mixture with diesel. Out of four isomers, n-butanol holds the largest share of the global butanol market and equals 75% [5]. In the situation of rising oil prices, it might represent a reasonable bio-fuel solution due to its high energy content (33.1 MJ/kg being higher than the lower heating value of ethanol: 26.8 MJ/kg) and compatibility with existing infrastructure [6].

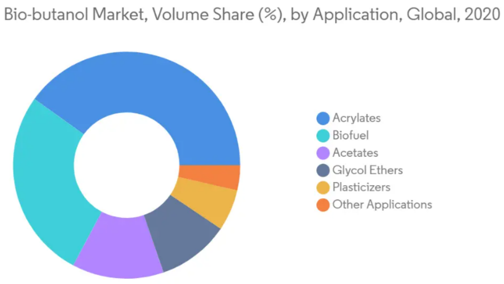


Figure 2: Bio-butanol market share in 2020 [7]

The global demand for butanol (including all isomers) was estimated as 5.5 million tons in 2019, and it is expected to reach approximately 7.5 million tons by 2024, growing at a compound annual growth rate (CAGR) of 6.4% [8]. The area of interested of the report is to facilitate the production of n-butanol and find adequate application in EU, specifically Greece. The import of butanol in Greece is set to reach €2,955,500 by 2026 from €2,122,000 in 2021, with an increase of 137.6% per year [9]. Greece is in top 10 EU countries with highest import of this chemical. Developing an independent production line of n-butanol in the country would enforce the economy and induce savings. Having in mind its location that would facilitate maritime transport, investing in a sustainable n-butanol production in Greece is expected to attract investors.

Greece generated approximately one million tonne of plastic waste in 2018 (Figure 3). Only 27% was recycled, while the remaining 73% was land filled, incinerated, or otherwise treated [10]. This represents huge opportunity for the process development in this area, having in mind the fact that technology designed is adjustable to mixed and non-recyclable plastic waste streams. Life cycle of plastic in Greece from 2018 took a form as shown in Figure 3 and emphasises the need for finding an effective end-of-life solution for plastic waste in order to avoid land filling. Furthermore, enforcing chemical recycling in Greece would offer the opportunity to effectively deal with the plastic sea debris which accounts for the biggest share in the mistreated plastic waste globally. A solution such is chemical recycling offers the possibility to treat the highest fraction of waste plastic which is not sorted and in some cases non-recyclable by turning it into propylene that serves as a platform in the desired butanol production.

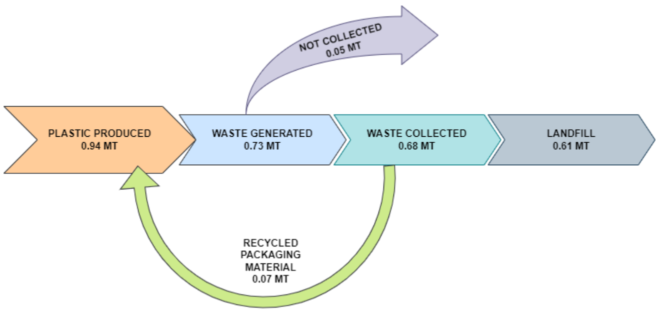


Figure 3: Mass balance of plastic in Greece in 2018; modified from [10]

The following chapters will focus on representing the key process characteristics and how its constituent subprocesses were successfully integrated to a high degree using different modelling techniques.

2 Process design

n-Butanol production process was designed in such a way that enabled high inter-connectivity of its constituent sub-processes which further lead to the efficient mass and energy exchange. The overall process consists of:

1. Co-electrolysis to produce syngas
2. Pyrolysis to produce propylene
3. Oxo synthesis to produce butanol

Typical single-site butanol production rate of 100 000 tonnes per year was taken as the reference for the process design. This requires 32 422 kg/hr of non-recyclable plastic waste input (corresponds to 0.3 MT which is half the amount represented in Figure 3). In order to be able to run the process, 21 793 kg/hr of water and 2 150 kg/hr of CO_2 are required to produce syngas in the CO-SOEC. Water is readily available and can be purified using standard desalination techniques, while the plant location should be such as it would enable direct CO_2 utilization from a fermentation or hydrogen refining line (i.e. CO_2 recovery) or capture the exhaust of a power plant (i.e. CO_2 capture) and then further purified CO_2 by absorption [11]. This would significantly reduce transportation costs and would offer new possibilities for both mass and energy integration on a larger scale.

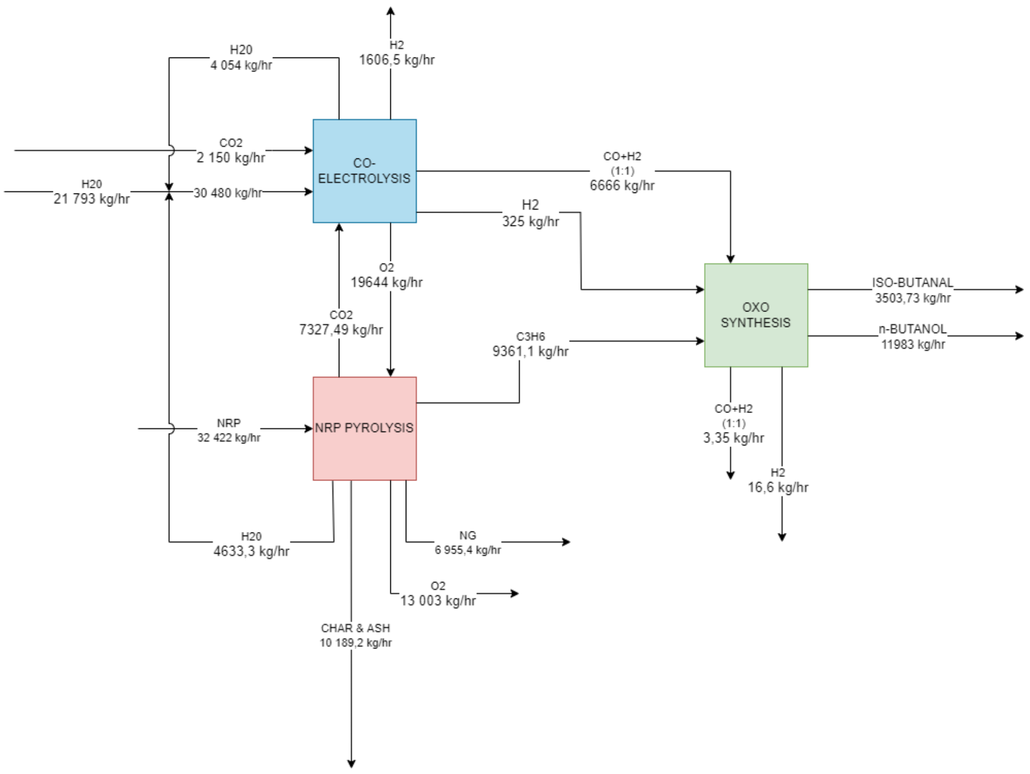


Figure 4: Block-flow diagram of the process configuration

Oxo synthesis is currently the most important process for the manufacturing of 1-butanol and 2-methyl-1-propanol (isobutanol) [5]. The classic process consists of hydroformylation of propylene to a mixture of 1-butanal and 2-methylpropanal (isobutanal). The aldehydes are then converted to alcohols through a hydrogenation step. It is most common to start the synthesis from propylene, although it is also possible to use ethylene as the starting olefin. Both propylene and ethylene are most commonly sourced from crude oil, but can also be produced from more sustainable carbonaceous feedstocks such as biomass or plastic waste, although this requires additional processing. The oxo reaction involves the addition of hydrogen and carbon monoxide to the carbon-carbon double bond in the presence of a catalyst. The syngas ratio and the choice of catalyst both affect the ratio of the two alcohol products.

Using NRP (non-recyclable plastic) as feedstock requires chemical recycling of the polymers to retrieve the monomers, which can then be used as building blocks for the oxo-synthesis. The composition of plastic in the feedstock determines the product distribution of short chain hydrocarbons. Decontamination is necessary as a preliminary step in order to remove contaminants such as sulphur and chlorine. This is especially important if PVC is part of the feed composition. One strategy to remove chlorine is through hydrodechlorination. By adding hydrogen to the plastic mixture prior to the pyrolysis process one can remove the chlorine as hydrochloric acid. The decontamination was modeled in a RYield reactor. The sorting of the plastic, as well as shredding and washing of the waste is not included in the design or simulation of the plant, although these are necessary steps to prepare the plastic for chemical recycling.

Chemical recycling can be done in numerous ways, but non-catalytic pyrolysis was chosen as it is a robust method to process the heterogeneous plastic feed. The data and methods used for the design of the plastic recycling process are based on a senior design report by students at the University of Pennsylvania [12]. The report is a comprehensive study of chemical plastic recycling, with the main end products being ethylene and propylene.

As the pyrolysis not only produces a fraction of short hydrocarbon chains, but also pyrolysis oil and char (C7+), The oil can be burned to supply energy to the plant, as well as provide CO_2 for a co-electrolysis unit producing syngas for the oxo-synthesis.

2.1 Process Simulation

The synthesis of butanol from plastic waste was modeled in Aspen Plus. The plastic pyrolysis, SOEC, hydroformylation and hydrogenation was modeled in separate files, and reconciled afterwards. The SOEC model as completely pre-made [13], and only linearly scaled to accommodate the desired production of syngas. As Electrolyzer cells are scaled up by adding more cells to a stack, this approximation is acceptable. The model of the plastic pyrolysis was based on a pre-made AspenTech support model [14], that was modified to meet the production needs. The hydroformulation and hydrogenation models were created from scratch.

2.1.1 Solid oxide electrolysis cell

Electrolysis of water and CO_2 separately is not a new technology, but co-electrolysis of both compounds together to form syngas poses some significant advantages [15]. It is both more energy efficient and in turn more cost efficient to produce syngas this way due to the fast overall electrochemical kinetics. Compared to the separate processes, the performance of the co-electrolysis reaction is close to that of sole steam electrolysis, while dry CO_2 electrolysis has a much higher activation energy. This means that co-electrolysis has a lower overpotential compared to sole CO_2 electrolysis. In addition to the electrochemical reactions inside the cell, there is a substantial amount of CO_2 being converted to CO through the reverse water gas shift reaction as seen in equation 1, which reduces the total electrical consumption required to produce syngas.

$$H_2 + CO_2 \rightarrow CO + H_2O \tag{1}$$

The solid oxide electrolysis cell (SOEC) unit for co-electrolysis would consist of several stacked electrolyzer cells in order to obtain the necessary volume of syngas, it is however modeled as a single cell in Aspen Plus consisting of several virtual units that models the behaviour accurately, which was later scaled linearly in order to estimate the cost, as well as integrate the heating and cooling needs with the rest of the plant. There would also be the need for a supporting water purification process to prepare the water for electrolysis, but this was not designed or modeled as part of the process.

Figure 5 shows the real units of the SOEC and the separation processes associated with the purification of the syngas. The flowsheet is based on the model created in Aspen Plus, but the SOECs are depicted how they would appear in a plant, and the virtual units that simulate the reactions are represented by these. A full overview of the virtual units used in the modeling of the SOEC are presented in Figure 18.

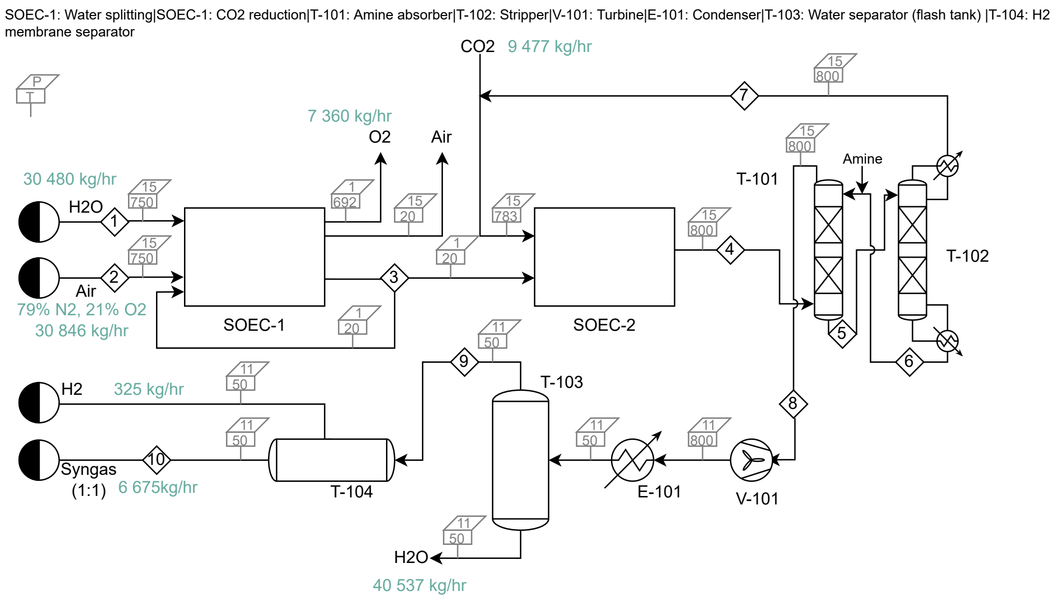


Figure 5: Process-flow diagram of the co-electrolysis

A SOEC is comprised of three distinct and porous layers: the cathode where the reduction happens, usually made out of porous nickel or a mixture of nickel and yttria stabilized zirconium YSZ, the solid electrolyte which allows the diffusion of O^{2-} oxide species and the anode where the oxidation happens, usually a mixture of lanthanide, strontium and manganese oxide associated with YSZ material.

Two reduction reactions can occur at the cathode:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \tag{2}$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \tag{3}$$

Due to favorable thermodynamical conditions, the reduction of CO_2 can be mostly due to the reverse water gas shift (RWGS) reaction and not through the eletrochemical reduction of CO_2.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{4}$$

The oxygen ions migrates through the electrolyte thanks to the process operating at high temperatures (800°C), removing solid-state diffusion limitations and arrive at the anode surface and are reduced to gaseous oxygen following equation ().

$$2O^{2-} \rightarrow O_2 + 4e^- \tag{5}$$

Electrolyzing at high temperatures allows to considerably reduce the electricity needed for the reaction, thus making the process more efficient.

The syngas from the SOEC contains too much CO_2 to be sent directly to the hydroformylation reactor. The carbon dioxide is removed with an amine scrubber, but because of time restraints the separation was modeled with a simple separation unit in Aspen Plus, and the cost calculations for this unit was done separately.

The model made to simulate this part of the process was pre-made, and modified to accommodate the required H_2:CO ratio, as well as the right purity of syngas. A H_2:CO ratio of 1.73 is required for the Oxo-synthesis.

The electrochemical reactions are modeled using a RStoic reactor in Aspen Plus, while the reverse water gas shift was modeled with a RGibbs reactor. The thermodynamic package used for the simulation was Soave-Redlich-Kwong (SRK).

2.1.2 Pyrolysis of non-recyclable plastic (NRP)

Although pyrolysis is almost an outdated technique of depolymerization, in the case of fluctuating feedstock composition (Table 1), it is the best option. Additionally, it does not require expensive and highly sophisticated equipment and the waste produced can be used as a fuel for the process. Screening of different chemical recycling techniques on disposal, thermal pyrolysis showed as least expensive and most powerful having in mind combination with other process sub-sections that could potentially mitigate its high energy requirements.

The composition of the NRP is likely to change as it is usually sourced from municipal waste. For the sake of the simulation and design of the process, an assumed composition of some of the most common packaging plastics were used as feedstock. Table 1 shows the weight average of the plastic feed composition.

Plastic Type	Percent by weight [%]
High-Density polyethylene	23.2
Low-Density Polyethylene	27.9
Polypropylene	37.2
Polystyrene	11.6

Table 1: Plastic feed composition

The proposed chemical recycling process consists of three main steps and is shown in Figure 6.

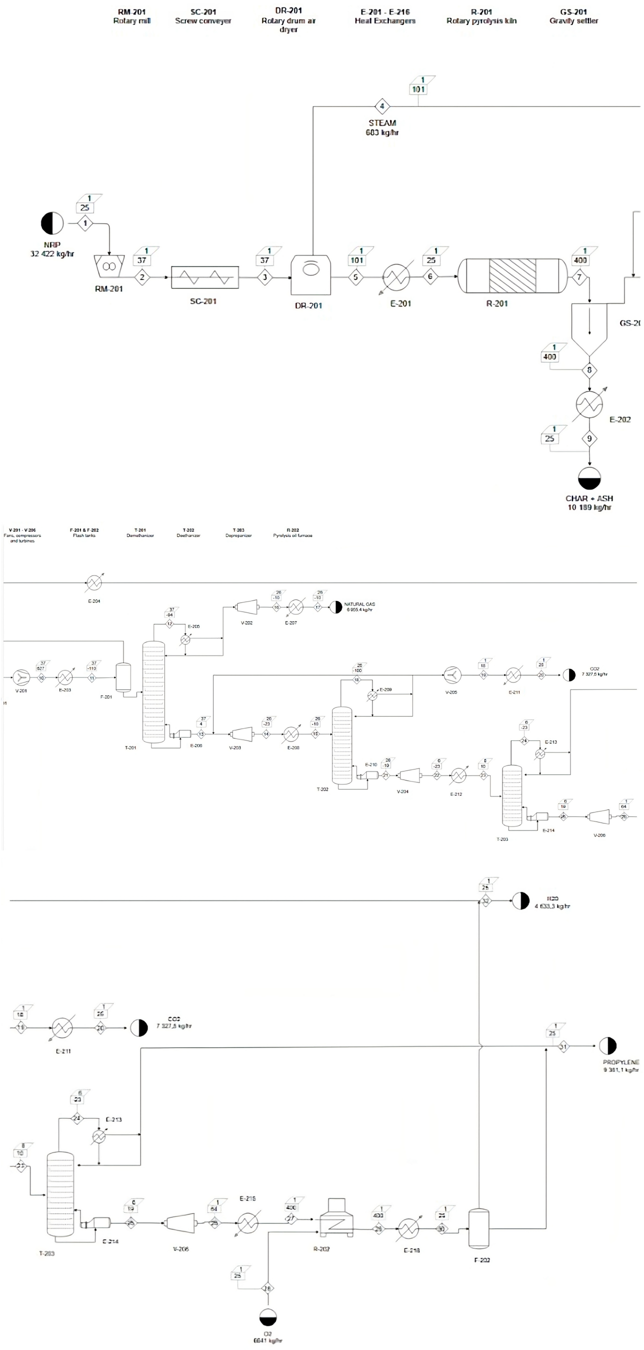


Figure 6: Process-flow diagram of NRP Pyrolysis process

Figure 6 presents the units used in more detail. First the plastic dried before it is pre-melted in an extrusion screw, and leaves the screw with a temperature of 250° C. This ensures efficient heat transfer in the next step, as all of the plastic is in the same phase. The melted plastic then goes directly into a rotary kiln, where it is heated to 400°C under anaerobic conditions. As there is no oxygen present, the high temperatures cause the polymer chains to break down without getting oxygenated, and the result is a mix of various length hydrocarbons in three different phases: oil, gas and char. The pyrolysis oil is sent to a furnace where it produces CO_2 for the co-electrolyzer as well as heat for the rotary kiln and steam cracker where the pyrolysis gas is sent, for further cracking.

The steam cracking unit has three sections: a preheating section, a radiant section, and a quenching section. In the preheating section the incoming gas from the pyrolysis kiln is being heated with recycled steam from the quenching tower. The radiant section is the part of the unit where the actual cracking is taking place. In the quenching tower, the cracked gas is cooled, and goes into a compressor train before the components can be separated. As in reality the preheating and radiant sections are part of a single unit, for the simulation purposes the constituent parts were modelled as separate units to be able to represent the physics of the system. As such, for the actual decomposition of the hydrocarbons, a kinetic model was used to represent the randomness of the pyrolysis process. [16] was used as the basis for the simulation of the NRP pyrolysis assuming the similarity in behaviour among different feed stock. By tuning the kinetic parameters to accurately represent the production of propylene, the values from the experimental study in [12] were successfully reproduced, making the pyrolysis process yield 29.7% raw propylene.

The resulting cracked gas still consists of varying length hydrocarbon chains (C1-C6), although the hydrocracking process to get the gas from the initial plastic feedstock produces mostly propylene and ethylene. Since these are the desired products, they need to be separated from the rest of the hydrocarbon chains. In order to have a chemical grade product, the purity of the bulk chemical needs to be at least 95%.

In total there are four separation processes, each consisting of column, condenser, reflux drum, kettle-reboiler, and pumps for the reflux streams. The major challenge with the separation of short chain hydrocarbons in the cracked gas, is their volatility. The temperature needs to be very low in order to keep the heavier compounds in the liquid phase. The separation is achieved using cryogenic distillation. Ethylene, which is the lightest of the heavy hydrocarbons in the gas, has a boiling point of -103.7°C, while methane has a boiling point of -161.6°C at atmospheric pressure. To completely separate methane and ethylene one would need a lot of energy to maintain such a low temperature. Therefore it is more economical to let some of the ethylene exit with the light hydrocarbons, even if this means some of the product will be lost.

The plastic pyrolysis was modeled using a rigorous approach based on a kinetic model developed by H. Ismail et al.[16]. The kinetic model was a applied in a plug flow reactor, while plastic decomposition and production of lighter compounds such as CO and CO_2 are modeled with the HCOALGEN and DCOALGIT model in a RYield and RGibbs reactor respectively.

2.1.3 Oxo synthesis

The oxo synthesis consists of two steps. First, propylene reacts with syngas to produce aldehydes that later react with hydrogen to form butanol. There are also extensive separation processes associated with each reaction, and the modeling was therefore divided into two separate files, and will be presented separately in this section.

Hydroformylation

The hydroformylation process is presented in Figure 7.

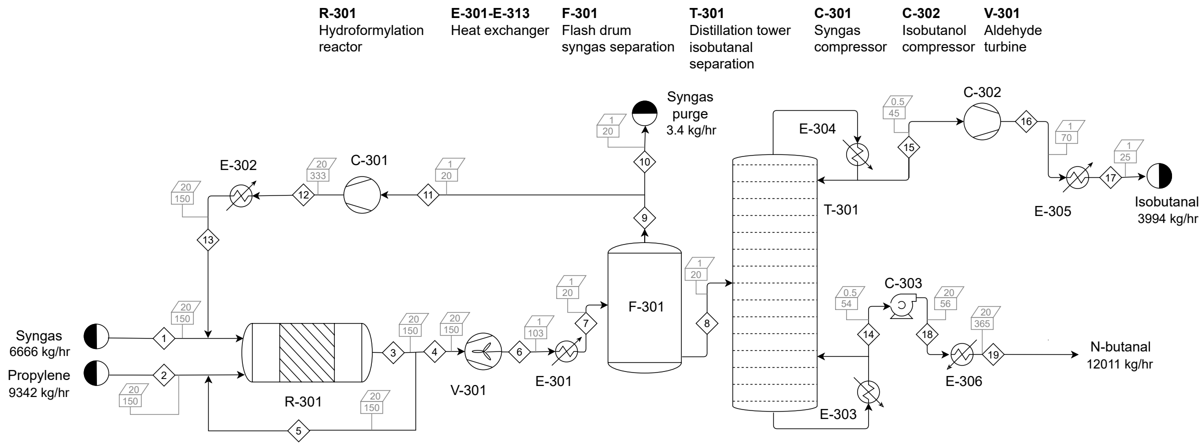


Figure 7: Details of the PFD of Oxo synthesis, hydroformylation section

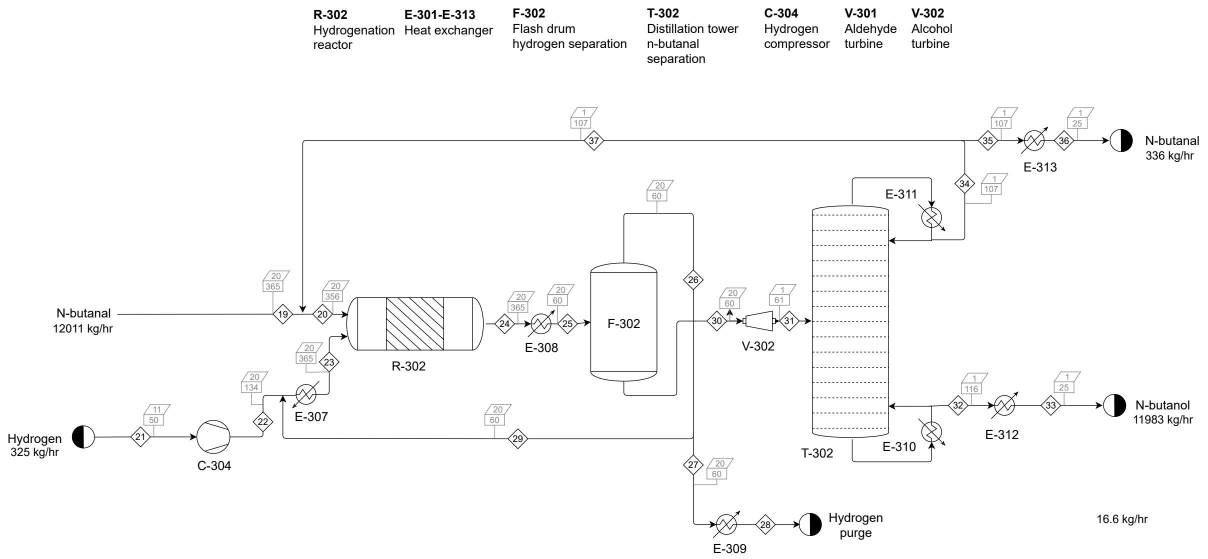


Figure 8: Details of the PFD of Oxo synthesis, hydrogenation section

The first step in the oxo-synthesis is the hydroformylation of propylene with syngas to form 1-butanal and 2-methylpropanal in the presence of a rhodium catalyst. The catalyst solution is in a liquid phase, while the reactants are in the gas phase. In order to ensure that there are no mass transfer limitations, there has to be a large contact area between the two phases.

Hydroformylation reaction

$$CH_3CH = CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO \quad (6)$$

- $\Delta G = -41kJ/mol$
- $\Delta H = -149.42kJ/mol$

A kinetic model following paper [17] has been implemented with the following parameters, fitting into equation 7 which follows the power law : $k_{n-butanal} = 7.984 \frac{m^8}{kmol^2 h}$, $k_{isobutanal} = 26.77 \frac{m^8}{kmol^2 h}$, E_a= 68.1 kJ/mol, n_5 = 0.544 (for n-butanal), m_5 = 0.298 (for isobutanal), [Rh]=100 ppm (mass fraction of 10^{-4}), [TPP]=0.5wt% (mass fraction of 0.005). The article reports kinetics for a liquid-gas phase reaction but article [18] claims that a supported catalyst in gas-phase reaction shows similar activation energies, partial pressure dependencies and reaction rates to those observed in liquid-phase reactions. It was thus assumed that the kinetic model could be applied to the envisioned gas-phase reactor suggested from the patent. Gas-phase reaction has the advantage of not relying on a solvent, which needs to be bought and separated, contributing to more environmental impact (product footprint and energy use for separation) and additional costs.

$$r = kc_{propylene}c_{H_2}c_{CO}[Rh][TPP]^{-m_5 or -n_5} \quad (7)$$

where concentrations are expressed in kmol/m^3 and [Rh] and [TPP] in mass fractions.

Catalyst Traditionally both cobalt and rhodium catalysts has been used in the hydroformylation of olefins. The drawback of Co catalysts is that they operate best under high temperature and pressure conditions, which is energy intensive to maintain. Cobalt catalysts also make a high branched/straight aldehyde ratio, which is undesired when making 1-butanol. Rhodium on the other hand operates under ambient conditions, and gives a much better branched/linear ratio. The biggest problem with rhodium catalyst is the high cost of the metal. Another concern is the scarcity of the metal in the earth crust, which makes it a less sustainable option than catalysts made of more abundant metals.

Hydrogenation

The hydrogenation step consists of the hydrogenation reaction itself, where the aldehydes react with hydrogen over a cobalt catalyst. The products from this reaction as well as unwanted compounds and impurities then need to be separated in a distillation column.

Hydrogenation reaction

$$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH \quad (8)$$

- $\Delta H = -275.6kJ/mol$

The reaction was modeled in Aspen Plus using a PPlug reactor and the Langmuir - Hinshelwood - Hougen - Watson kinetic model. The kinetic model was based on data from a research paper describing the hydrogenation of n-butanal to n-butanol[19].The kinetic model can be expressed as

$$r = \frac{k' P_{MA} P_{H_2}}{P_{MA} + k_1' P_{H_2}^{0.5} + k_2' P_{H_2}^{0.5} P_{MA}} \quad [\frac{mmole}{g \cdot h}] \tag{9}$$

where

$$k' = 1.26 \cdot 10^3 e^{-\frac{2760}{T}} \quad [\frac{mmole}{g \cdot h \cdot kPa}] \tag{10}$$

$$k_1' = 0.114 e^{\frac{999}{T}} \quad [kPa^{0.5}] \tag{11}$$

$$k_2' = 7.55 \cdot 10^{-5} e^{\frac{3891}{T}} \quad [kPa^{-0.5}] \tag{12}$$

Catalyst A wide variety of catalysts are used in industrial hydrogenation reactions. Also in this part of the process a cobalt catalyst can be used, and it is possible for hydroformylation and hydrogenation to happen simultaneously in the same reactor over the same catalyst.

Separation process Depending on the catalyst there will be various co-products produced. By-products, co-products and impurities needs to be separated from the main product, n-butanol. For a cobalt catalyst there has been reported formation of di-n-butylether (DBE)[20]. This leads to challenges in the separation after the hydrogenation reaction. Although the reaction produces little DBE, this needs to be removed in order to obtain the pure products. Pure DBE has an atmospheric boiling point of 142°C, but in the presence of n-butanol it creates a binary azeotrope with a boiling point of 177.6°C. As the boiling point of pure n-butanol is 177.2°C, this makes it very hard to separate the two compounds. The problem can be solved by adding water to the distillation column. If water is present, the three compounds will create a tertiary azeotrope with a boiling point of 90.6°C, which makes it possible to separate the n-butanol from DBE.

2.2 Material and energy balance

2.2.1 Material balance

Process efficiency To achieve the desired production of 100 000 tons/year, an outlet flow of 11 983 kg/h of n-butanol is needed, considering that the plant will function continuously during the year. This would require a propylene feed of 78 634 tons/year (which entails 272 345 tons/year of plastic) and a mixed CO and H_2 feed (ratio: 1:1) of 56 070 tons/year. Figure 4 shows the simplified Block Flow Diagram (BFD) of the overall process with the most critical mass flows.

The generalized reaction mass efficiency was calculated to be 21%. As the process is mainly in gas phase, it does not require any solvents except for the amine used in the CO_2 scrubber, and so does not have a lot of waste associated with solvent use. There are however substantial losses associated with the plastic recycling to propylene, mostly in the form of ash and char.

However, a stream is only considered a loss if it cannot be reused. Table 2 presents solutions to valorize every by-product and waste stream of the process. Overall, there is little material wasted, provided that measures are taken to store and market the waste streams.

Content	Flow	Possible areas of use
Isobutanal	4 tonnes/hr Purity: 87.5% isobutanal	Vitamins, perfumes, flavorings, rubber, additive to gasoline Depending on the end use, the stream can be purified further, or left as is
N-butanal	0.3 tonnes/hr Purity: Chemical grade (95%)	rubber accelerators, synthetic resins, solvents, plasticizers
Water(Clean)		Dispose of without treatment
Ash and Char	10 tonnes/hr	Gasify to produce syngas as an alternative source to the SOEC Produce activated carbon Sequestration
Syngas	3.35 kg/hr	Burn with the pyrolysis oil to generate energy and CO2 for the co-electrolysis unit
Oxygen	617 kg/hr (100%)	Release in the atmosphere
Natural gas	7.4 tonnes/hr	Sell (8 USD/MMBtu) Burn in a boiler to provide energy to the plant

Table 2: Type and amount of waste generated within the process with the proposition of possible use

Carbon balance

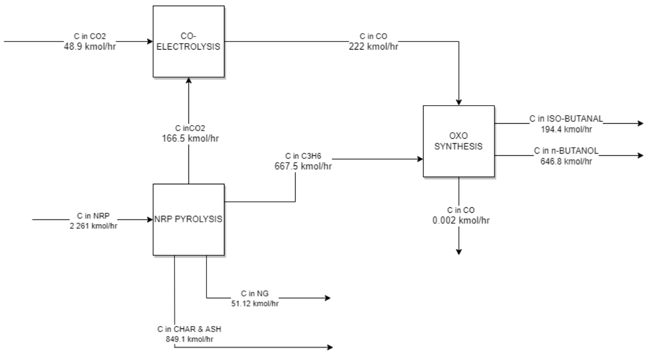


Figure 9: BFD of the carbon flow within the process

The carbon balance is calculated to provide an understanding on the atomic flow of the materials. As carbon is the main element of the process and that it is of interest to compute the amount of carbon captured and used by the process, the carbon balance is of interest compared to other elemental balances. Figure 9 shows that the total process has a carbon efficiency of 28%, where the largest carbon sink is the ash and char produced in the plastic pyrolysis which accounts for 36.8% of the initial carbon content in the NRP and CO_2. The natural gas also accounts for a substantial amount of the carbon loss, about 27.1%. If the natural gas is burned in the boiler, this carbon would be reintroduced to the process, and the natural gas would not represent a loss of carbon. The CO_2 released from burning the natural gas in the boiler to produce heat to close the heat balance is 2 216.8 kg/hr assuming total combustion of the gas. This is enough to cover the carbon dioxide need of 2 150 kg/h for the SOEC, which would make the plant completely self reliant on CO_2 for the process. The remaining CO_2 emissions are 67 kg/hr, which means the yearly emissions are 570 tonnes CO_2/year, and 5.6 g CO_2/kg n-butanol, which is considered to be low.

2.2.2 Energy balance

The energy requirements of the envisioned process is presented and several major energy integration processes are used.

Table 3: Total heating and cooling demand

Process part	Cooling [MW]	Heating [MW]
Plastic pyrolysis	81.30	41.40
Co-electrolysis	22.37	10.15
Oxo-synthesis	20.11	15.44
TOTAL	123.78	67.00

Heating and cooling demand Table 3 presents the heating and cooling requirements for the different parts of the process. It can be seen that most of the energy use is in cooling as the plastic pyrolysis generates enough waste heat to cover all heating needs.
The total energy need amounts to 190MW.

Electricity demand The electrical consumption comes mainly from the use of pumps and compressors.

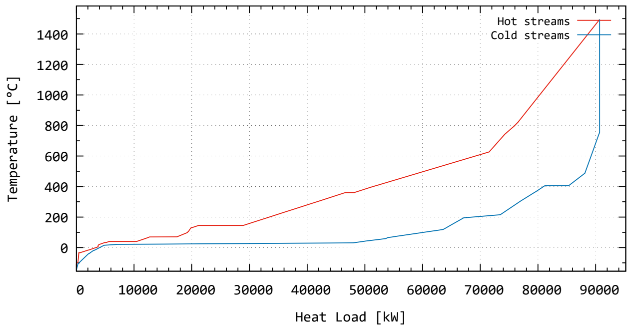
The electrical consumption of an SOEC is taken as 3.37kWh/m^3 of H_2 produced (at NTP) [21]. The total flow of H_2 produced is 412 mol/h which corresponds to 10m^3/h. The average power for the SOEC is thus 33.7 kW.This value is low and some uncertainty of its accuracy remains. However, it is known that using a high-temperature process such as an SOEC considerably lowers the electricity demand for the electrolysis [22].

Table 4 summarizes the different electricity-consuming units from the process. One compressor PDMETCOM (which in reality would be several units) in the pyrolysis part constitutes most of the electricity demand. The total electricity demand is 21.2 MW.

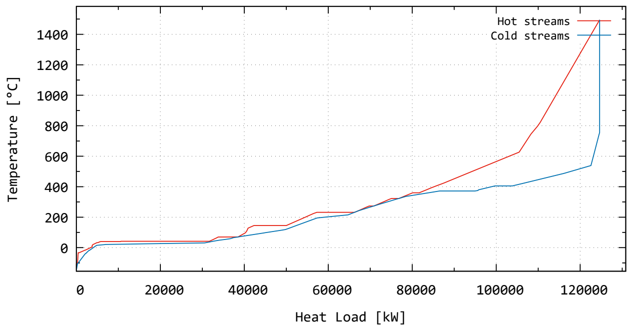
Table 4: Electrical consumption of the pumps and compressors in the process. It can be seen that the pyrolysis of the plastic is the most electricity consuming part of the process.

Process part	Unit	Type	Power [kW]
Oxo Synthesis	C101	Pump	17
	C102	Compr	39
	C103	Compr	110
	C104	Compr	20
Pyrolysis	PDMETCOM	Compr	20979
SOEC	SOEC	SOEC	34
		Total	21199

Heat and electricity integration To prevent excess energy use, heat can be recovered and transferred between streams. Pinch analysis is used to evaluate the heat recovery potential.
Pinch analysis is an useful tool to quantify the amount of heat that can be recovered while being thermodynamically consistent. It is a visual technique using Temperature-Enthalpy (T-H) diagrams. The enthalpy change of each stream (the differential heat flow dQ [kW]) is represented as the product of the heat capacity flowrate CP [kW/K] multiplied by the differential temperature change dT [K] ($dQ = CP.dT$). By drawing the composite curves of the hot and cold streams (with the minimum temperature difference between the two curves set at 10°C), the overlap of them gives us precious information on the potential of heat exchange and recovery. Figure 10 present two examples of shifted composite curves.
To achieve this energy recovery, steam cycles coupled with steam turbines have been implemented following the method presented by Kermani [23] in their thesis "Methodologies for simultaneous optimization of heat, mass, and power in industrial processes". This energy recovery system for high temperature (>600°C) not only allows to recover and transfer heat from different streams, but also to generate electricity. The remainder of the cooling needs is provided by a cooling water circuit at 20°C.
To visually compare the advantages of using the steam cycles, the shifted composite curve (SCC) of two scenarios are presented in Figure ??. Scenario a) considers only using cooling water to close the energy gap, while scenario b) possesses both the cooling water circuit and the steam cycles.



(a) Scenario without steam cycle



(b) Scenario with steam cycle

Figure 10: Shifted composite curves for a scenario with and without steam cycle integration

The area between the composite curves for the hot and cold stream is drastically reduced from introducing the steam cycle. Without it, the total cooling provided by the cooling water is 39.6MW. With it, it is only 22.2MW, which represents a 44% decrease in cooling requirement. About 85.3MW of heat is exchanged through the steam cycle. An additional 17.4MW is produced through the steam turbines, which covers 82% of the electricity requirement.

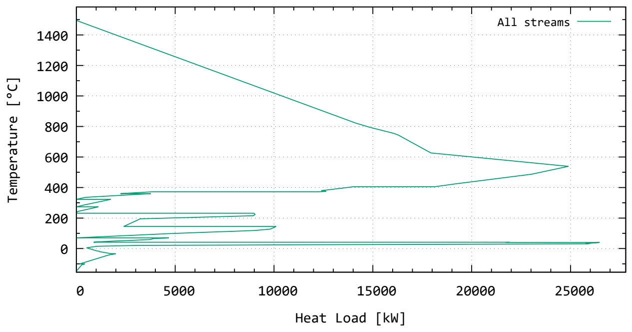


Figure 11: Grand composite curve of the process with steam integration

The grand composite curve gives another representation of the heating and cooling requirement of the process, as seen on figure 11. The cooling requirement from the NRP pyrolysis can be more clearly observed from the area under the curve between 300°C and 1500°C. The linear increase of the hot stream composite curve can be explained from the self-fueling behavior of the NRP pyrolyis as the pyrolysis will not only sustain the temperature but also increase it.

To further recover energy to generate electricity, gas turbines can be installed wherever the process calls for expansion valves. The fluid power could be used to provide electricity for the process.

The electricity generated from those turbines have been approximated as a fraction of the fluid power. The power was calculated using Equation 13, which is the efficiency multiplied by the fluid power. Gas turbines have been considered as gaseous mixtures are going through the expansion valves.

$$P_{turbine} = C_p \cdot T_{in}(1 - \frac{P_{out}}{P_{in}}^{\frac{\gamma}{\gamma-1}}) \cdot \dot{n} \cdot \eta \qquad (13)$$

where $P_{turbine}$ is the power generated by the turbine [kW], C_p is the heat capacity of the gas stream [kJ/(kmol.K)], T_{in} is the inlet temperature [°K], $\frac{P_{out}}{P_{in}}$ is the pressure ratio [-] for the expansion valves, γ is the heat capacity ratio [-] (1.33 for gases), $\dot{n}$ is the mole flow of the gas stream [kmol/s], η is the turbine efficiency [-] (considered to be 0.3).
The turbines can thus produce a maximum of 8.4MW, which covers 40% of the total electricity needs.

By integrating both steam and gas turbines throughout the process, it is possible to cover 122% of the electricity requirement. This means that electricity is produced in excess, which can be redistributed through the grid. The process is thus entirely self-sufficient for electricity generation, which is a great advantage considering the high price of electricity in Greece [24].

Our process show self-sufficiency in energy in the form of natural gas and of electricity, increasing its resilience and decreasing dependency on a highly fluctuating energy market. The only inputs needed are the NRP waste and CO_2. The former will unfortunately not see its production decrease in the close future while the latter sees an increasing demand in its capture.

2.3 Economic and profitability analysis

A detailed economic analysis is performed on the process to assess the feasibility and the profitability of the project. The method used and the results are presented in this section.

Process costs calculations The total cost (TOTEX) [USD/year] is comprised of two elements : the capital expenses (CAPEX) [USD/year] and the operating expenses (OPEX) [USD/year]. The CAPEX takes into account the cost of the units and the installation cost, annualized over the lifetime of the plant. The OPEX takes into account the cost of resources (natural gas, electricity, etc.), the maintenance, manpower and taxes for each year.

While the OPEX is expressed per year in its definition, the capital investment cost is usually paid at once when the plant in built. This cost thus needs to be annualized by multiplying the unit cost by the annualization factor $\frac{1}{\tau}$ [-] described in Equation 14.

$$\frac{1}{\tau} = \frac{i(1+i)^n}{(1+i)^n - 1} \qquad (14)$$

where i is the interest rate over the years which is taken as 6% and n is the lifetime of the plant [years] which is taken as 20 years. [25]
The capital costs can be found in literature and several methods are used to adapt them to the designed process. However, as the data is often outdated, it needs to be actualized. This is done by using the CEPCI (Chemical Engineering Plant Cost Index), which is a composite index assembled from a set of four sub-indexes: Equipment, Construction Labor, Buildings and Engineering Supervision. These indexes follow the change in net transaction prices over the year and allow the comparison on prices over widely economically different periods. The CEPCI of 2022 is 797.6, the one of 2003 (year of publication of the main reference used) is 402, the one from 1998 is 389.5 (for the steam turbines) and the one from 1995 (for the cryogenic refrigeration system) is 381.1. [26]

The size of the unit may have to be adapted from values from literature. Due to economy of scale, the cost per size unit often decrease when the size increase. The ratio of the size is thus not sufficient as a multiplier to properly scale up or down a unit. A capacity exponent γ is needed to account for this effect. The actualization and equipment sizing are described in equation 15

$$C_u = C_{u,ref} \cdot (\frac{A_u}{A_{u,ref}})^{\gamma} \cdot \frac{I_{project}}{I_{ref}} \qquad (15)$$

where C_u is the sized, actualized unit cost [USD], $C_{u,ref}$ is the cost found from literature [USD], A_u is the size of the unit in the process [kW, m^2, ...], $A_{u,ref}$ is the size of the unit found in literature [kW, m^2, ...], γ is a capacity exponent with typical values between 0.6 and 0.8, $I_{project}$ is the CEPCI from the year where the project is planned, I_{ref} is the CEPCI from the year where the unit cost from literature was recorded. [25]

For each unit, as it is complicated to give an accurate value for the OPEX except of the resource cost, its value was fixed at 10% of the annualized CAPEX. This would take into account the manpower, the maintenance and taxes. [25]

For the installation of a plant, a lot of parameters are not described just in the unit cost. The Bare module cost factor F_{BM} is a multiplier that takes into account those additional costs. These cost can be additional materials required for installation, foundation and piping costs, labor and engineering work, cost for the integration with other equipments, equipments and adaptation of control and security systems, taxes and royalties and the purchase of land. F_{BM} is taken as 3.63 in this process [25].

In the end, the CAPEX [USD/year] is described in equation 16.

$$CAPEX = C_{u,ref} \cdot (\frac{A_u}{A_{u,ref}})^{\gamma} \cdot \frac{I_{project}}{I_{ref}} \cdot \frac{1}{\tau} \cdot F_{BM} \qquad (16)$$

Unit cost derivation One way to derive the cost of a unit is from cost correlations. Those correlations are found in handbooks such as Turton's "Analysis, Synthesis and Design of Chemical Processes" which was used in this project [25]. The correlation has a general shape described by eq. 17.

$$C_{u,ref} = 10^{(k1+k2log(A_u)+k3(log(A_u))^2} \qquad (17)$$

where $C_{u,ref}$ is the cost of the unit [USD], k1, k2, k3 are empirical constants from the cost database, A_u is the size of the unit [kW, m^2, ...].

A detailed cost analysis table can be found in the annex, where the exact size of the unit, the corresponding unit found in literature, the k constants can be found.

Reactors have been imagined to be jacketed and non-agitated as tubular reactors are thought to be used.
Distillation columns had to be sized in two parts: first the tower in itself and then the trays. The tower is considered to be tray and packed. For the trays, sieve or valve trays were chosen as they're usually quite cost-effective and can be flexibly used in a variety of conditions. Valve trays are slightly more expensive but also more efficient.
The flash tanks have been modeled as vertical process vessels. For the volume, it has been considered that the vessel should be able to hold the volume of chemicals that go through the vessel in 10min, multiplied by two to account for the volume of gases (50% liquid and 50% gases.[27] Concerning the dimensions of the towers and the trays, the design function in Aspen Plus has been used to derive the tray spacing and diameter.
Compressors and pumps are both taken as centrifugal. The necessary power has been taken from Aspen Plus simulations.
The cost from the rest of the units have been found from literature.

Process cost By using the aforementioned methods, the costs for each part of the process has been calculated. Details can be found in the Appendix. For the plastic pyrolysis, every unit except the screw conveyor, the rod mill and the storage silo could be calculated from the Turton handbook [25]. The total cost amounts to 5.69 Mio USD/year. For the SOEC, as the Aspen simulation doesn't correspond to reality but only serve to approximate the results from a real co-electrolysis unit, the cost had to be derived from literature. Except one flash tank that was sized using the Aspen simulation, the co-electrolysis is comprised of the SOEC cell and the amine scrubber. The cost of the amine scrubber has been adapted from ref. [28] and amounts to 0.466 Mio USD/year for the amount of CO_2 removed. For the SOEC, the area has been determined by comparing to the Aspen model. The total area of the SOEC cell is 6648m^2 from the assumptions used in the Aspen simulation. From ref. [22], the cost of an SOEC per area is 5140 €/m^2. Thus the SOEC cost is approximated to be 12.36 Mio USD/year. As SOEC is still a relatively new technology and is still in its research stage, its cost is expected to go down as the technology becomes more widely spread. According to ref. [29], the price of SOEC units is expected to go down four-fold by 2030. Taking this into consideration, the process would become significantly more competitive by 2030 with a decrease of the total cost from 25.49 Mio USD/year to 16.22 Mio USD/year. This decrease is visually represented by figure 12.

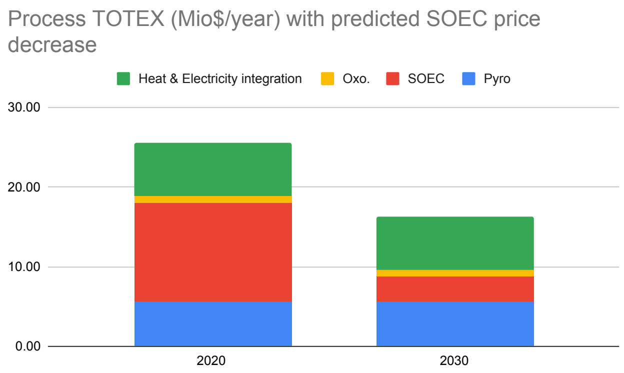


Figure 12: Decrease in the TOTEX [USD/year] with expected price decrease for SOEC technology by 2030

The Oxo synthesis is a well known process that is relatively inexpensive in terms of equipment, with the majority of the cost coming from the distillation column and the Rhodium catalyst. The Cobalt catalyst has been neglected as it was expected that its cost was relatively negligible, as Cobalt is inexpensive. A Rhodium catalyst is needed for the hydroformylation of propylene into butanals. Rhodium is a precious metal whose price has been fluctuating a lot in the past few years. The reference market value that was taken for this process is 360,289 USD/kg [30]. As the rhodium loading is equal to 100ppm, it was calculated that the required mass of rhodium in the reactor is 6.853kg. This brings the cost of the catalyst to be 2,499,063 USD in total. The processing of the catalyst is considered negligible in comparison to the raw material cost. With appropriate regeneration, the catalyst can be reused for multiple year.

For the heat and electricity integration, the cost of the water cooling system is estimated at 0.001USD/kWh. The calculations were based on a power requirement of 22.17MW and a run time of 8000h/year. The cost of the steam cycle is derived from process equipment cost estimations from ref. [31]. By taking advantage of all the gas expansions that are needed in the process, 8.4MW of electricity can be generated with the use of gas turbines. The cost of turbines are derived from cost correlations from the Turton handbook [25].

Considerable cost savings are achieved by the integration of both steam and gas turbines due to the relatively high price of electricity in Greece (0.23 USD/kWh was the price of electricty for business in 2022). The heat and electricity integration would cost 6.57 Mio USD/year with the cooling water circuit and both steam and gas turbines. If all the electricity was provided from the grid, the cost of the cooling water circuit (which needs to be scaled up) would be 3.36 Mio USD/year and the cost of electricity would be 40.57 Mio USD/year. Thus, by valorizing waste heat and mechanical energy, not only energy can be saved but money as well. It would save approximately 85% of the heat and integration cost.

Table 5: Cost summary

Plastic Pyrolysis	5,694,617
Oxo synthesis	861,300
SOEC	12,363,205
Heat integration	13,925,334
Electricity integration	6,709,960
Total [USD/year]	39,554,417

Table 5 summarizes the cost for each part of the process. In total, the cost would amount to 39.6 Mio USD/year. Figure 13 represents this table in a more visual manner.

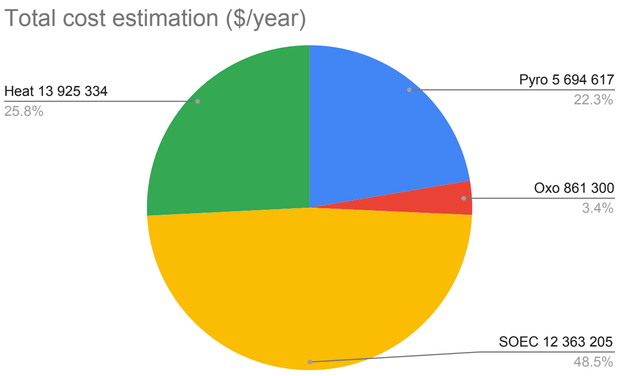


Figure 13: TOTEX [USD/year] pie chart with each sector corresponding to a process part

Subsidies A common procedure in the recycling industry is to ask for a gate fee for the service of disposing of wastes.

By comparing to the legal landfill gate fee for a ton of non-recyclable plastic (NRP), which is around 50USD/ton in Europe [32], the gate fee for the chemical plant can be assumed to be the same. As 272,000 tons of NRP is expected to be consumed a year, the total revenue generated from the gate fee would be around 13.6 Mio USD/year.

A CO_2 gate-fee can be introduced as well. The average carbon price in Greece in 2019 was 15.72 USD/ton CO_2 [33]. With a need for 18 060 tons of external CO_2/year, the revenue generated from introducing this gate fee would be equal to 283'903 USD/year or 0.283 Mio USD/year. This source of revenue is relatively small as the amount of CO_2 consumed is also small. A lot of CO_2 is already produced during the pyrolysis which is further used as a feedstock in the co-electrolysis process.

Profitability The production cost of 1 ton of n-butanol is 254.94 USD/ton without gate fees. This means that the profit generated from the is equal to 670 USD/ton (market price) minus the production price 254.94 USD/ton, so 415.06 USD/ton of n-butanol. As the production quantity is predicted to be 100,000 tons/years, the total profit would be 41.5 Mio USD/year (and the revenue 67 Mio USD/year). This indicates that the process is generating revenue.

However, profit, while already useful, isn't sufficient as an economic indicator. For this report, four economic indicators have been chosen: the payback time, the net present value (NPV), the return on investment (ROI) and the internal rate of return. All indicator calculation were referenced from ref. [34], though plenty of literary resources exist to explain such basic metrics.

Payback time The payback time is defined as the cost of investment divided by the average annual income. It represents the time needed for an investment to be repaid. This means that during the payback time, no benefit is actually produced. The cost of investment is calculated to be 234.7 Mio USD (actualized and installed cost of the chemical plant, not annualized) and the average income is 41.5 Mio/year as mentioned in the previous paragraph. The payback time would thus be 5.66 years. As this value is considerably shorter than the lifetime of the plant (assumed 20 to 30 years), benefit can be made after the payback period.

Net present value (NPV) The NPV is a way to calculate today's value of future streams of payments. It is defined in eq. 18, where R_t is the net cash inflow-outflow during 1 year (so for the first year it would be all the investment cost + 1 year worth of revenue (-193.2 Mio USD) and for all other years it would be only the revenue (41.5 Mio USD)), t is the lifetime of the plant in years and i is the interest rate which is usually taken as 8%. The calculated NPV is thus 190.2 Mio USD. As this is a positive value, the investment is assumed to be profitable.

$$NPV = \sum_{t=1}^{n} \frac{R_t}{(1+i)^t} \tag{18}$$

Return on investment (ROI) ROI measures the amount of return on a particular investment, relative to the cost of investment. It is defined in eq. **??**. The current value of investment refers to the revenue generated from the investment, so 67 Mio USD/year. The cost of investment is 41.1 Mio USD/year (annualised CAPEX). The calculation can also be done over the whole lifetime of the plant, but the calculation per year has been chosen here. The ROI is thus 0.63%. As the ROI is positive, the investment is worthwhile. However, the ROI is relatively small so the profitability can be easily compromised.

$$ROI = \frac{I_{CV} - C_{inv}}{C_{inv}} \tag{19}$$

where I_{CV} is the current value of investment and C_{inv} is the cost of investment.

Internal rate of return (IRR) The IRR is a discount rate that makes the NPV of all cash flows equal to 0. The higher the IRR, the more desirable. Eq. 20 explains the IRR mathematically. It is based on the NPV equationt (eq. 18), the only added parameter is C_0 which is the total initial investment cost (200 Mio USD). The IRR calculated is 20.9%, which is a good number as it is higher than the interest rate (8%).

$$0 = NPV = \sum_{t=1}^{n} \frac{R_t}{(1+IRR)^t} - C_0 \tag{20}$$

With gate fees If gate fees are implemented, the indicators can be bettered. This would add 13.6 Mio USD/year in the revenue. The yearly profit would thus become 55.4 Mio USD/year. Table 6 summarizes the results obtained with or without the implementation of gate fees.

Table 6: Economic and profitability indicators

	Without gate fees	With gate fees
Profit (USD/t_butanol)	415.06	553.90
Payback time (years)	5.66	4.32
ROI (-)	0.63	1.93
NPV (USD)	190'201'674	326'469'244
IRR (%)	20.90	30.69

The process is overall profitable in both cases, with a considerable increase in profitability with the introduction of gate fees. As the main idea behind the process was to pursue the recycling of plastic and emphasize on the innovation of the process, the economics weren't expected to be good. However, it is a pleasant surprise to see that the process can indeed be profitable, with further cost decrease in perspective in future years due to the predicted decrease of SOEC cost. Also, the price of n-butanol can perhaps be expected to increase in future years as most of the market bases itself on propylene coming from fossil sources. The price of fossil fuels are known to fluctuate but the general trend is an increase in price. [35]

2.4 HAZOP

Due to a high degree of interconnectivity between the process sub-units, the individual process risks are amplified. The highest of the chemical risks is associated with detonation caused by hydrogen outburst from the SOEC and Oxo sub-processes. If mixed with a gaseous stream from another part of the process, it can cause even more harm and ignite even without the outburst.

Another issue related to the operation of pyrolysis kiln is mechanical in nature: heating failure scenario or any other that would lead to the reactor clogging could result in an explosion.

Butanal, a key intermediate of butanol is highly flammable aldehyde, thus needs to be handled with great caution.

In order to avoid these and many other scenarios considered in this work, an effective control system needs to be installed (Figure 19). An example is provided on a single unit of highest risk in the process, namely Hydrogenation reaction as the second step in the Oxo-synthesis route, as it combines hydrogen and highly flammable butanal streams at extreme reaction conditions.

A more elaborate HAZOP study is obtained based on the presented diagram and is included in the Appendix.

3 Conclusion

Energy self-sufficient production of 11 983 kg/hr n-butanol using half of the available amount of waste non-recyclable plastic in Greece as reported in 2018 and CO_2 is proven not only to be possible, but also profitable by achieving 41.5 Mio USD/year net profit. Unique process design has been obtained on the basis of a well-known, industrially established process: Oxo synthesis, by shifting the source of carbon from fossil to waste plastic and making the process more sustainable. In such way, this process aims at treating two problems at the same time, and offers a great opportunity for Mediterranean countries, such is Greece, to enforce independent chemical production from readily available sources.

Three sub-processes whose integration forms the overall process configuration have been modelled in Aspen Plus:

- co-electrolyzer cell to produce syngas
- non-recyclable plastic pyrolysis to produce propylene
- oxo synthesis (hydrogenation and hydroformulation) to produce butanol

The process was further optimized in terms of energy integration in OSMOSE using MILP resolution. This enabled for the high degree of inter-connectivity between the process units and significantly reduced the energy intensity and operating costs. More specifically, heating needs of the process were completely satisfied, while the cooling needs were reduced by 44% by integrating steam cycles into the process. Additional amount of 17.4 MW of electricity is produced suing steam turbines, which covers 82% of the overall electricity requirement.

Proposed process is of specific interest due to the type and amount of waste and side-products it produces: almost all waste can be either freely discharged in the environment (oxygen) or further valorised in terms of energy production (natural gas, char and ash). Main side product, isobutanal can be sold to the market as an important intermediate in chemical industry. There are no inherent CO_2 emissions from the process, as CO_2 produced is used in co-electrolysis and even additional amounts are required, which makes this process a carbon sink and increases its position on the sustainability ladder.

Investing in further development of the proposed process in the context of Greece is of interest both from the aspect of economy enforcement and waste problem treatment. The adequate design of the process enables robust operation under the fluctuating change in type and amount of feedstock. The costs are expected to decrease based on the projections made on CO-SOEC costs that make up for the largest fraction in the cost distribution.

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Appendix

Process Selection

Processes industrially relevant for butanol production [5] were screened and three of the most promising ones in terms of sustainability and profitability were further ranked in the selection matrix. The processes are as follows:

1. Oxo synthesis using sustainable feedstocks (non-recyclable plastic waste, CO_2 and water)
2. Optimized ABE fermentation process
3. Hydrogenation of crotonaldehyde derived from ethanol coupled with the direct CO_2 capture

Process 1 has the advantage of using a very well-known technology (oxo synthesis) and changing the source of carbon to valorize waste product (waste plastic). This will thus increase the residence time of oil-based product in the global economic system. However, the process is known to be energy intensive and also utilizes some rare earth metal catalysts.

Process 2 is milder in its process conditions due to the use of fermentation technology (ABE fermentation). It also has the potential to use biomass in the form of lignocellulosic waste, which is abundant, low-cost and doesn't compete with food crops. The drawbacks are the complex upstream and downstream processing and the low productivity.

Process 3 uses CO_2 in its raw form through electrolysis to produce ethanol. Ethanol is then used in a well-known process known as the Guerbet reaction, but the overall combination of the chosen processing routes is evaluated as inefficient (and thus not sustainable) due to the very low end yields.

Criteria which determine the selection among different production routes - key performance indicators (KPI) are a subject to specific process, so not universal. In the particular case, the accent has been put on innovation and sustainability as this work takes the opportunity to consider industrially relevant processes and reconsider the feed stocks.

Tables 8 and 9 show the evaluation procedure for each of the three processes, while Table 7 gives detailed explanation of the KPI chosen.

KPI	Weight	Explanation
Cost	0.05	The total cost of the plant will consist of both the operating and investment cost.It is assumed that the investment cost can roughly be estimated by the complexity of the process, while the operation cost depends mostly on the required energy supply.
Environmental impact	0.15	The total environmental impact depends on the raw materials used, the energy consumption, the emissions from the plant and the waste products.
Safety	0.1	One of the most important points to evaluate is the safety of the process. This encompasses everything from the thermal safety to hazardous chemicals used in the process.
Efficiency	0.08	In this context the efficiency of the process was evaluated as the ability to convert the raw materials to the end product. The efficiency was calculated as percentage yield, but atom economy can also be used to estimate the efficiency of the process
Configuration complexity & engineering ease	0.08	Simplicity of a process can be a huge advantage when it comes to the design and operation. The configuration complexity can also influence the investment cost of the plant.
Greenness	0.15	The greenness of a process is a component of its environmental impact, but focused on the chemicals' impact on the environment.
Innovation	0.2	In order to solve the problems the world is facing with respect to energy demand, emissions and waste, it is not enough to rely on true and tested processes any longer.
Raw materials	0.04	The raw materials were evaluated based on abundance, price and from an environmental viewpoint.
Energy intensity	0.15	The energy intensity of a process both influences the cost and the environmental impact. Keeping the energy consumption low therefore has several advantages.

Table 7: Explanation of the key process indicators

In total, it can be seen that the highest score is achieved for the first process: Oxo-synthesis from waste plastic (7.02), while Process 2 and 3 have similar scores of 6.21 and 6.19 respectively.

KPI	Weight factor	Process 1	Justification	Process 2	Justification
Cost	0.05	4	- The energy needed will result in a high operational cost - SOECs are not commercially implemented in large scale yet, and are quite expensive	5	- Expensive separation - cheap raw materials
Environmental impact	0.15	8	- Plastic waste treatment is a big challenge that needs to be overcome - minimal emission - No hazardous waste	8	- Reduce and valorize waste - No dependency on petroleum products
Safety	0.1	6	- Large differences in operating conditions	8	- Low temperature and pressure
Efficiency	0.08	5	- A lot of carbon is lost in the plastic treatment	3	- Milling and steam explosion and separation takes a lot of energy
Configuration complexity & engineering ease	0.08	5	- Complex separation of the pyrolysis oil and gas - Using processes that are not yet established in large scale industry	7	- Straightforward process - Maintenance can be complicated - Use of membranes can complicate the process
Greenness	0.15	9	- No hazardous raw materials, solvents or products	7	- Little waste - Lignin can be reused for combustion
Innovation	0.2	9	- Very innovative as plastic pyrolysis and co-electrolysis are currently not used in large scale production of chemicals	5	- Room for improvement, but has been done before as a whole
Raw materials	0.04	8	- Valorizing waste - Using CO2 to prevent emissions	9	- Biomass is widely available - Cheap (as it is considered a waste product) - Renewable source of raw materials
Energy intensity	0.15	5	- Requires a lot of cooling and heating	5	
Total	1	7.02		6.21	

Table 8: Selection Matrix for processes 1 and 2

KPI	Weight	Process 3	Justification
Cost	0.05	3	- Low efficiency conversion induces a big demand on resources, energy and investment
Environmental Impact	0.15	9	- Sustainable feedstocks and low-hazard emissions
Safety	0.1	7	- Mild operating conditions due to low thermal effect of the reactions
Efficiency	0.08	2	- Very low yield of n-butanol meaning a lot of waste
Configuration complexity & engineering ease	0.08	6	- More than five reaction steps, making it complicated to be integrated
Greenness	0.15	6	- Emissions present, but not evaluated as extremely hazardous
Innovation	0.2	6	- Innovative from the viewpoint of introducing different processes together
Raw materials	0.04	5	- Highly abundant materials
Energy intensity	0.15	7	- Particular steps are not as energy intensive, nevertheless, it is not ideal due to the low process efficiency
Total	1	6.19	

Table 9: Selection Matrix for Process 3

Aspen simulation

Overall simulation in Aspen Plus is divided in three sections:

1. Co-electrolysis by upgrading an existing in-house made model [13]
2. Plastic Pyrolysis to produce Propylene by upgrading a pre-made model provided by AspenTech [16]
3. Oxo-synthesis (hydroformylation of propylene and hydrogenation of butyraldehyde) model made from scratch

Thermodynamic properties package

Non-recyclable plastic In plastic pyrolysis and in oxo synthesis, PR-BM thermodynamic property package is used to estimate the properties of the conventional components. PR-BM property method uses the Peng Robinson cubic equation of state with the Boston-Mathias alpha function for all thermodynamic properties. This property method can be used for non-polar or mildly polar mixtures (hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen) over the wide range of both temperatures and pressures but is not consistent near the mixture critical point. It is recommended for gas-processing, refinery, and petrochemical applications such as gas plants, crude towers, and ethylene plants. Since Aspen Physical Property System does not have built-in binary parameters for this property method, they had to be estimated.

For plastic which is defined as non-conventional component (together with ash), HCOALGEN and DCOALIGT were used to calculate the enthalpy and density based on its proximate and ultimate analysis (Figure **??**) as was done in the example of AspenTech.

Oxo-synthesis PENG-ROB was used to simulate the oxo-synthesis of propylene to n-butanol. The property method is based on the peng-robinson cubic equation. As PR-BM, which is also based on the same equation of state, PENG-ROB is well suited for non-polar mixtures, for example hydrocarbons and light gases, which is exactly what this part of the process describes.

Process Flowsheet

All of the flowsheets hereby presented are screenshots of the process configuration as simulated in Aspen Plus V11.

NRP Pyrolysis

All the units shown in Figures 14 and 15 and for which modeling was performed are hereby listed:

- PDRY (RStoic as a dryer): Valid phases=vapor-liquid-liquid — T=38°C—p=1 atm— moisture removal as stoichiometric reaction provided in [14]— amount of moisture present = 5%
- PDRYFLASH (Flash2 as flash tank): p=1bar — vapor fraction = 1
- PDECOMP (RYield as a virtual unit): T= 482.2°C— P=0bar — decomposition component yields for ash, carbon and hydrogen are 0.2, for nitrogen, chlorine, oxygen, water and sulfur 0.1
- PPLUG (RPlug as the actual plug flow reactor/pyrolysis kiln): constant T=400 — p=1bar — L=9.144m — Dc= 0.914m — process stream=vapor only — assembly reaction defined as pyrolysis kinetics based on [14]
- PPYRO (RGibbs as a virtual unit): T = 400 — p= 1 bar — considering all components as products — all inerts except C_6H_6 and C_6H_6O — restricted equilibrium set as temperature approach for the reaction:

$$5C_6H_6O + 3C \rightarrow 5C_6H_6 + CO + 2CO_2 \tag{21}$$

- PSPLIT (SSplit as gas-solid splitter/settler): CHAR split fraction = 1 in the CISOLID stream — ASH split fraction = 1 in NC (non-conventional component) stream
- PDMETCOM (Compressor): isentropic — p=37bar
- PVENTDEM (FSplit as a venting unit): split fraction of PPURGE containing mostly methane = 0.2
- PDMFLASH (Flash2 as a flash tank): T= -110 — p=37 bar
- PDMETHAN (RadFrac as demethanizer cryogenic distillation column): 30 stages — reflux ratio = 0.5 — distillate to feed ratio = 0.35 — feed stream on stage 14 — distillate vapor fraction = 0.5 — no pressure drop
- PVALVE1 (Valve): adiabatic with a specified outlet pressure of p=1bar
- PVALVE2 (Valve): p=20bar
- PDETHAN (RadFrac as deethanizer cryogenic distillation column): 20 stages — reflux ratio = 3.7 — D/F = 0.08 — feed on stage 10 — distillate vapor fraction = 0.5 — no pressure drop
- PDESPLIT (FSplit as a venting unit): DERECYCL split fraction of 0.9
- PDEPROP (RadFrac as depropanizer cryogenic distillation column): 10 stages — reflux ratio = 1.2 — D/F = 0.7 — feed on stage 6 — distillate vapor fraction = 0.5 — no pressure drop
- PSEP3 (Separator unit): RECPROP stream contains only propylene
- PPROPCO2 (Separator unit): PCO2 stream contains only CO_2
- PFURNAC (RStoic as a furnace unit): T= 400 — p=1bar — combustion reaction as described by the Equation **??** and assuming 100% conversion
- PPPP (Flash2 as a flash tank): T=25 — p=1 bar — used to separate CO_2 and H_2O

As the list of units is already extensive, heaters, coolers, mixers and vents are not included as they provide the desired conditions to the stream in order to perform the operations in the other units as hereby listed.

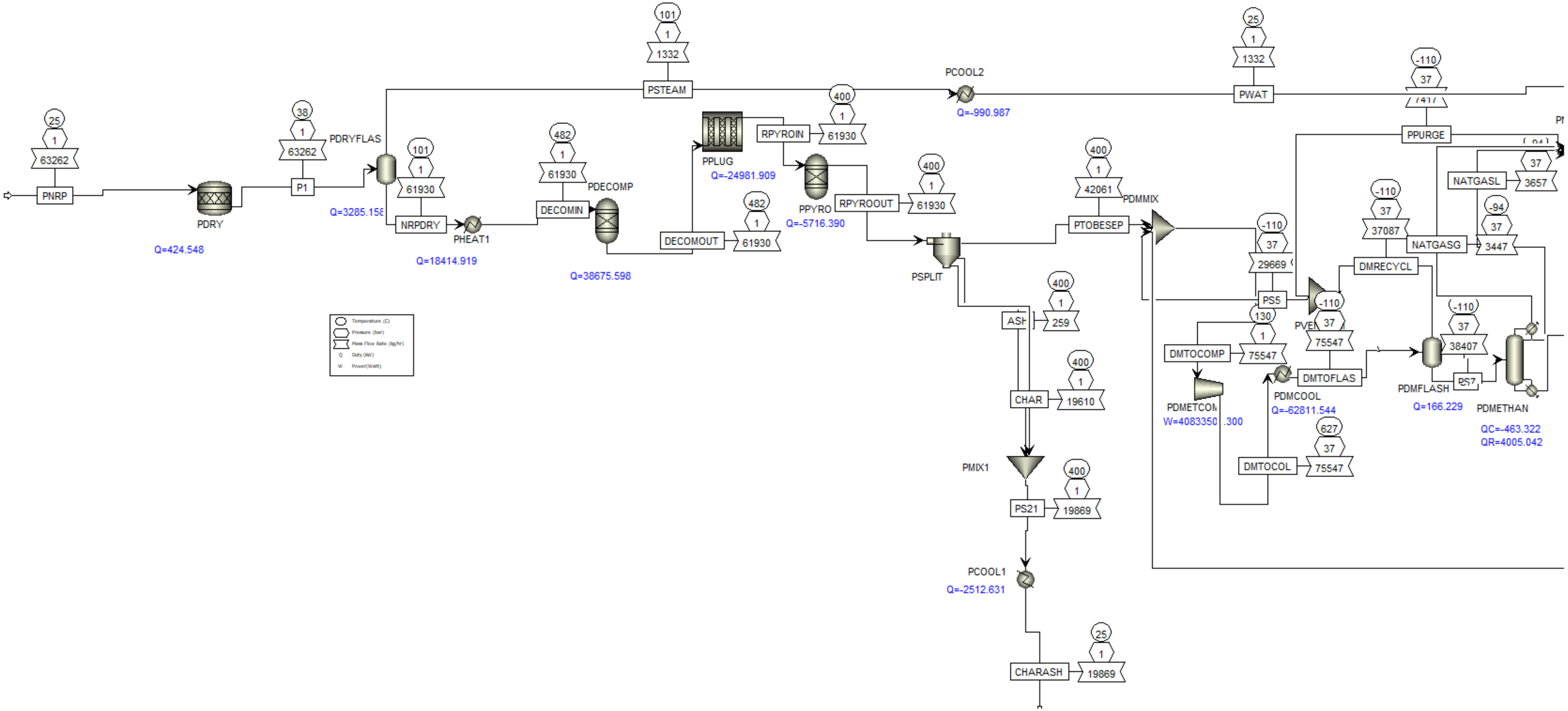


Figure 14: Aspen flowsheet for Section 1: NRP Pyrolysis, part 1

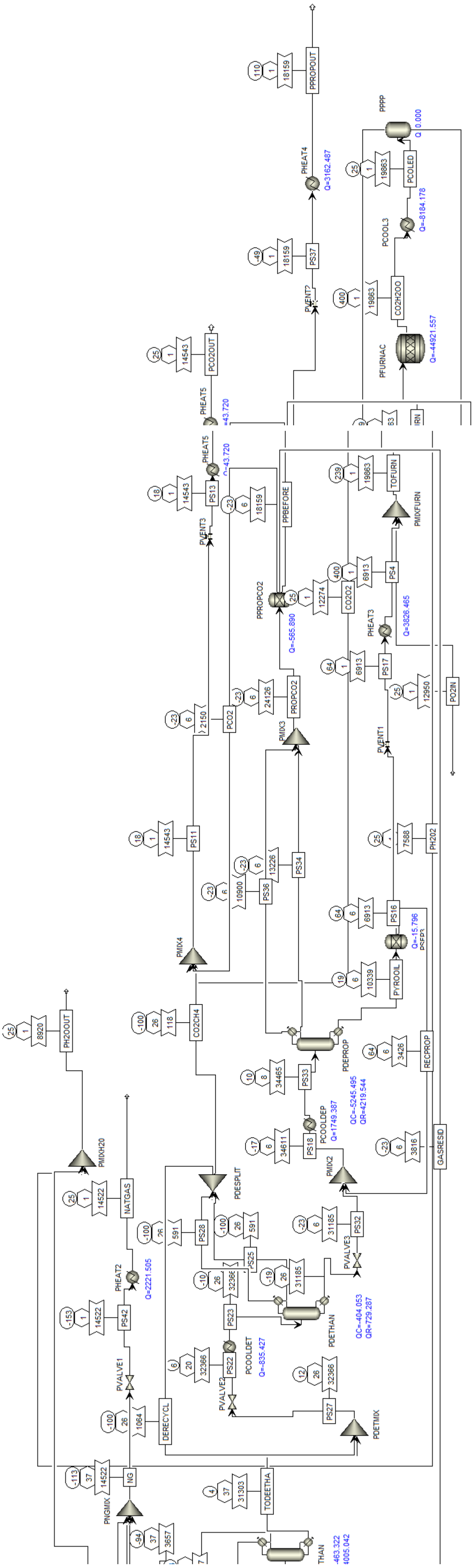


Figure 15: Aspen flowsheet for Section 1: NRP Pyrolysis, parts 2&3

Oxo synthesis

The following list explains the units given in Figures 16 and 17:

- **M101** (Mixer): Valid phases=Vapor-Liquid
- **R101** (Tubular reactor PPLUG): T=150°C—P=20 bar—Length=10m, Diameter=0.5m—Vapor-only—Hydroformylation reaction
- **S101** (Splitter FSplit): Split fraction=0.9 (0.1 recycled)
- **V101** (Expansion valve): Outlet pressure = 1bar—Valid phases:Vapor-Liquid
- **E101** (heater): T=20°C—P=1bar—Valid phases=Vapor-liquid
- **S102** (Splitter Fsplit): Split fraction=0.03 purged
- **C104** (Isentropic compressor Compr): Discharge pressure = 20bar
- **E107** (Heater): T=150°C—P=20°C—Valid phases=Vapor-only
- **T101** (Flash tank Flash2): T=20°C—P=1bar—Valid phases=Vapor-Liquid
- **T102** (Distillation column RadFrac): Number of stages=35—Condenser=Partial-Vapor—Valid phases=Vapor-liquid—Reflux ratio= 10—Distillate to feed ratio=0.25—Feed on stage 19—Condenser pressure=0.5bar
- **C102** (Isentropic compressor Compr): Discharge pressure=1bar
- **E103** (Heater): T=25°C—P=1bar—Valid phases=Vapor-liquid
- **C101** (Pump): Discharge pressure= 20 bar
- **E102** (Heater): T=365°C—P=1bar—Valid phases= Vapor-Liquid
- **M102** (Mixer): Valid phases=Vapor-Liquid
- **M104** (Mixer): Valid phases=Vapor-Liquid
- **C103** (Isentropic compressor): Discharge pressure= 20 bar
- **M103** (Mixer): Valid phases=Vapor-Liquid
- **E104** (Heater): T=365—P=20 bar
- **R102** (Tubular reactor PPLUG): T=365°C—P=20bar—L=7m, D=0.5m—Vapor-only—Catalyst loading=350kg, Bed voidage=0.4—Hydrogenation reaction
- **E108** (Heater): T=60°C—P=20bar—Valid phases=Vapor-liquid
- **T103** (Flash2): T=60°C—P=20bar—Valid phases=Vapor-liquid
- **V102** (Expansion valve): Outlet pressure=1bar—Valid phases= Vapor-liquid
- **S103** (Splitter Fsplit): Split fraction=0.97 recycled
- **E105** (Heater): T=25°C—P=1bar—Valid phases= Vapor-Liquid
- **T104** (Distillation column RadFrac): Number of stages=9—Condenser=Partial-Vapor—Reflux ratio=3.429—Distillate to feed ratio=0.492—Feed on stage 3—Condenser pressure=1bar
- **E109** (Heater): T=25°C—P=1bar—Valid phases=Liquid-Only
- **S104** (Splitter FSplit): Split fraction=0.97 recycled
- **E106** (Heater): T=25°C—P=1bar—Valid phases=Vapor-Liquid

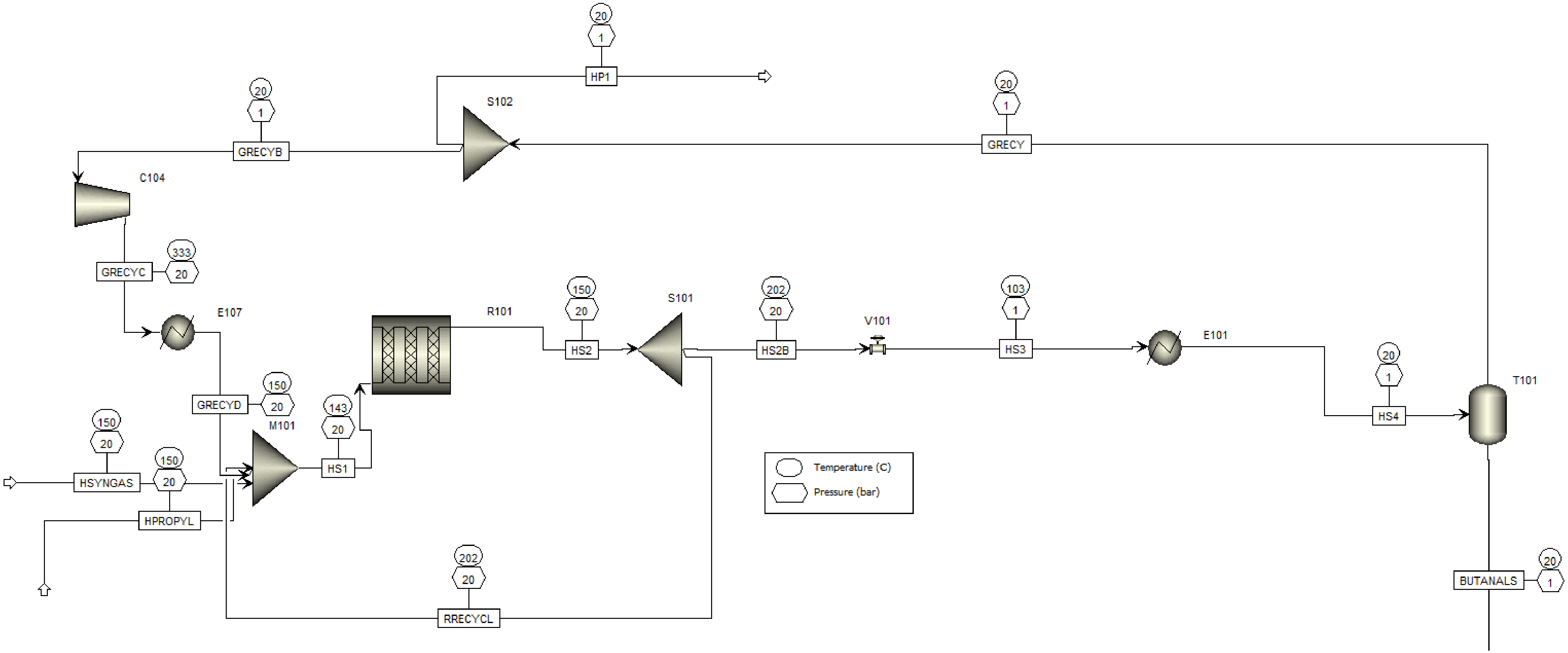


Figure 16: Aspen simulation of the hydroformylation of propylene section

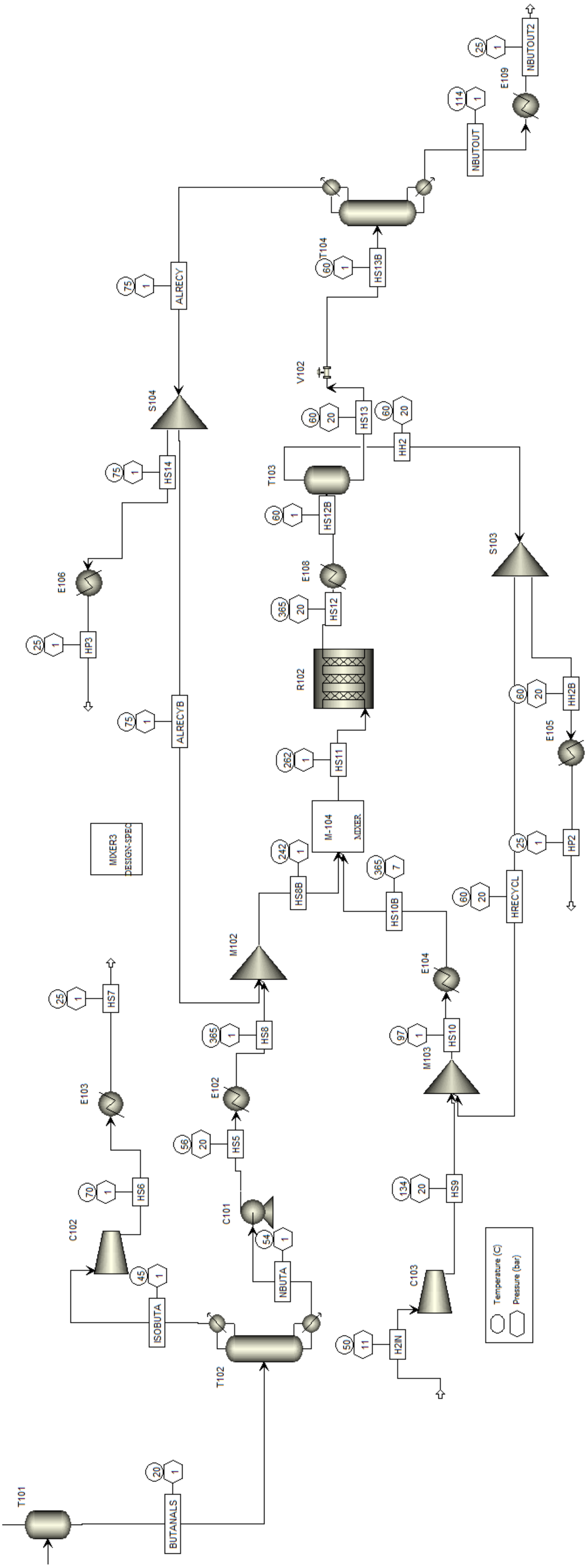
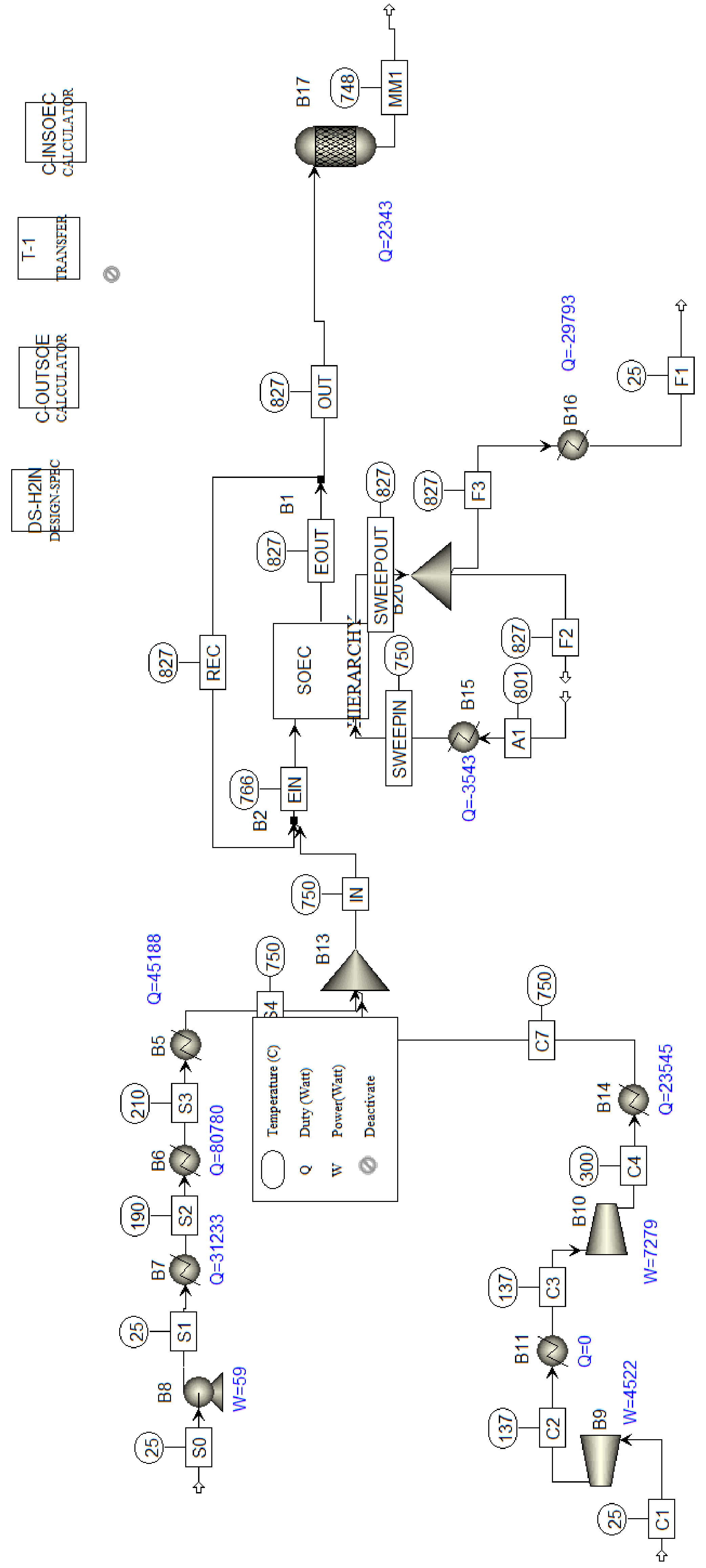


Figure 17: Aspen simulation of the hydrogenation of butanals

Co-electrolysis

Since the electrolysis unit is modelled in such a way to virtually represent the reactions occuring at the electrodes, none of the units included in the flowsheets (e.g. compressors, reactors, mixers etc.) are real. For this reason, a detailed explanation of the individual units is not included in the Appendix, but can be found in [13].

Furthermore, in order to be able to close the material balance of the overall process, the CO-SOEC model needed to be upscaled by a factor of 70, which did not affect the operating conditions but increased the magnitude of flows and duties, assuming linear scale-up.


DS-H2IN
DESIGN-SPEC
C-OUTSOE
CALCULATOR
T-1
TRANSFER
C-INSOEC
CALCULATOR
B17
748
MM1
Q=2343
827
OUT
B1
827
EOUT
827
SWEEPOUT
827
F3
B16
Q=-29793
25
F1
827
REC
SOEC
HIERARCHY
B20
750
827
F2
801
A1
B15
SWEEPIN
Q=-3543
766
EIN
B2
750
IN
B13
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S4
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B5
210
S3
B6
Q=80780
190
S2
B7
Q=31233
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S1
B8
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25
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W Power(Watt)
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B14
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B9
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C1

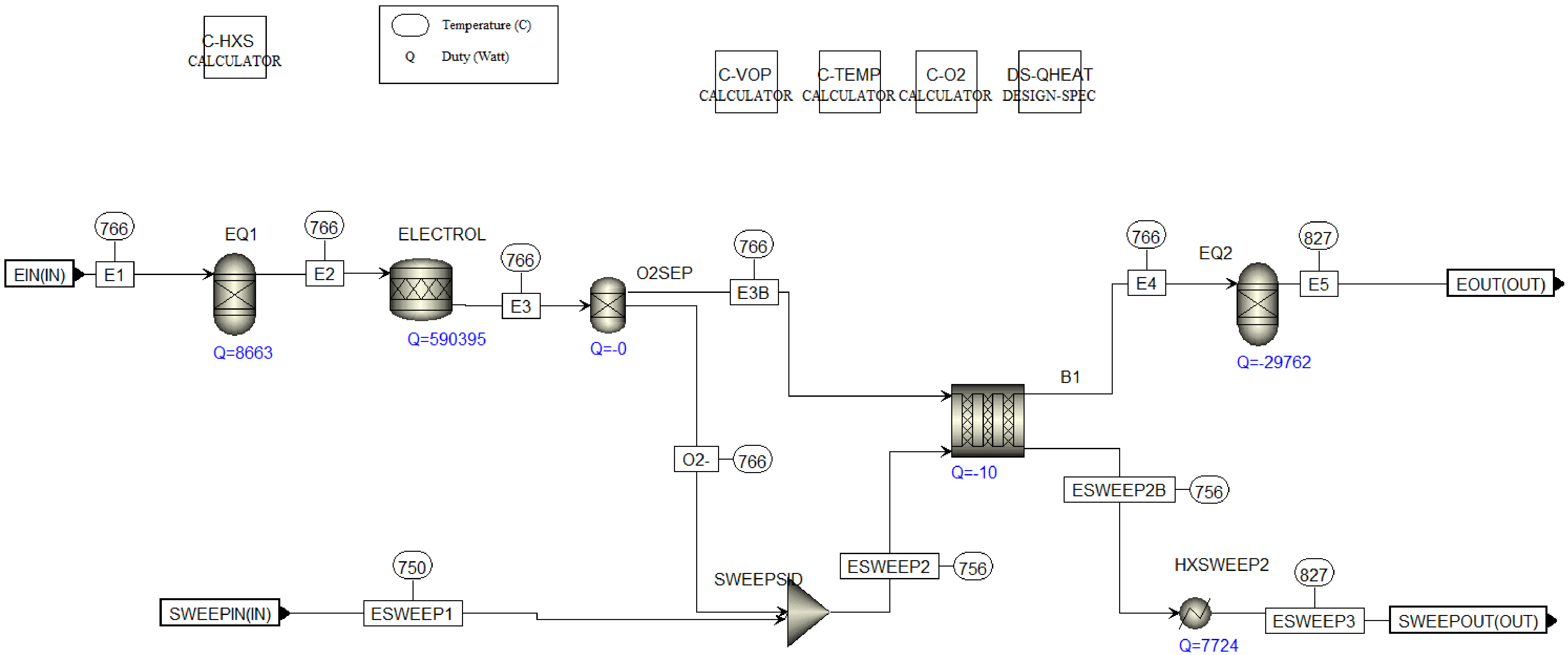


Figure 18: Aspen flowsheet for CO-SOEC

Main flows

This section describes a few characteristics and the composition of the main flows of the process. Refer to figures 14& 15 (plastic pyrolysis), 16 & 17 (Oxo synthesis) and 18 (co-electrlysis) for the matching between names and streams on the flowsheet.

Table 10: Main flows in the pyrolysis of plastic part

Description		PNRP (solid)	PPROPOUT	PCO2OUT	NATGAS	PH2OOUT
Temperature	C	25.00	110.00	25.00	25.00	25.00
Pressure	bar	1.01	1.00	1.00	1.00	1.00
Molar Vapor Fraction	-	0.00	1.00	1.00	1.00	0.00
Mass Enthalpy	kJ/kg	-3063.67	623.45	-8913.27	-4273.70	-15962.00
Mass Density	kg/cum	660.24	1.33	1.73	0.41	848.66
Enthalpy Flow	kW	-27751.10	1631.68	-18570.30	-8879.52	-20351.30
Mass Flows	kg/hr	32609.28	9421.84	7500.38	7479.77	4589.95
Mass Fractions						
NRP		1				
ASH						
Mole fraction						
C3H6		0	1	1.41E-14	0.000595	0
O2		0	0	0.005172	0	1.04E-08
C2H6		0	0	5.78E-05	0.000843	5.73E-11
CH4		0	0	0.02279	0.573467	2.55E-15
CO2		0	0	0.949465	0.001846	1.07E-05
H2O		0	0	0.022516	0	0.999989
H2		0	0	0	0.421248	0
CO		0	0	0	0.002001	0

Table 10 describes the main flows in the plastic pyrolysis section.PNRP is the stream of entering NRP waste, PPROPOUT is the main output of propylene and PCO2OUT, NATGAS and PH2OUT are respectively the waste streams of CO_2, CH_4/H_2 mixture and water.

Table 11: Main flows in the co-electrolysis part

Description		IN	O2	CO2	WATER2	HYDROGEN	SYNGASS
Temperature	C	750	691.5757	783.3333	50	50	50
Pressure	bar	15	1	15	11	11	11
Molar Vapor Fraction		1	1	1	0	1	0.983169
Mass Enthalpy	kJ/kg	-11935.8	671.0057	-8113.39	-15912.7	363.1275	-3989.17
Mass Density	kg/cum	3.185053	0.39883	7.481864	939.0809	0.820876	6.252541
Enthalpy Flow	kW	-36105.8	1837.81	-21940	-17603.4	32.78235	-7396.59
Mass Flows	kg/hr	13266	9860	9735	3982.5	325	6675
Mole Fractions							
H2O		1			0.999994		0.026185
O2			1				
CO2				1			
H2					5.89E-06	1	0.487261
CO					3.54E-07		0.486554

Table 11 describe the main flows in the co-electrolysis section. IN is the inlet stream of water, O2 the outlet stream of oxygen, CO2 the inlet stream of CO_2, WATER2 is the waste water stream and HYDROGEN and SYNGASS are the main product streams for hydrogen ad syngas.

Table 12 describe the main flows in the Oxo synthesis section.HSYNGAS and HPROPYL are the inlet streams of syngas and propylene coming from the co-electrolysis and the plastic pyrolysis, GRECYD is the recycle stream of syngas and propylene from the hydroformylation reaction, HS2 is the product stream after the hydroformylation reactor, RRECYCL is the recycle stream right after the hydroformylation reaction, HP1 is the purge of the recycle stream GRECYD, HS7 is the isobutanal-rich waste stream after the separation of n-butanal and isobutanal, NBUTA is the stream of n-butanal for the hydrogenation reaction, H2IN is the hydrogen stream coming from the co-electrolysis for the hydrogenation reaction, HRECYCL is the hydrogen recycle stream after the hydrogenation reactor, ALRECYB is the recycled stream for butanals, HP2 is the purge for the hydrogen recycle stream, HS12 is the product stream out of the hydrogenation reactor, ALRECY is the recycle stream of butanals before the purge, HP3 is the purge of the butanal recycle stream, NBUTOUT2 is the final product of the process, the 95% purity n-butanal stream.

Table 12: Main flows in the Oxo synthesis part

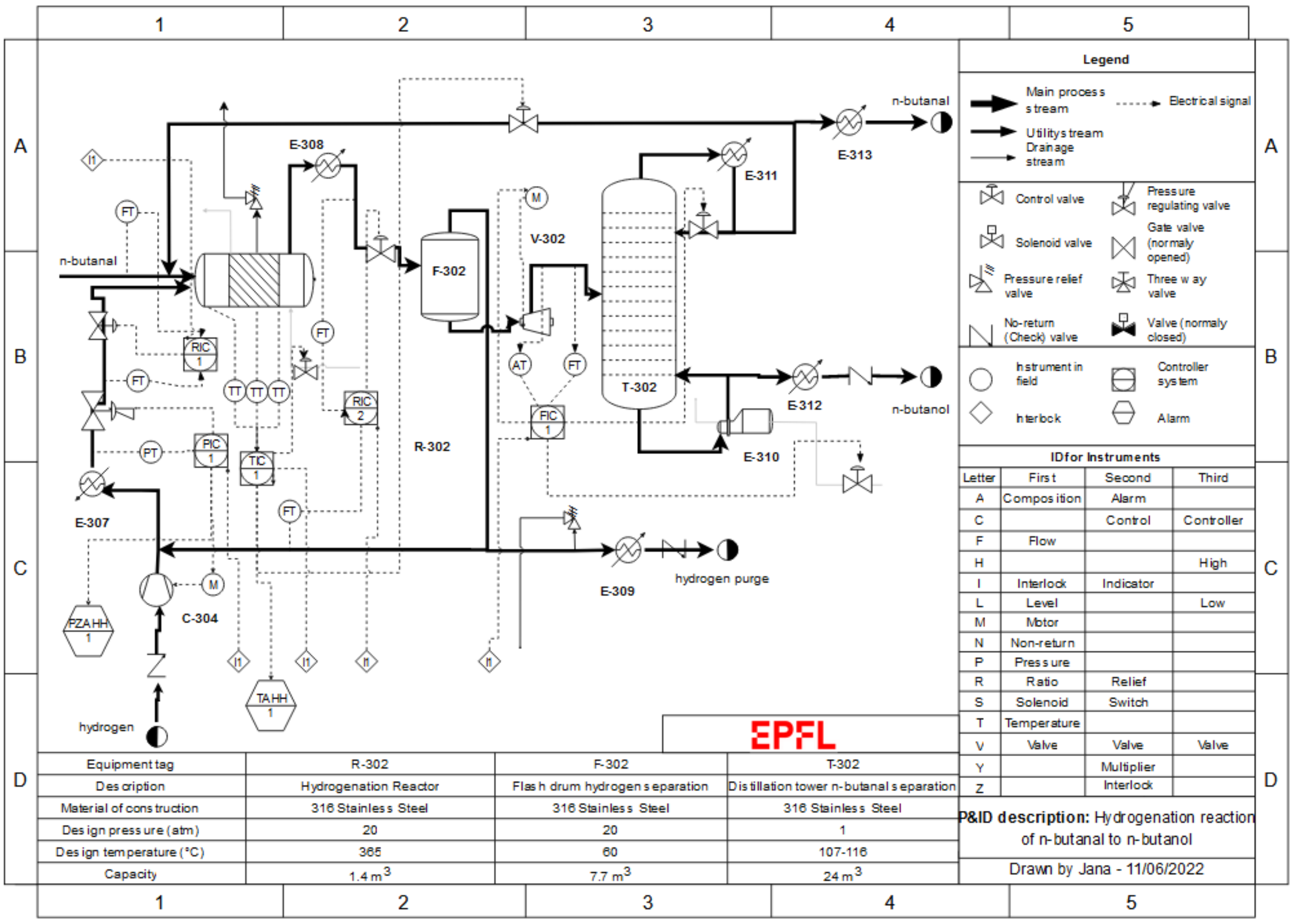
Description		HSYNGAS	HPROPYL	GRECYD	HS2	RRECYCL	HP1	HS7 (isobutanal)	NBUTA	H2IN	HRECYCL	ALRECYB	HP2	HS12	ALRECY	HP3	NBUTOUT2
Temperature	C	150	150	150	150	202.0707	20	25	53.91766	50	60	74.76511	25	365	74.76511	25	25
Pressure	bar	20	20	20	20	20	1	1	0.5	11	20	1	1	20	1	1	1
Molar Vapor Fraction		1	1	1	1	0.517547	1	0.001952	0	1	1	1	1	1	1	0.013257	0
Mass Enthalpy	kJ/kg	-3438.55	672.4969	-2963.24	-2774.68	-2774.68	-3213.11	-3411.82	-3263.29	361.7035	-938.524	-2793.28	-1253.08	-2515.04	-2793.28	-3326.48	-4318.45
Mass Density	kg/cum	8.466311	26.82987	11.98549	80.68221	88.51665	0.865532	518.3627	767.3402	0.821147	2.437326	2.54238	0.865532	19.23227	2.54238	170.78	806.1145
Enthalpy Flow	kW	-6366.88	1745.111	-89.2164	-13801.8	-1380.18	-2.99194	-3785	-10887.6	32.61907	-140.22	-8430.43	-2.99194	-16584.4	-8691.16	-310.505	-14374.4
Mass Flows	kg/hr	6665.834	9341.902	108.3876	17907.18	1790.718	3.352195	3993.765	12010.96	324.6545	537.8557	10865.18	3.352195	23738.69	11201.22	336.0366	11982.98
Mole Fractions																	
CO		0.5		0.347953	0.008477	0.008477	0.347953	0.001479									
H2		0.5		0.506671	0.01197	0.01197	0.506671	0.000624		1	0.980258	0.011478	0.980258	0.335089	0.011478	0.011478	1.01E-26
C3H6			1	0.006111	0.000704	0.000704	0.006111	0.002301									
n-butanal				0.094736	0.753693	0.753693	0.094736	0.120461	0.985754		0.016901	0.981908	0.016901	0.337614	0.981908	0.981908	0.03496
isobutanal				0.04453	0.225155	0.225155	0.04453	0.875134	0.014246								
n-butanol											0.002776	0.006247	0.002776	0.322231	0.006247	0.006247	0.950385
isobutanol												0.000368	6.50E-05	0.005065	0.000368	0.000368	0.014656

HAZOP

Example of a HAZOP study on a specific hazard: hydrogen leak

In general, the consequences of presented hazards are evaluated by performing simple calculations. The overall risk is obtained by multiplying the frequency (probability) of the event by its consequence expressed numerically. The parts of the process with the highest hazard are the furnace operation next to the cold box in NRP Pyrolyis and hydrogenation step of the Oxo synthesis (even though hydroformylation reaction step is also exothermic, it has a lower enthalpy of reaction). Due to the higher significance of the Oxo synthesis to the overall process, the example of control loop implementation and HAZOP study will be performed upon that node.

In Figure 19 the P&ID of the process node is presented. Note that elements such as indicators and recorders are omitted from graphical representation for the purpose of clarity (as these elements of control systems are assumed to be present and do not represent the main elements of actions, usually they are not directly represented). Based on the preliminary P&ID constructed, HAZOP study can be performed in order to determine the highest risks and possible mitigation strategies and is presented in Figure 20.



Equipment tag	R-302	F-302	T-302
Description	Hydrogenation Reactor	Flash drum hydrogen separation	Distillation tower n-butanal separation
Material of construction	316 Stainless Steel	316 Stainless Steel	316 Stainless Steel
Design pressure (atm)	20	20	1
Design temperature (°C)	365	60	107-116
Capacity	1.4 m^3	7.7 m^3	24 m^3

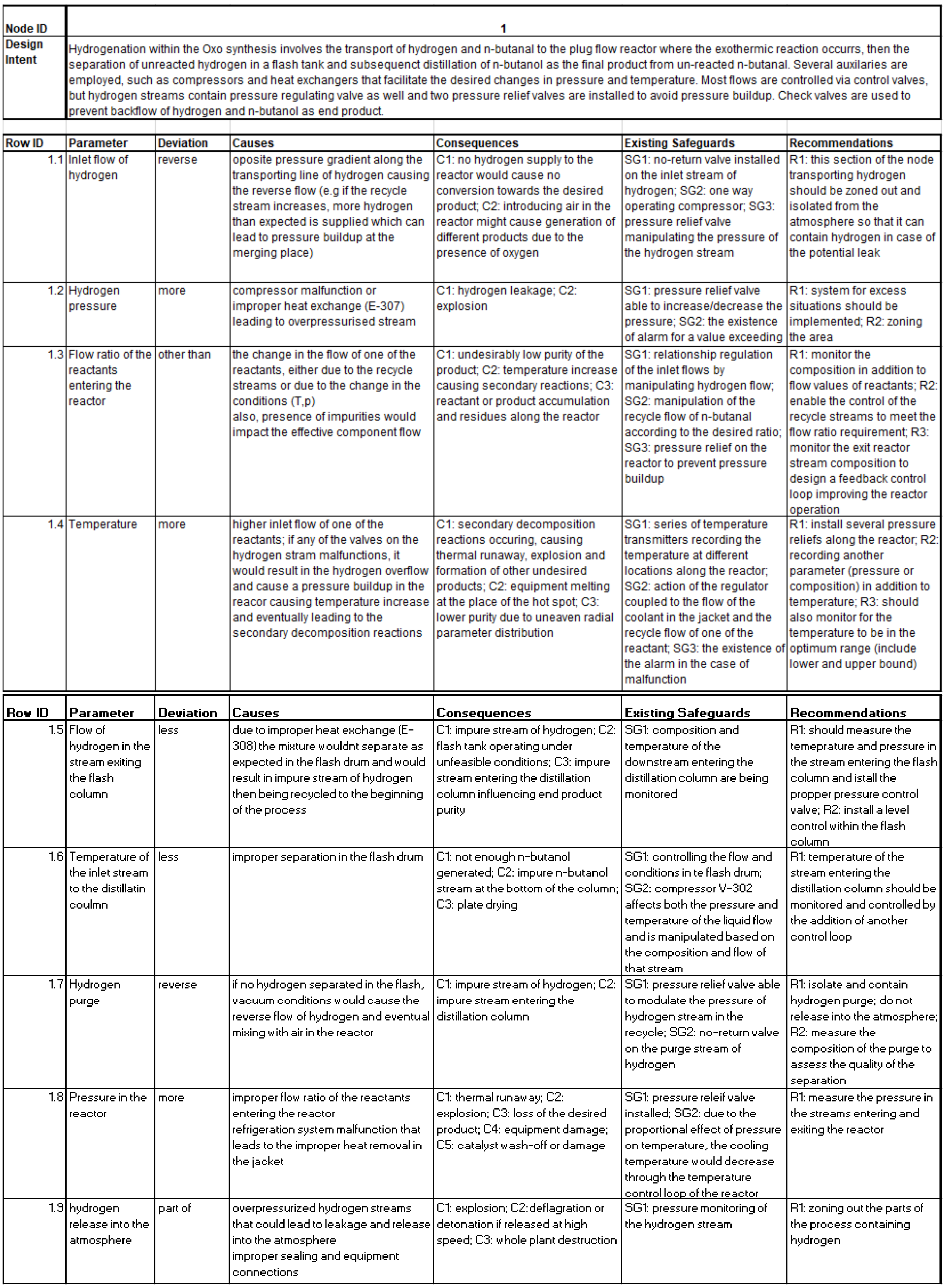
ID for Instruments

Letter	First	Second	Third
A	Composition	Alarm	
C		Control	Controller
F	Flow		
H			High
I	Interlock	Indicator	
L	Level		Low
M	Motor		
N	Non-return		
P	Pressure		
R	Ratio	Relief	
S	Solenoid	Switch	
T	Temperature		
V	Valve	Valve	Valve
Y		Multiplier	
Z		Interlock	

P&ID description: Hydrogenation reaction of n-butanal to n-butanol

Drawn by Jana - 11/06/2022

Figure 19: Piping and instrumentation diagram for the chosen node with the highest hazard



Node ID	1
Design Intent	Hydrogenation within the Oxo synthesis involves the transport of hydrogen and n-butanal to the plug flow reactor where the exothermic reaction occurrs, then the separation of unreacted hydrogen in a flash tank and subsequenct distillation of n-butanol as the final product from un-reacted n-butanal. Several auxilaries are employed, such as compressors and heat exchangers that facilitate the desired changes in pressure and temperature. Most flows are controlled via control valves, but hydrogen streams contain pressure regulating valve as well and two pressure relief valves are installed to avoid pressure buildup. Check valves are used to prevent backflow of hydrogen and n-butanol as end product.

Row ID	Parameter	Deviation	Causes	Consequences	Existing Safeguards	Recommendations
1.1	Inlet flow of hydrogen	reverse	oposite pressure gradient along the transporting line of hydrogen causing the reverse flow (e.g if the recycle stream increases, more hydrogen than expected is supplied which can lead to pressure buildup at the merging place)	C1: no hydrogen supply to the reactor would cause no conversion towards the desired product; C2: introducing air in the reactor might cause generation of different products due to the presence of oxygen	SG1: no-return valve installed on the inlet stream of hydrogen; SG2: one way operating compressor; SG3: pressure relief valve manipulating the pressure of the hydrogen stream	R1: this section of the node transporting hydrogen should be zoned out and isolated from the atmosphere so that it can contain hydrogen in case of the potential leak
1.2	Hydrogen pressure	more	compressor malfunction or improper heat exchange (E-307) leading to overpressurised stream	C1: hydrogen leakage; C2: explosion	SG1: pressure relief valve able to increase/decrease the pressure; SG2: the existence of alarm for a value exceeding	R1: system for excess situations should be implemented; R2: zoning the area
1.3	Flow ratio of the reactants entering the reactor	other than	the change in the flow of one of the reactants, either due to the recycle streams or due to the change in the conditions (T,p) also, presence of impurities would impact the effective component flow	C1: undesirably low purity of the product; C2: temperature increase causing secondary reactions; C3: reactant or product accumulation and residues along the reactor	SG1: relationship regulation of the inlet flows by manipulating hydrogen flow; SG2: manipulation of the recycle flow of n-butanal according to the desired ratio; SG3: pressure relief on the reactor to prevent pressure buildup	R1: monitor the composition in addition to flow values of reactants; R2: enable the control of the recycle streams to meet the flow ratio requirement; R3: monitor the exit reactor stream composition to design a feedback control loop improving the reactor operation
1.4	Temperature	more	higher inlet flow of one of the reactants; if any of the valves on the hydrogen stram malfunctions, it would result in the hydrogen overflow and cause a pressure buildup in the reacor causing temperature increase and eventually leading to the secondary decomposition reactions	C1: secondary decomposition reactions occuring, causing thermal runaway, explosion and formation of other undesired products; C2: equipment melting at the place of the hot spot; C3: lower purity due to uneaven radial parameter distribution	SG1: series of temperature transmitters recording the temperature at different locations along the reactor; SG2: action of the regulator coupled to the flow of the coolant in the jacket and the recycle flow of one of the reactant; SG3: the existence of the alarm in the case of malfunction	R1: install several pressure reliefs along the reactor; R2: recording another parameter (pressure or composition) in addition to temperature; R3: should also monitor for the temperature to be in the optimum range (include lower and upper bound)
1.5	Flow of hydrogen in the stream exiting the flash column	less	due to improper heat exchange (E-308) the mixture wouldnt separate as expected in the flash drum and would result in impure stream of hydrogen then being recycled to the beginning of the process	C1: impure stream of hydrogen; C2: flash tank operating under unfeasible conditions; C3: impure stream entering the distillation column influencing end product purity	SG1: composition and temperature of the downstream entering the distillation column are being monitored	R1: should measure the temeprature and pressure in the stream entering the flash column and istall the propper pressure control valve; R2: install a level control within the flash column
1.6	Temperature of the inlet stream to the distillatin coulmn	less	improper separation in the flash drum	C1: not enough n-butanol generated; C2: impure n-butanol stream at the bottom of the column; C3: plate drying	SG1: controlling the flow and conditions in te flash drum; SG2: compressor V-302 affects both the pressure and temperature of the liquid flow and is manipulated based on the composition and flow of that stream	R1: temperature of the stream entering the distillation column should be monitored and controlled by the addition of another control loop
1.7	Hydrogen purge	reverse	if no hydrogen separated in the flash, vacuum conditions would cause the reverse flow of hydrogen and eventual mixing with air in the reactor	C1: impure stream of hydrogen; C2: impure stream entering the distillation column	SG1: pressure relief valve able to modulate the pressure of hydrogen stream in the recycle; SG2: no-return valve on the purge stream of hydrogen	R1: isolate and contain hydrogen purge; do not release into the atmosphere; R2: measure the composition of the purge to assess the quality of the separation
1.8	Pressure in the reactor	more	improper flow ratio of the reactants entering the reactor refrigeration system malfunction that leads to the improper heat removal in the jacket	C1: thermal runaway; C2: explosion; C3: loss of the desired product; C4: equipment damage; C5: catalyst wash-off or damage	SG1: pressure releif valve installed; SG2: due to the proportional effect of pressure on temperature, the cooling temperature would decrease through the temperature control loop of the reactor	R1: measure the pressure in the streams entering and exiting the reactor
1.9	hydrogen release into the atmosphere	part of	overpressurized hydrogen streams that could lead to leakage and release into the atmosphere improper sealing and equipment connections	C1: explosion; C2:deflagration or detonation if released at high speed; C3: whole plant destruction	SG1: pressure monitoring of the hydrogen stream	R1: zoning out the parts of the process containing hydrogen

Figure 20: HAZOP study upon one of the process nodes performing hydrogenation reaction and subsequent separation within the Oxo synthesis

Detailed cost calculation table

The following section presents the detailled cost calculations. Table 13 presents the cost of each unit based on the cost derivations from the Turton handbook [25]. table 14 presents the actualized, annualised TOTEX (CAPEX+OPEX) of the units.

Table 13: Unit costs for the process

Process	Unit code	Unit type	Size	Size unit	Unit name in Turton	K1	K2	K3	min size	max size	log(cost)	Purchased Cost($)
Plastic Pyrolysis	PDRYFLASH	Plastic drier	18.93	m2	rotary, gas fired dryer	4.5472	-0.7269	0.134	5	100	3.837	6877.1
	PDECOMP+PPLUG+PPYRO	rotary kiln	35576.36	kW	pyrolysis furnace	2.3859	0.9721	-0.0206	3000	100000	6.383	2417657.7
	PDMETCOM	compressor (7 units)	3000.00	kW	Centrifugal compressor	2.2897	1.3604	-0.1027	450	3000	5.778	4201385.8
	PDMFLASH	flash tank	104.00	cum	vertical process vessel	3.4974	0.4485	0.1074	0.3	520	4.839	69022.1
	PDMETHAN	distillation column	29.00	cum	tray tower	3.497	0.4485	0.1074	0.3	520	4.383	24130.8
		the trays	1.54	/	sieve trays	2.9949	0.4465	0.3961	0.07	12.3	3.092	1237.2
	PDETHAN	distillation column	5.49	cum	tray tower	3.497	0.4485	0.1074	0.3	520	3.887	7714.6
		the trays	0.45	/	sieve trays	2.9949	0.4465	0.3961	0.07	12.3	2.888	772.2
	PDEPROP	distillation column	16.03	cum	tray tower	3.497	0.4485	0.1074	0.3	520	4.193	15610.5
		the trays	2.63	/	sieve trays	2.9949	0.4465	0.3961	0.07	12.3	3.252	1787.7
	PSEP3	flash tank	2.76	cum	vertical process vessel	3.4974	0.4485	0.1074	0.3	520	3.716	5200.3
	PFURNAC	furnace	22414.61	kW	nonreactive fired heater	7.3488	-1.1666	0.2028	1000	100000	6.112	1293869.8
	PPPP	flash tank	1.49	cum	vertical process vessel	3.4974	0.4485	0.1074	0.3	520	3.578	3787.0
	PSPLIT	S/V splitter (settler)	0.17	m2	disk and drum filter	4.8123	-0.7142	0.042	0.9	300	5.381	240365.2
	Screw conveyor	screw conveyor (3 units)	2.25	m2	screw conveyor	3.6062	-0.7341	0.1982	0.5	30	3.372	7069.2
	Rod mill	rod mill (open wet)			roller mill	/	/	/	/	/	/	230000.0
	Storage	storage silo	825.24	cum		/	/	/	/	/	/	100000.0
Oxo synthesis: Hydroformylation	R101	Hydrofor reactor	1.96	m3	Jacketed nonagitated reactor ?	3.3496	-0.2765	0.0025	5	45	3.269	1856.9
	V101	Expansion valve	1.00	kW fluid power	Turbines -Radial gas/liquid expanders ?	2.2476	1.4965	-0.1618	100	1500	2.248	176.8
	T101	Flash	5.32	m3	Process vessel, vertical	3.4974	0.4485	0.1074	0.3	520	3.880	7578.2
	T102	Distillation column	139.86	area m2*nb of trays	Valve trays	3.2353	0.4838	0.3434	0.7	10.5	5.854	715179.8
			90.19	m3	Towers: tray and packed	3.497	0.4485	0.1074	0.3	520	4.784	60877.7
	C104	Compressor	19.87	Fluid power, kW	Centrifugal compressor	2.2897	1.3604	-0.1027	450	3000	3.883	7634.9
		Rhodium catalyst	6.85	kg		/						2469063.0
Oxo synthesis: Hydrogenation	C101	Pump	8.48	Shaft power, kW	Pumps, centrifugal	3.3892	0.0536	0.1538	1	300	3.572	3728.2
	C103	Compressor	109.58	Fluid power, kW	compressor, centrifugal etc.	2.2897	1.3604	-0.1027	450	3000	4.637	43377.0
	R102	Reactor	1.37	volume, m3	jacketed nonagitated	3.3469	-0.2765	0.0025	5	45	3.309	2035.9
	T103	Flashdrum	7.73	volume, m3	vessel, vertical	3.4974	0.4485	0.1074	0.3	520	3.981	9562.2
	T104	Distillation tower	68.29	volume, m3	Towers, tray and packed	3.4974	0.4485	0.1074	0.3	520	4.681	48025.3
			12.45	area, m2 (9 stages)	trays, sieve	2.9949	0.4465	0.3961	0.07	12.3	3.959	9095.0
SOEC	B7	Flash	0.28	volume, m3	vessel, vertical	3.4974	0.4485	0.1074	0.3	520	3.284	1921.7
	B4	Amine scrubber	/									1338862.0
	Cell	SOEC										34170720.0
Heat recovery		Steam Turbines	17426.90	kW, elec	/	/	/	/	750	22400	/	1500000.0
		Water cooling (w steam turbines	22169.7	kW	/	/	/	/	/	/	/	192876.4
		Water cooling (wo steam turbines	39596.6	kW	/	/	/	/	/	/	/	344490.4
Electricity recovery		Turbines(8 units)	3525.00	kW fluid power	Axial gas turbine	2.7051	1.4398	-0.1776	100	4000	5.578	3025286.4

Table 14: Cost details for all units of the process: CAPEX+OPEX=TOTEX [USD/year].

Process	Unit code	Unit type	Purchased Cost($)	Installed Cost [$]	actualized	CAPEX [$/year]	OPEX [$/year]	TOTEX [$/year]
Plastic Pyrolysis	PDRYFLASH	Plastic drier	6877.1	24964.1	49530.7	4318.3	431.8	4750.1
	PDECOMP+PPLUG+PPYRO	rotary kiln	2417657.7	8776097.5	17412476.1	1518099.0	151809.9	1669908.9
	PDMETCOM	compressor (7 units)	4201385.8	15251030.6	30259258.8	2638140.1	263814.0	2901954.1
	PDMFLASH	flash tank	69022.1	250550.2	497111.5	43340.5	4334.0	47674.5
	PDMETHAN	distillation column	24130.8	87594.9	173795.2	15152.3	1515.2	16667.5
		the trays	1237.2	4491.2	8910.8	776.9	77.7	854.6
	PDETHAN	distillation column	7714.6	28003.9	55561.9	4844.1	484.4	5328.6
		the trays	772.2	2802.9	5561.3	484.9	48.5	533.3
	PDEPROP	distillation column	15610.5	56666.0	112429.9	9802.2	980.2	10782.4
		the trays	1787.7	6489.4	12875.4	1122.5	112.3	1234.8
	PSEP3	flash tank	5200.3	18877.0	37453.5	3265.4	326.5	3591.9
	PFURNAC	furnace	1293869.8	4696747.3	9318720.4	812448.5	81244.9	893693.4
	PPPP	flash tank	3787.0	13746.8	27274.8	2377.9	237.8	2615.7
	PSPLIT	S/V splitter (settler)	240365.2	872525.6	1731160.3	150930.4	15093.0	166023.5
	Screw conveyor	screw conveyor (3 units)	7069.2	25661.0	50913.5	4438.9	443.9	4882.8
	Rod mill	rod mill (open wet)	230000.0	834900.0	1656508.1	144421.9	14442.2	158864.1
	Storage	storage silo	100000.0	363000.0	720220.9	62792.1	6279.2	69071.4
Oxo synthesis: Hydroformylation	R101	Hydrofor reactor	1856.9	6740.6	13373.9	1166.0	116.6	1282.6
	V101	Expansion valve	176.8	642.0	1273.7	111.0	11.1	122.2
	T101	Flash	7578.2	27508.8	54579.7	4758.5	475.9	5234.4
	T102	Distillation column	715179.8	2596102.7	5150874.5	449076.7	44907.7	493984.4
			60877.7	220986.1	438454.0	38226.4	3822.6	42049.1
	C104	Compressor	7634.9	27714.5	54987.8	4794.1		4794.1
		Rhodium catalyst	2469063.0	2469063.0	2469063.0	215264.2	21526.4	236790.6
Oxo synthesis: Hydrogenation	C101	Pump	3728.2	13533.4	26851.3	2341.0		2341.0
	C103	Compressor	43377.0	157458.4	312410.0	27237.3	2723.7	29961.1
	R102	Reactor	2035.9	7390.3	14662.9	1278.4	127.8	1406.2
	T103	Flashdrum	9562.2	34710.7	68868.7	6004.3	600.4	6604.7
	T104	Distillation tower	48025.3	174331.7	345887.9	30156.1	3015.6	33171.7
			9095.0	33014.8	65504.0	5710.9	571.1	6282.0
SOEC	B7	Flash	1921.7	6975.7	13840.4	1206.7	120.7	1327.3
	B4	Amine scrubber	1338862.0	4860069.1	4860069.1	423723.0	42372.3	466095.3
	Cell	SOEC	34170720.0	124039713.6	124039713.6	10814347.5	1081434.7	11895782.2
Heat recovery		Steam Turbines	1500000.0	5445000.0	11150018.0	972109.4	97210.9	1069320.3
		Water cooling (w steam turbines	192876.4	700141.3	1465318.0	127753.1	2999018.4	3126771.5
		Water cooling (wo steam turbines	344490.4	1250500.2	2617158.2	228175.8	2999018.4	3227194.2
Electricity recovery		Turbines(8 units)	3025286.4	10981789.5	21788744.6	1899642.0	189964.2	2089606.2