CPD NR 3300
Conceptual Process Design

Process Systems Engineering
DelftChemTech - Faculty of Applied Sciences
Delft University of Technology

Subject

Propylene production by heat integrated dehydrogenation of propane with selective hydrogen oxidation (Hipphox)

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Preface

The course Conceptual Process Design (CPD, CE3811) [23] is part of the 4th year's curriculum for students studying Chemical Engineering and Biochemical Engineering at the DelftChemTech (DCT) Department of the Faculty of Applied Sciences (TNW) at Delft University of Technology. The Conceptual Process Design (CPD) is coordinated by the section Process Systems Engineering (PSE) of the DelftChemTech Department.

With this course, students are expected to produce an innovative process design, where they have to creatively integrate their knowledge, gathered so far in their study. The design work is performed by five students as a team, with full responsibility for design quality, planning and communications. Moreover, the course requires approximately 12 consecutive full working weeks, hardly leaving room for other activities.

CPD 3300 would like to thank Dr G. Rothenberg and Dr. A.C. Dimian for their availability at all times, the readiness for answering questions and the guidance throughout the project. We also enjoyed our visit to Amsterdam. It was a challenging experience to successfully test the feasibility of implementing the SOC.

Summary

The objective of this CPD project is to make a conceptual process design for the production of 250 kta propylene using a solid oxygen carrier (SOC). This SOC is recently developed by scientists of the University of Amsterdam (UvA). The problem statement is defined as follows:

How can propylene be produced by using the new solid oxygen carrier in the dehydrogenation of propane coupled with selective hydrogen combustion?

Market analysis shows an increasing demand of propylene over the next decennia. Propylene will be made from propane, the main component of LPG. The difference in price between propane and propylene allows a high enough margin for profitable production of propylene from propane. Therefore the Heat Integrated Propylene Production with Hydrogen OXidation (Hipphox) process has been developed.

Major differences of the Hipphox process compared to another propane dehydrogenation process, UOP's Oleflex, are the reactor and regeneration sections. The use of a SOC increases the conversion per pass from 29 mole% to 57 mole%. Furthermore the selectivity of the propane conversion is increased from 90 mole% to 99 mole% due to better heat integration and thus minimizing selectivity loss due to thermal cracking. The product quality is met; propylene is produced with a purity of 99.5 wt%.
Any components in LPG heavier than propane are removed in the first separation section. The resulting mixture is sent to the reactor, where it is mixed with a solid SOC stream. The gas-solid mixture is continuously passed through a monolith reactor, where the self-regenerating platinum catalyst is immobilized. After reaction the solid SOC stream is separated. The gas mixture contains mainly propylene, propane and water. After separation of the solids from the gas polymer grade propylene is produced in the second separation section. The SOC is continuously regenerated in a riser reactor, which is fed by air.
Only few waste products are formed and carbon dioxide emissions are reduced compared to Oleflex. Therefore it is expected that future environmental legislation like carbon dioxide emission reduction favour the Hipphox process.

The Fire & Explosion Index showed that all processing units have a moderate or intermediate degree of hazard. The conclusions from the Hazard and Operability study (HAZOP) are implemented in the process control and the risks are minimized.
The Hipphox plant lifetime is estimated at 20 years for 8000 operational hours per year (of available 8760 hours). This new plant will use a combined dehydrogenation and selective hydrogen combustion reactor. This new process is currently not applied in chemical industry.
Economic analysis shows a positive cash flow. Total investments are estimated at 36.4 M€, the payback time is 7.4 years and the discount cash flow rate of return (DCFRR) is 16.6%. An economical comparison is made with Oleflex and the economic potential of Hipphox is more promising.
Several creativity techniques have been used throughout the project in order to design an innovative process design. "Plant design Improvement by QUAlity Review" or "Piquar" was used to comply with the goals that were set in the beginning of the process. Piquar shows a

positive trend in the process development throughout the process design, finally resulting in this report.

A problem encountered in the design was the non-availability of data about the thermodynamics and kinetics of the SOC. It is therefore strongly recommended for future work to do a number of experiments with the SOC that determine the heat effect and entropy change of the SOC reactions and kinetics of the SOC reaction separately of and mixed with the dehydrogenation reaction.

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1 Introduction

At the University of Amsterdam scientists have recently developed a new solid oxygen carrier (SOC). This SOC can be applied in the combustion of hydrogen in a hydrocarbon mixture, because of the high selectivity to hydrogen. Furthermore the dehydrogenation (DH) of propane can be combined with the combustion of hydrogen (SHC) using this SOC. The objective of this project is to make a conceptual process design for the production of 250 kta propylene using this SOC. The problem statement is defined as follows:

How can propylene be produced by using the new solid oxygen carrier in the dehydrogenation of propane coupled with selective hydrogen combustion?

The principals of this project are dr. G. Rothenberg and dr. A.C. Dimian from the Chemical Engineering department at the University of Amsterdam. Their interest in the project is a feasibility study for the application of SOC in the dehydrogenation of propane.

Propylene is one of the principal light olefins. About 75% of the propylene produced in Western Europe is derived from steam crackers. The other 25% is derived from refinery and dehydrogenation of propane (~5%) [1]. As most of the propylene is produced as a by-product of gasoline and ethylene from petroleum refineries, the production of propylene is dependent on the demand for gasoline and ethylene. A supply/demand imbalance can occur. The dehydrogenation of propane is independent of the demand for gasoline and ethylene and can bring a solution to the supply/demand imbalance.
The main application of propylene is the production of polypropylene. Polymer grade propylene has a purity of 99.5 wt%. The growth in propylene production is therefore primarily driven by the industry demand for polypropylene. The growth rate of polypropylene is expected to be 5% per year [49], therefore the dehydrogenation of propane will become more important in the future.

The industrial dehydrogenation suffers from unfavourable thermodynamics. It is an equilibrium that favours the reactants and consumes a lot of energy.
A closed cycle can be envisaged where the energy is supplied by the combustion of the hydrogen by-product, also shifting the equilibrium to the desired side (figure 1.1).

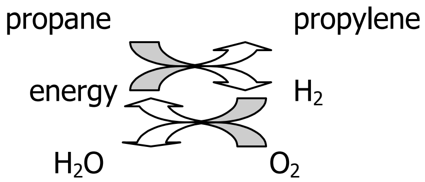


Figure 1.1 Cycle for oxidative dehydrogenation [9]

In practise no oxygen combustion is used because of explosion risks. Instead of oxygen a solid oxygen carrier can be used. In this project this is $Ce_{0.9}W_{0.1}O_y$. The selective oxidation of hydrogen with a SOC is an endothermic reaction. Therefore the energy will not be provided directly by the reaction of H_2 with oxygen, but indirectly during the regeneration of the SOC with oxygen. Hence the cycle diagram shown in figure 1.1 is not complete. A main goal in the design is to optimise the heat integration, which closes the cycle for oxidative dehydrogenation of figure 1.1.

The SOC offers major opportunities in the dehydrogenation of alkanes, due to the possibility to shift the equilibrium. If further research is done on the SOC composition, even better conversions can be achieved, which offers major advantages in the downstream processing. In the product recovery a propane/propylene-splitter (P/P-splitter) is inevitable, since not all propane can be converted and needs to be separated from the propylene product stream. With the objective of this process the costs can be greatly reduced, if the size of the P/P-splitter can be further reduced. Furthermore the SOC offers an opportunity to render interstage heaters obsolete, since the heat of regeneration can be integrated with the DH and SHC reaction.

The propylene price has fluctuated over the last 15 years (see figure 1.2). As the demand will be growing in the future, the assumption is made that the price of propylene will not decline much further. It is expected to fluctuate between 250 $/ton and 500 $/ton. The price of propylene in the design is therefore set at 375 $/ton. The price of propane is more or less stable and is taken at 190 $/ton.

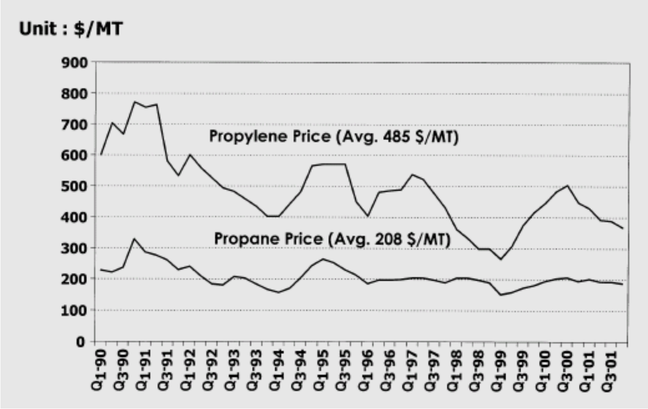


Figure 1.2 Price levels of propane and propylene [2]

In Western Europe 13 million tonnes of propylene have been produced in 2001 [1]. The production from dehydrogenation is 650 kta (5%) in 2001. With the objective of this process design (250 kta), this is a considerable contribution to the dehydrogenation production of propylene.

In industry, there are four commercial selective propane dehydrogenation processes [3]: Oleflex (UOP), Catofin (ABB Lummus), STAR (Philips) and FBD (Snamprogetti).
Oleflex uses adiabatic radial flow moving beds in series with intermediate heating in external furnaces. Catofin uses adiabatic fixed-bed reactors in parallel. They are alternately on and off stream for reaction and regeneration; the required reaction heat is stored in the catalyst bed. The STAR process uses fixed bed multi-tubes in fired furnaces; the reaction regeneration procedure is the same as the Catofin process. FBD is a staged fluidized bed with the catalyst continuously circulating from the bottom of the reactor to the top of the regenerator; the catalyst supplies the heat to the reactor.
The Oleflex process is taken as a reference process. It was first commercialized in 1990 in Thailand by UOP. Currently there are a number of UOP Oleflex units industrially applied.

Most of the plants are located in Asia and the Middle East. The units produce between 250 and 350 kta, the largest existing plant is located in Tarragonna, Spain, producing 350 kta [72]. New Oleflex units are being planned, for example a propane dehydrogenation plant is announced at Yanbu, Saudi Arabia for start-up in 2006, producing 420 kta [68]. The Oleflex unit can also produce isobutylene. In Appendix 1.1 a description of the Oleflex process is given.

Patent situation & competition's development

DH:

There are several patents on dehydrogenation catalysts; one example is given here. In Voskoboynikov et al. [4] promoted noble metal-alumina catalysts for dehydrogenation of alkanes and branched alkanes to alkenes are discussed, they consist of Group VIII noble metal component, 0.9-1.1 wt% of an alkali (earth) metal component, and a third component selected from Sn, Ge, Pb, In, Ga, and Tl, supported on θ-Al_2O_3.

The dehydrogenation process, or parts of the process, is also patented. For example in Cottrell [6] a method for improving the operation of a P/P-splitter is discussed.

SHC:

The selective hydrogen combustion can also be carried out with other metal oxides. With a bismuth oxide Bi_2O_3/SiO_2 a similar selectivity and conversion can be achieved than with using $Ce_{0.9}W_{0.1}O_y$ [44]. However this solid oxygen carrier deactivates quickly due to loss of dispersion on the support. Several other combinations of dopants with CeO_2 are tested [9], for example with Pb and Sn. These metal oxides however do not have a high selectivity.

DH+SHC:

There are also some patents on the catalytic dehydrogenation of alkanes to alkenes with simultaneous combustion of hydrogen, e.g. [7]. Schindler et al. [5] discuss a method and catalysts for the dehydrogenation of C2-30 hydrocarbons into alkenes with hydrogen combustion for the generation of reaction heat. However there are currently no commercial processes combining the DH and SHC process and the SHC is not as selective as with the use of the SOC.

Alternatives for removing hydrogen:

Concurrent research is being carried out to remove hydrogen in situ in a permeable ceramic reactor. Efforts are also directed at developing high temperature catalytic membrane reactors containing palladium and its alloys in the pores [73].

Data availability

A solid oxygen carrier with composition $Ce_{0.9}W_{0.1}O_y$ is not used in any commercial process. As a result the available data are limited. The mechanism of the SHC reaction and especially the oxygen exchange in the lattice is unknown. The thermodynamical calculations are therefore educated guesses. These are based on literature about thermodynamic measurements on non-stoichiometric CeO_{2-x} used as electrolyte in solid oxide fuel cells [47].

CeO_2 is often used for oxygen storage and also as a three-way catalyst. Therefore a lot of data is given for CO conversion in CO_2 with a CeO_2 based catalyst. The kinetic calculations are based on models of such a CeO_2 based catalyst. In experiments in literature an excess

amount of hydrogen is used with SOC limitation. In our reaction an excess of SOC is used with possible hydrogen limitation.
The Oleflex process will be taken as a reference mainly for a economic evaluation, since there is no detailed information available on reactor volumes, in and outgoing streams, amount of utilities and other design factors of the Oleflex process. A limited comparison of the two processes is made as well.

Solutions to key design problems

In the design of the process several design problems were encountered. The equilibrium conversion is low. A goal in the design is to shift this equilibrium to propylene by reacting the hydrogen formed with SOC. In the design it is chosen to combine the dehydrogenation and selective hydrogen combustion in one reactor to have an optimal shift in equilibrium.
As described above the dehydrogenation reaction is endothermic. Therefore heat integration by coupling the regeneration with the dehydrogenation reaction is desired and needs to be optimised. However the oxygen stream required for the regeneration of the SOC cannot be brought in contact with hydrogen, because of explosion risks. In the design it is chosen to use the SOC as heat carrier to supply the heat from the regeneration to the reaction unit. In this way of operation the regeneration is done separately and the risks of explosions are minimised.
To use the SOC as a heat carrier the solids have to be transported between the reaction and regeneration unit. This transport and the regeneration with air can be integrated by the use of a riser reactor. For an optimal heat integration and sufficient reaction rate, based on kinetic calculations, an excess of SOC is needed.
The DH reaction requires a catalyst to obtain an acceptable selectivity. This catalyst cannot withstand a high oxygen pressure, which is necessary for the regeneration of the SOC. Therefore the catalyst needs to be separated from the SOC. The solution in this design is to immobilize the catalyst by use of a monolith. In this way the regeneration of the catalyst requires a switch between the hydrocarbon stream and the catalyst regeneration environment. For a continuous production reactor units in parallel would be required.
The catalyst used, Pt-Sn-K/γAl_2O_3, can be regenerated with water [70]. Water can also be used as a diluent to prevent coke formation [17]. As water is formed in the reactor the coke formed during the reactor reacts with water in the reactor. Because the deactivation of the catalyst is minimal due to the presence of potassium, it is assumed that no regeneration is required during the continuous process [71]. The catalyst is therefore assumed to be self-regenerating.
Because water is formed in the SHC reaction and the recovery of propylene from light ends and propane is difficult, the effluent compression and product purification sections account for nearly 85% of total capital required [73]. In the optimalization of the separation section, energy efficiency is the primary goal. Due to the high cooling water requirements and reboiler duty for the P/P-splitter, a heat pump installation is implemented in the design.

In the design the emphasis lies on the new aspects of this process, compared to existing propylene production plants. The challenge of this design lies in the application of the SOC and thus in the design of the units for the reaction and regeneration. Existing units like water separation from a hydrocarbon stream are not designed in detail. The depropanizer and the column for the light ends removal are not fully optimised, since these columns are standard technology and also applied in the Oleflex process.

In the creativity sessions (see chapter 13) a brainstorm session led to a name for the new process: Hipphox, which stands for Heat Integrated Propylene Production with Hydrogen OXidation.

2 Process options and selection

In this chapter the process options and selection will be treated. First the input information for the process such as the stoichiometry, reactions, raw materials and other specifications will be explained. From these specifications process options are generated, one option is selected and explained in more detail.

2.1 Input information

All input information that is needed for the design is given in this paragraph. First the stoichiometry and reactions will be given, followed by information about the raw materials and catalysts. At last the constraints for temperature, pressure and oxygen concentration are given.

2.1.1 Stoichiometry and reactions

Propylene will be produced from propane, which is stoichiometricly presented in equation 2.1.

$$C_3H_8(g) \rightleftarrows C_3H_6(g) + H_2(g) \tag{2.1}$$

This reaction will be referred to as the dehydrogenation (DH) reaction. This is an endothermic reaction and it is equilibrium limited. The reaction only occurs at higher temperatures and therefore will compete with thermal cracking reactions, because these reactions also occur at higher temperatures. Thermal cracking consists of several parallel and sequential reactions, which will be analysed in detail in chapter 4. The main side reactions are propane cracking, coke formation (C_6) and C_4-formation as presented in equation 2.2 to 2.4.

$$C_3H_8(g) \rightleftarrows C_2H_4(g) + CH_4(g) \tag{2.2}$$

$$2C_3H_6(g) \rightleftarrows 0.5Coke(s) + 3CH_4(g) \tag{2.3}$$

$$C_3H_6(g) + C_2H_6(g) \rightleftarrows C_4H_8(g) + CH_4(g) \tag{2.4}$$

In order to improve the conversion of propane to propylene, the hydrogen is selectively burned with oxygen, present in the SOC. This is shown in equation 2.5.

$$5\,Ce_{0.9}W_{0.1}O_y(s) + H_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + H_2O(g) \tag{2.5}$$

This reaction is referred to as selective hydrogen combustion (SHC). In this reaction oxygen in the lattice reacts with hydrogen. Here y has a value of approximately 2. In the design only the amount of oxygen freed per mole SOC is important. Therefore the exact value of y is not known, but also not important. Only a small amount of oxygen in the SOC can react due to enthalpy and entropy change of the lattice. In the Hipphox design it is assumed that 10% of the oxygen in the lattice can react. This is explained in chapter 4.2.2, reaction kinetics. This corresponds to the value of 0.2, in reaction 2.5. The reaction is highly selective towards hydrogen (97%), the remaining 3 percent of the SOC burns hydrocarbons. The main side reactions are burning of propane and propylene (reactions 2.6 and 2.7) to form CO are:

$$3.5O_2(g) + C_3H_8(g) \rightleftarrows 3CO(g) + 4H_2O(g) \tag{2.6}$$

$$C_3H_6(g) + 3O_2(g) \rightleftarrows 3CO(g) + 3H_2O(g) \tag{2.7}$$

The SOC that has been developed by Rothenberg et al. [9], is a Ceriumoxide doped with Tungsten. The structure of the SOC is as follows: $Ce_{0.9}W_{0.1}O_y$ [42]. Because hydrogen reacts with oxygen present in the SOC-lattice the amount of oxygen atoms changes.

2.1.2 Raw materials

LPG

LPG will be used as a propane source. Since it is readily available, a constant supply of LPG is considered achievable. LPG is commercially available at 80-100 wt% propane, with light ends of 0-10 wt% and heavy ends of 0-10 wt%. The LPG in this design consists of 95 wt% propane, 3 wt% ethane and 2 wt% butane.

SOC [9, 42]

Cerium oxide and ceria-based mixed metal oxides ($Ce_xM_{1-x}O_y$) are known as versatile solid oxygen exchangers. The redox cycle $Ce^{3+} \leftrightarrow Ce^{4+} + e^-$ facilitates oxygen storage and release from its fluorite lattice. This makes them ideal for direct oxidation applications, such as automotive three-way catalysis [8] and hydrocarbon fuel cells [9, 10]. The selectivity of pure CeO_2 in hydrogen oxidation is poor, but the redox chemistry of doped cerium oxides is sensitive to crystal structure defects and may be tuned, in principle, by substituting some Ce-ions with ions of different size and/or charge. This enhances selectivity and stability of the cerium oxide. Cerium tungsten oxide ($Ce_{0.9}W_{0.1}O_y$) is discovered to be an excellent hydrogen oxidation catalyst, with practically zero coking levels, good thermal stability, and a selectivity of 97 mole%.

Catalyst

As there are different catalysts available for the dehydrogenation, the right catalyst has to be selected. This is done in paragraph 2.1.3. For the dehydrogenation a Pt-Sn-K on γ-AlO_3 catalyst is required. This catalyst is also used in the Oleflex process. More information about this catalyst can also be found in paragraph 2.1.3.

Air

In order to regenerate the SOC, regular air (21 vol% oxygen) will be used to reoxidize the SOC.

2.1.3 Catalyst for dehydrogenation

For the selective dehydrogenation of propane a number of catalysts can be used. A selection of the most commonly used catalysts is given below [10]. From this selection, one catalyst is chosen.

Platinum based catalysts

Industrial uses of Pt-based catalysts are:

1) Pt-Sn with alkali metals on alumina as support.

2) Pt-Sn doped with alkali elements on either $ZnAl_2O_4$ or $MgAl_2O_4$ as support.

In general, all platinum-based catalysts are characterized by the presence of tin, which has a promoting effect. It improves the activity, selectivity and stability of the catalyst.

$ZnAl_2O_4$ and $MgAl_2O_4$ are slightly basic or neutral and do not need any alkali promoters. In contrast, alumina-based catalysts need additional alkali promoters in order to minimize the acid properties of the system, responsible for lowering selectivity and catalyst life.

The main properties of the support are the following:

- Surface acidity
- Intrinsic stability during reaction and regeneration
- Stabilization of Pt dispersion during all the stages of catalyst treatments
- Chemical interaction with promoters
- Pore-size distribution

The main role of the support is to stabilize the dispersion of Pt, especially during regeneration (coke burn-off). Pt on silica sinters during this oxidation treatment, whereas little sintering occurs for Pt on alumina. No sintering at all occurs for Pt on $MgAl_2O_4$. The optimal alumina support has relatively large pores to avoid plugging by coke. Alkali metals are necessary to suppress the acidity of alumina; optimal promoters are Cs, Li and K. Potassium doping also prevents coke formation.

The platinum-based catalysts are proven to have uniform activity with time-on-stream and a constant yield in the dehydrogenation reaction, but they do not tolerate oxygenate compounds. They form PtO_2 solids that melt at high temperatures. Catalyst lifetime is 1-3 years for Pt-Sn on alumina, 1-2 years for Pt/Sn on $ZnAl_2O_4$ or $MgAl_2O_4$.

Chromium oxide based catalysts

Two types of chromium oxide catalysts are used in dehydrogenation of lower alkanes:

1) Cr_2O_3 supported on alumina, doped with alkali metal.
2) Cr_2O_3 supported on ZrO_2. This catalyst has been investigated for its lower acidity and higher thermal stability with respect to alumina.

The formation of solid solutions of chromia and alumina is responsible for irreversible deactivation of the catalyst. Alkali metals have been indicated as promoters of activity and selectivity, but only Cs, Rb and K are effective. Potassium doping prevents coke formation on the catalyst. This has attributed to the fact that the larger alkali cations stabilize the structure of alumina. Chromium oxide based catalysts are reactivated by treatment with air, which improves the dispersion of Cr_2O_3 crystallites and coke is combusted off the catalyst. The chromium oxide based catalysts are proven to have a high thermal stability, attrition and breakage resistance, and they have a high tolerance to poisons such as heavy metals. Catalyst lifetime is 1-2 years.

A Pt-Sn-K on alumina catalyst will be used in Hipphox, the reasoning of this is as follows. The performance of the catalysts is more or less the same: all are capable of dehydrogenation of propane with high selectivity; they are applicable in the same temperature and pressure range and catalyst life is comparable [3, 10]. All catalysts can withstand different reactor types, like a fluid bed, fixed bed or monolith.

The Pt based catalysts are generally more expensive, and they do not tolerate high oxygen concentrations. The chromium oxide based catalysts are more harmful to nature, and the formation of solid solutions of chromia and alumina on the reactor walls causes much problems. Because the dehydrogenation catalyst and the SOC are used in the same reactor

(see chapter 2.3), the formation of these solids on the SOC can cause severe damage to the SOC. These two disadvantages of the chromium oxide catalyst are considered to be less easy to overcome and therefore a Pt catalyst will be used.
Since there is no large difference in performance in the two types of Pt catalysts, the Pt-Sn-K on alumina catalyst, which is also used in the Oleflex process, will be used.

Reactivation

The Pt catalyst deactivates due to coke formation on the catalyst. In the regeneration section the formed coke can be burned off. To prevent formation of PtO_2 a low partial oxygen pressure is necessary. For reactivation the Pt catalyst is subjected continuously or batchwise to different in situ treatments with gases such as oxygen and chlorine. Treatment with oxygen is required for burning off the coke. It must be carried out at relative low temperature, approximately 720 K, and with low oxygen pressure concentration to minimize overheating of the catalyst and sintering. Treatment with chlorine is necessary to transform the surface oxides of Pt and Sn into chlorides, which help the dispersion. This however also creates acid sites, which are coke precursors. Therefore steam treatment is necessary to eliminate surface chlorine.

In the Hipphox design the reactivation is not taken into account. The catalyst is assumed to be self-regenerating [71], because of the following reasons:

- Presence of potassium in catalyst
- Short residence time
- Steam as gasifier for coke
- Steam as diluent to prevent coke formation

The potassium is added primarily to neutralize the acid sites of alumina and thereby to inhibit the cracking reaction of hydrocarbons on the support. Improved conversions are observed for catalysts containing amounts of potassium in excess of that required to neutralize the support. In addition, these catalysts exhibited lower extents of coke formation [56].
The coke formation reaction has a lower reaction rate compared to the DH reaction; this is explained in chapter 4. Since the residence time in the reactor is short, see chapter 4.2.7, minimal coke formation occurs.
In the SHC reaction steam is formed. It has been suggested that the Pt catalyst can be regenerated with steam [70]. In this reaction the coke is reacted in several steam-reforming reactions.
Steam can also be used as a diluent to prevent coke formation [17]. In the SHC reaction steam is formed, which can prevent coke formation on the catalyst during the DH reaction.

During the selection of process options, the fact that the Pt catalyst is self-regenerating was not yet known. Regeneration of the Pt catalyst has therefore been taken into account in the selection of a process option. The paragraph on process options in this chapter, 2.3, is not updated with this new information, since the selection was already made in an earlier stage of the design. The influence this self-regeneration of the Pt catalyst has on the selection procedure is discussed in paragraph 2.3 as well.

2.1.4 Constraints

Temperature constraints

Due to an increased rate of thermal cracking at high temperatures (e.g. > 800°C) the DH reaction is favoured at lower temperatures. This also improves the catalyst selectivity. However, since the DH reaction is highly endothermic, the equilibrium is favoured by high temperatures. Therefore a minimum temperature of approximately 500°C is assumed, as explained in chapter 4.2.7.

The regeneration of the SOC is an exothermic reaction and is favoured by low temperatures. The SOC can be reoxidated at a wide temperature range, from room temperature up to 800°C. In order to obtain optimal heat integration, the regeneration should be carried out at a higher temperature than the DH reaction.

Pressure constraints

Since the thermodynamic equilibrium for propylene production favours low pressure, the reactor pressure should be as low as economically possible. But due to pumping requirements in the downstream processing, the pressure cannot be "too low". Also for safety reasons the pressure should be higher than atmospheric pressure. An additional advantage is the lower volumetric flow rate and smaller equipment.

The regeneration of the SOC is preferably carried out at high oxygen pressure.

Oxygen constraints

The reactor operates at a temperature above the auto ignition temperature of several components. Therefore no molecular oxygen is allowed to enter the reactor.

2.2 Batch versus continuous

The decision batch versus continuous is based on the following criteria according to Douglas [24]: production rate, market forces and scale up problems. Because the production of propylene is $2.8*10^8$ kg/yr, which typically can be seen as bulk production, a continuous process would be preferable. The amount produced is much more than the guideline of $10*10^6$ lb/yr ($4.5*10^6$ kg/yr). On the plant mainly propylene is produced, therefore a continuous process is preferred as well. The market for propylene is constant during the year, therefore there are no large seasonal influences. The production can be the same during the different seasons.

There can be some scale up problems, because of the use of two types of solids: Pt catalyst and the SOC. Also some problems with safety aspects can occur.

The decision is made to design a continuous process.

2.3 Process options and selection

In order to make a well-founded selection between possible process options, some design bases have been formulated. Economical aspects are taken into account when formulating decision criteria. Also product quality, safety and sustainability played an important role.

The assumption that the Pt catalyst is self-regenerating is not updated in the process options, since the selection was already made in an earlier stage of the design. The influence this decision has on the process selection is reviewed at the end of this paragraph.

The combination of catalytic dehydrogenation (DH) and selective hydrogen combustion (SHC) can be done in several ways. However due to safety reasons the oxygen rich regeneration of catalyst and SOC must be separated from the hydrocarbon mixture to minimize explosion risk. This separation can be done in time and/or in space. Separation in time means that the regeneration is done semi-batch-wise, with a switch in hydrocarbon to oxygen-rich stream. Separation in space means a continuous regeneration and reaction, which means the solids are regenerated in the regeneration section, apart from the reaction section. This leads to four options, drafted using the following operating options:

- DH / SHC in series, alternating DH and SHC reactors, and
- DH / SHC combination in one reactor.

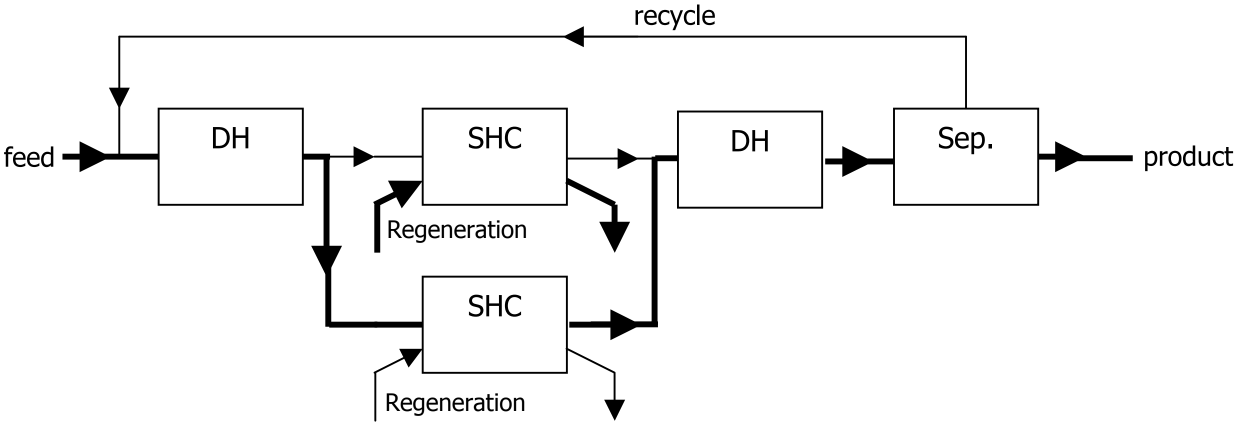
Together with:

- Continuous regeneration of the SOC, and
- Semi batch regeneration of the SOC.

The reasoning behind these operating options is that the regeneration of the SOC will provide heat, and the reaction of the SOC with hydrogen requires heat. The regeneration of the SOC should therefore be optimised with regard to heat exchange. Batchwise regeneration of the SOC has the advantage that the heat of the regeneration is kept inside the reactor. However the disadvantage is that an extra reactor unit is necessary for continuous production. In a continuous regeneration of the SOC the heat of the regeneration is carried by the SOC. The Pt catalyst has to be regenerated much less often than the SOC, therefore a semi batch regeneration of the Pt catalyst is not considered to be a good alternative, since it would require an extra reactor for a continuous operation to be possible, and the heat effect is much less. Only when the two reactions are combined, and the SOC and Pt catalyst could be regenerated at the same time, a semi batch regeneration of the Pt catalyst is considered a nice alternative.

Option 1

The first option is the DH and SHC in series, with a batch-wise regeneration of the SOC integrated in the SHC section. This means that one has to switch streams from the feed with the hydrocarbons and hydrogen to a oxygen-rich stream, which regenerates the SOC. This also implicates that a nitrogen purge is required to remove any hydrocarbons left, before the SOC is regenerated with oxygen. In figure 2.1 option 1 is drawn schematically. Three units are placed in series, first DH then SHC, followed by DH. Because the conversion will be low with just DH and SHC in series, another DH is required to make a good performance comparison with the other options.



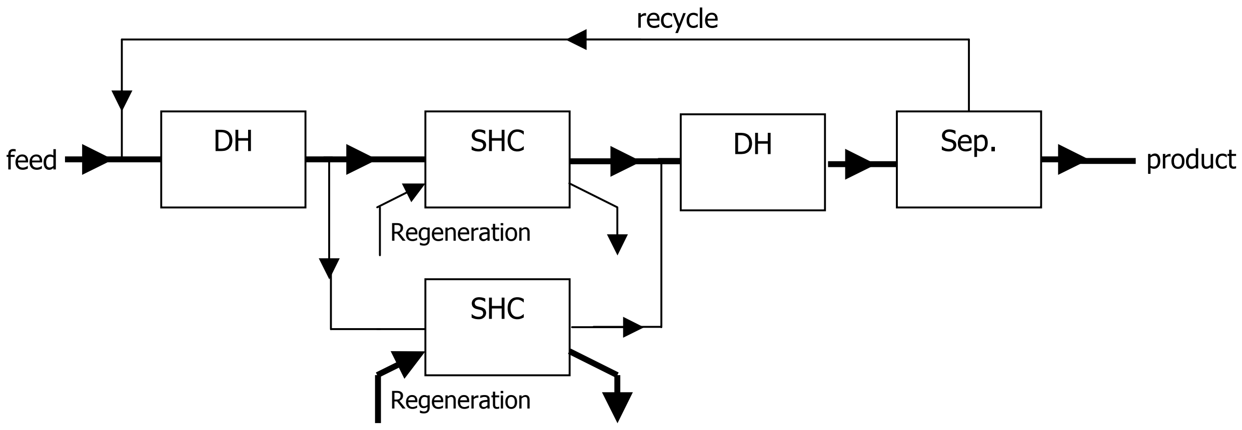


Figure 2.1 Schematic view of option 1: DH and SHC in series with semi-batch regeneration of the SOC and continuous regeneration of the DH catalyst, Sep. = separation.

Option 2

In the second option the DH and SHC will occur in one section, with semi-batchwise regeneration. In this section also the regeneration will take place. Here one also has to switch streams. If simultaneous regeneration of the SOC and the Pt catalyst can be assumed possible, this is a feasible process option. In figure 2.2 option 2 is drawn schematically.

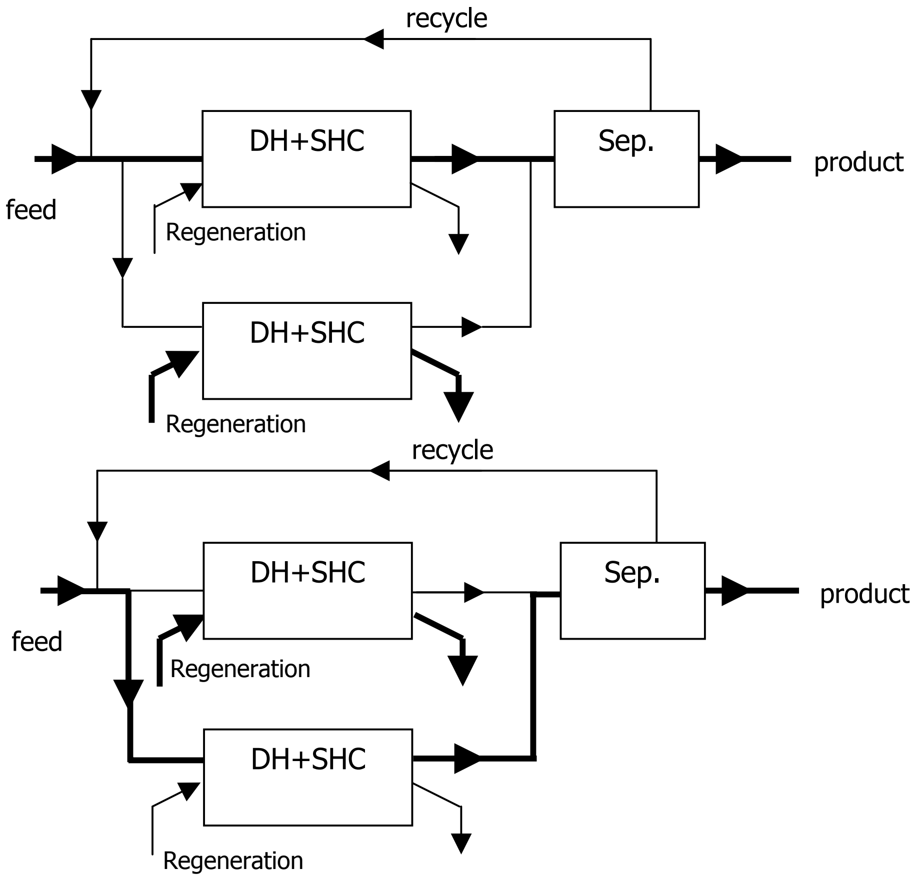


Figure 2.2 Schematic view of option 2: DH and SHC in one reactor with semi-batch regeneration of the DH catalyst and SOC. Sep. = separation.

Option 3

In the third option the DH and SHC will occur in one section, as in the second option. The main difference is that the regeneration in the third option will not occur in the same section but will be done continuously in a regeneration section. In figure 2.3 option 3 is drawn schematically. Since the DH catalyst and the SOC are regenerated in another section, it is also possible to separate them and regenerate them in two different regeneration sections.

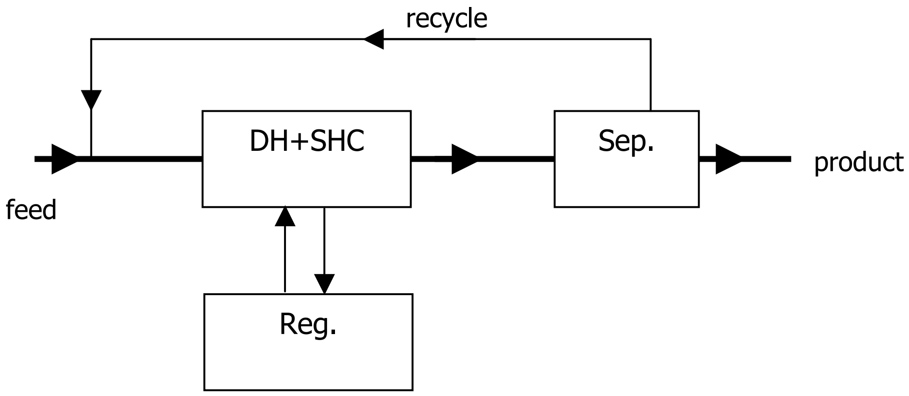


Figure 2.3 Schematic view of option 3: DH and SHC in one reactor with continuous regeneration of the DH catalyst and SOC. Reg. = Regeneration, Sep. = separation.

Option 4

In the fourth option the DH and SHC are in series again, and the regeneration of the SOC and DH catalyst will occur continuously in separate regeneration sections. In figure 2.4 option 4 is drawn schematically.

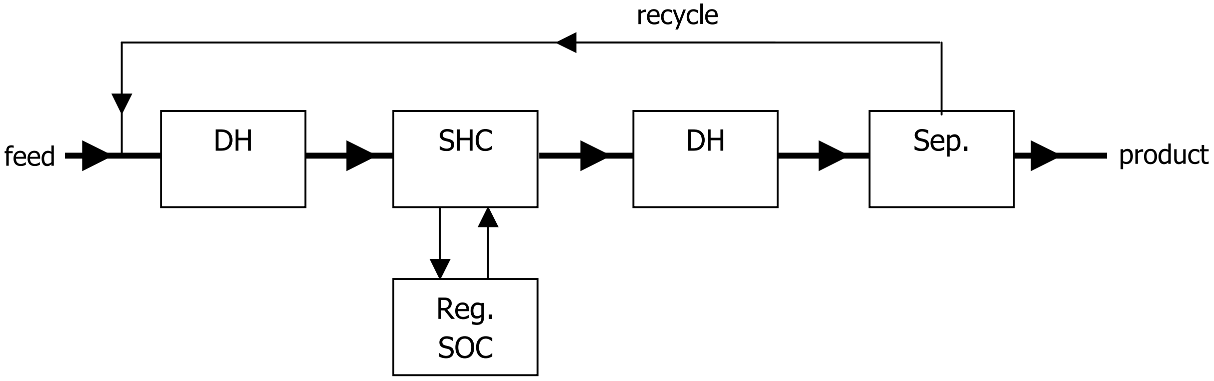


Figure 2.4 Schematic view of option 4: DH and SHC in series with continuous regeneration of the SOC. Reg. = Regeneration, Sep. = separation.

Of course there are a few variations of these options, which lead to new options. But first a decision must be made between the operating options mentioned above.

A number of decision criteria on which the process will be evaluated are obtained from a brainwriting session (see chapter 13.1). These criteria are based on the design bases. A list can be found in table 2.1. In a group discussion the criteria are evaluated for each process option. This is done by assigning a value to each process option ranging from –2 to 2 for each criterion, with 2 being the best score and –2 the worst for the specific criterion. Each criterion is coupled to one or two Piquar criteria, to allow an option that will satisfy Piquar design criteria. The Piquar method is described in more detail in chapter 13.4. A list of the Piquar criteria is shown in table 2.2, together with the weighing factors. The values assigned for each criterion to each process option are then multiplied by the weighing factors of the Piquar criteria to which they are coupled. So every criterion has its own weighing factor obtained from the Piquar criteria.

All criteria are explained in more detail in Appendix 2.1, in which also the reasoning behind the scores is discussed.

Table 2.1 Evaluation of process options

#	**Criterion**	**Piquar criteria assigned**	**Option 1**	**Option 2**	**Option 3**	**Option 4**
1	Energy integration reaction - regeneration	3	0	2	2	0
2	Conversion per reactor volume	2	0	1	1	0
3	Amount of equipment needed	2	0	1	1	0
4	Regeneration conditions optimal	3 5	1	-2	0	1
5	Dead time	1 2	-1	-1	1	1
6	Amount of N2 needed	2 5	-1	-2	0	1
7	Intrinsically safe	4 10	-1	-1	0	0
8	Proven technology (KRO factor)	4 10	1	-1	-1	1
9	Integration with existing plants	10	1	-1	-1	1
10	Coke formation on soc	6 5	0	-1	-1	0
11	CO formation by regeneration which reduces SOC	6 5	0	-2	0	0
12	Comply with (future) environmental legislation	6 9	0	0	0	0
13	Safety for operators in plant and surrounding	4 10	0	0	0	0
14	Controllability of the temperature	3 4	0	0	1	1
15	Controllability of the mass flows	1 4	1	0	0	1
16	Optimal conditions for DH and SHC possible	3 5	1	0	0	1
17	Scale-up easy	2	1	-1	-1	1
18	Control system/exchangeable streams	2 7	-2	-2	0	0
19	Separation solid gas necessary between reactor and regenerator	5	0	0	-1	-1
20	Possibility of regenerating Pt cat. + SOC simultaneously	5 2	0	1	1	0
21	SOC regeneration efficiency	5	0	-1	0	0
22	Process must be robust	2 7	0	1	2	0
23	Equilibrium composition	1 2	0	2	2	0
24	Veronica factor	8	0	1	2	0
	Final score multiplied with weighing factor		**-0.28**	**-0.70**	**2.59**	**1.99**

Table 2.2 Piquar criteria and weighing factor (WF), more information: see Chapter 13.3

#	**Piquar criterion**	**WF**
1	Product quality and quantity	0.319
2	Economically feasible	0.189
3	Energy efficient	0.099
4	Intrinsically safe	0.094
5	Efficient use of raw materials	0.088
6	Waste management	0.048
7	Process must be robust	0.045
8	Team spirit with an open mind	0.043
9	Comply with (future) environmental legislation	0.038
10	Safety for operators in plant and surrounding	0.037

From table 2.1 it can be concluded that option 3 is the most promising process scheme. In option 3 the heat of the regeneration of the SOC can directly be used by the DH and SHC reaction, because the SOC is continuously regenerated. Because the SHC and DH reaction are carried out in one reactor, the equilibrium conversion per reactor volume will be higher than the conversion reached by DH and SHC in series. This is also applicable for option 2, however in this option the regeneration cannot be performed at optimal conditions, because the regeneration of the SOC has to be done under low oxygen pressure to prevent PtO_2 forming on the Pt catalyst. The regeneration of the SOC needs a high partial oxygen pressure. Regeneration of the SOC with low oxygen pressure would require too much time for complete SOC regeneration because of the large amount of SOC needed. Fortunately in option 3 the regeneration section is separated from the reactor section and therefore can take place at optimal conditions.

The main disadvantage of option 1 is the batch-wise regeneration of the SOC. This means reactors in parallel are required to obtain a continuous production. Option 4 is then a better option. For option 4 thermodynamic calculations (see chapter 4.1.3) are made to compare the equilibrium conversion with option 3. From these calculations it shows that the equilibrium conversion for option 3 is higher than for option 4.

As the production rate of propylene is very high, it is very desirable to operate the process continuously. That is why in all the options the structure is drawn using parallel reaction sections in case of semi-batch operation. This is also a reason why option 3 and 4 are the most promising ones.

Influence of self-regenerating catalyst on the process selection

The main advantage of the self-regenerating catalyst is the possibility to immobilize the catalyst, which means in option 3 less solid transport is required. This does not influence the process selection since all options would still be feasible.

2.4 Block scheme of selected option

Now that a process option is selected, the input-output structure of the flow sheet can be generated, and from this structure a block scheme for option 3 can be drawn.

2.4.1 Input-output structure of selected option

The LPG feed consists of propane, ethane and butane. In the reaction section, the main side reactions are thermal cracking. Since butane is a higher alkane than propane, the butane reacts as well in the thermal cracking and coke formation reactions. This leads to additional by-products and a more complex separation system. Butane is therefore not inert, and since it is present in significant quantities. Therefore the decision is made to purify the LPG feed to remove the butane.

The primary product is of course propylene. The reaction to form propylene from propane is an equilibrium reaction; therefore the unconverted propane is recycled to the reaction system. The light by-products have to be separated from the primary product propylene and therefore they cannot be recycled with the reactant propane. This means no purge is necessary, but for the separation of the light ends expensive processing operations are required, since high pressure and refrigeration is needed. Since hydrogen is a valuable by-product, the separation of hydrogen from the light ends should be considered. A process alternative could be the use of membrane separation. The by-products from the process, light ends and C_4^+ have fuel value and are therefore not considered as waste.

The SOC reacts with hydrogen to form water and SpentSOC. The SpentSOC is recycled after regeneration to the reaction system. Water is considered a waste and needs to be removed and sent to waste water treatment. The air used for the regeneration of the SOC will not be recovered, since it is not valuable. In order to ensure a high enough conversion of the regeneration of the SOC, an excess of air is used; therefore the exhaust air will still contain some oxygen.

This leads to the input-output structure for the Hipphox process, defined below:

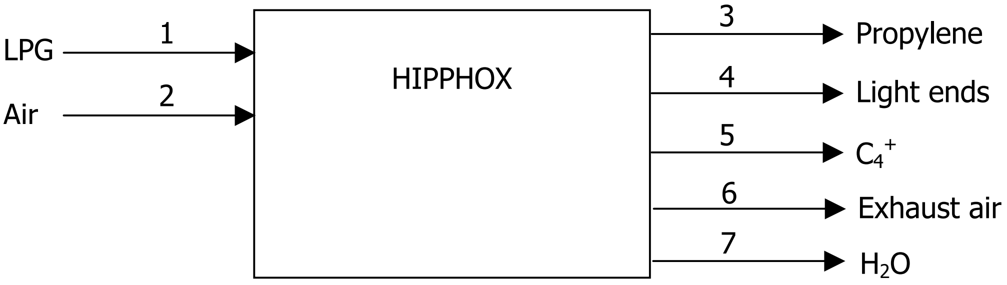


Figure 2.5 Input-output structure of the Hipphox process

This input-output structure is the same as in chapter 3.2.2, in which it is defined by the battery limits.

2.4.2 Block scheme of selected option

From this input-output structure the block scheme for option 3 is made, separating the 'black box' into a reaction section, two separation sections and a regeneration section, see Appendix 3.1. The LPG feed purification is represented in the first separation section. The second separation section is the recovery of the product. In chapter 5 the tasks represented in the block scheme will be translated into unit operations and equipment.

3 Basis of Design (BOD)

In this chapter all key data for the design are given and provided with background information. First a short description of the design will be given. Next the process definition will be given, followed by the basic assumptions like plant capacity, location, battery limits and the definition of in- and outgoing streams. Finally the economic margin will be treated and compared with the cash flow calculated in the economic evaluation (chapter 11).

3.1 Description of the design

In chapter 1 and 2 the Hipphox process is introduced. With this new process propylene can be produced by the dehydrogenation of propane (DH) combined with the selective hydrogen combustion (SHC). Liquefied petroleum gas (LPG) will be used to produce 250 kta polymer grade propylene. The process will be compared with a commercially available process, the Oleflex process.

The major difference of the Hipphox process compared to the Oleflex process is the use of a solid oxygen carrier (SOC). This SOC provides the oxygen in order to selectively combust the hydrogen, which will shift the equilibrium of the DH reaction towards propylene. Furthermore the regeneration of the spent SOC with air will provide energy that can be used in the DH and SHC reaction. Concluding the use of this SOC has two big advantages over the Oleflex process:

- Higher conversion per pass
- Energy integration

The challenge of this design is the application of the SOC to integrate the heat and to increase the conversion. The SOC is used as a heat carrier to transport the heat produced during the regeneration to the reactor. Thus the units for the reaction section and the regeneration section are fully designed. Existing units like the depropanizer and the P/P-splitter are well-known columns. For the dehydrogenation of the propane a Pt catalyst is used that does not need to be regenerated. The Pt catalyst is therefore immobilized in a monolith. Combining the DH and SHC reaction in one reactor, leads to a conversion of 57% of propane per pass compared to a conversion of 29% per pass in the Oleflex process.

3.2 Process Definition

In this paragraph a summary of chapter 2 will be given. The process concept chosen will be described, followed by the block schemes. Also the thermodynamic properties will be described, which is a summary of chapter 4. Finally the list of pure component properties is given.

3.2.1 Process concept chosen

In chapter 2 all the pros and cons were evaluated for 4 options. Option 3 is the most promising one. This means that the DH and SHC will be done simultaneously. One reactor is needed for reaction and one separate regeneration reactor is needed. Both sections will operate continuously. A platinum catalyst will be immobilized in a reactor and the solid SOC stream and a gaseous propane stream will flow through the reactor. In the reactor the propane will be converted to propylene and the formed hydrogen will be combusted to water. Since the SOC is used as a reactant, the SOC is regenerated with air.

3.2.2 Block schemes

In order to develop the block scheme first input-output diagrams are made, starting with the Oleflex process.

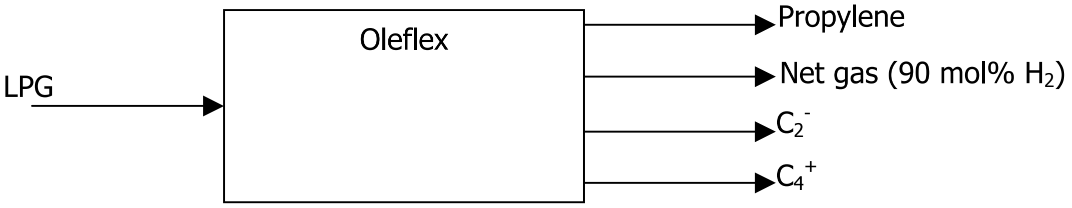


Figure 3.1 Input-output structure of the Oleflex process

This input-output diagram is based on the battery limits defined in chapter 3.3.3. The input-output structure for the Hipphox process is based on the input-output structure for the Oleflex process. There are two differences. An air stream is needed for the regeneration of the SOC and water is produced. Therefore the input-output structure for the Hipphox process looks as follows:

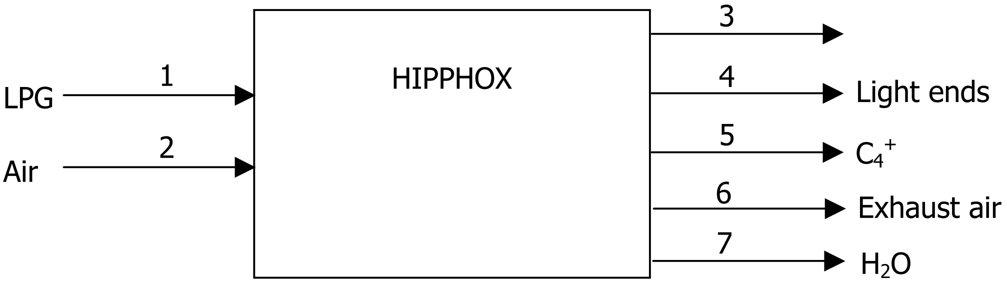


Figure 3.2 Input-output structure of the Hipphox process

From this input-output structure the block scheme was made, separating the 'black box' into a reaction section, two separation sections and a regeneration section. The LPG feed stream needs purification, as the C_4^+ components are not wanted in the reaction section, since C_4^+ components increase coke formation. This is represented in the first separation section. The second separation section is the recovery of the product. The mass balances are treated in chapter 5 and chapter 7. The numbers in the block scheme are calculated using simple mass balances.

The next step is to create a structure in more detail. Reactor and separation sections are developed. Since the conversion is estimated at 57% a propane recycle structure will be required. The simple process flow scheme (PFS) is developed as shown in figure 3.3.

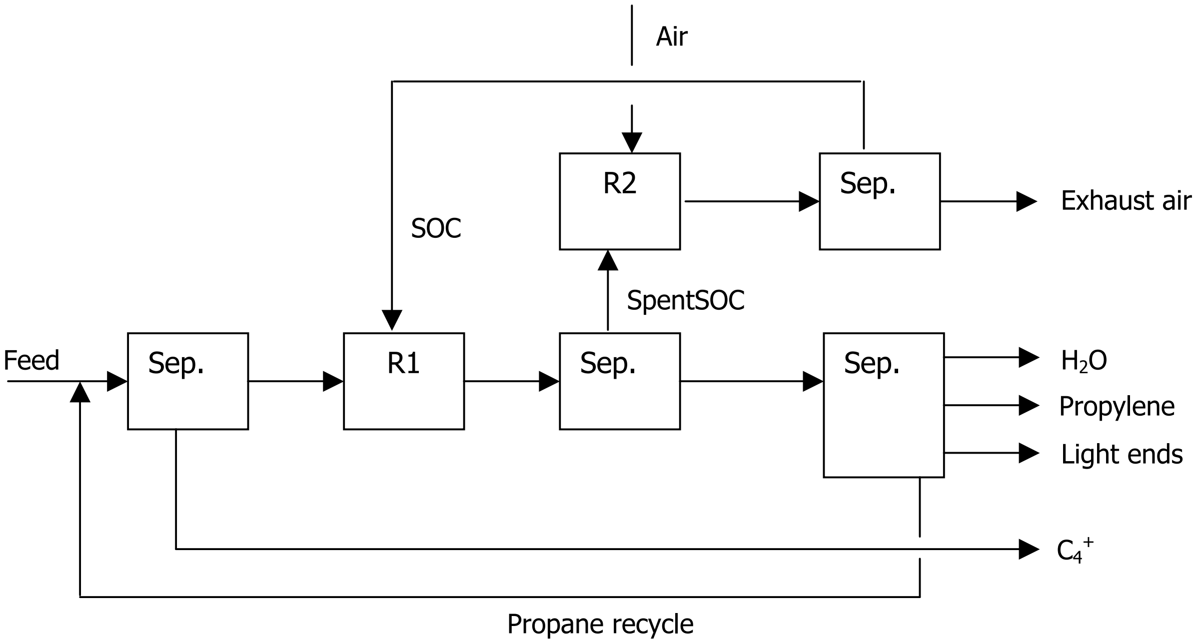


Figure 3.3 Simple block scheme of the Hipphox process; R1 and R2 are reaction systems, Sep. are separation systems.

After defining a block scheme the pressure and temperature of reaction system were determined. For the reactor a temperature of 873 K (600 ^{0}C) and a pressure not higher than 2 bara were estimated. Using mass balances all mass streams were determined as shown in Appendix 3.1 and figure 3.4.

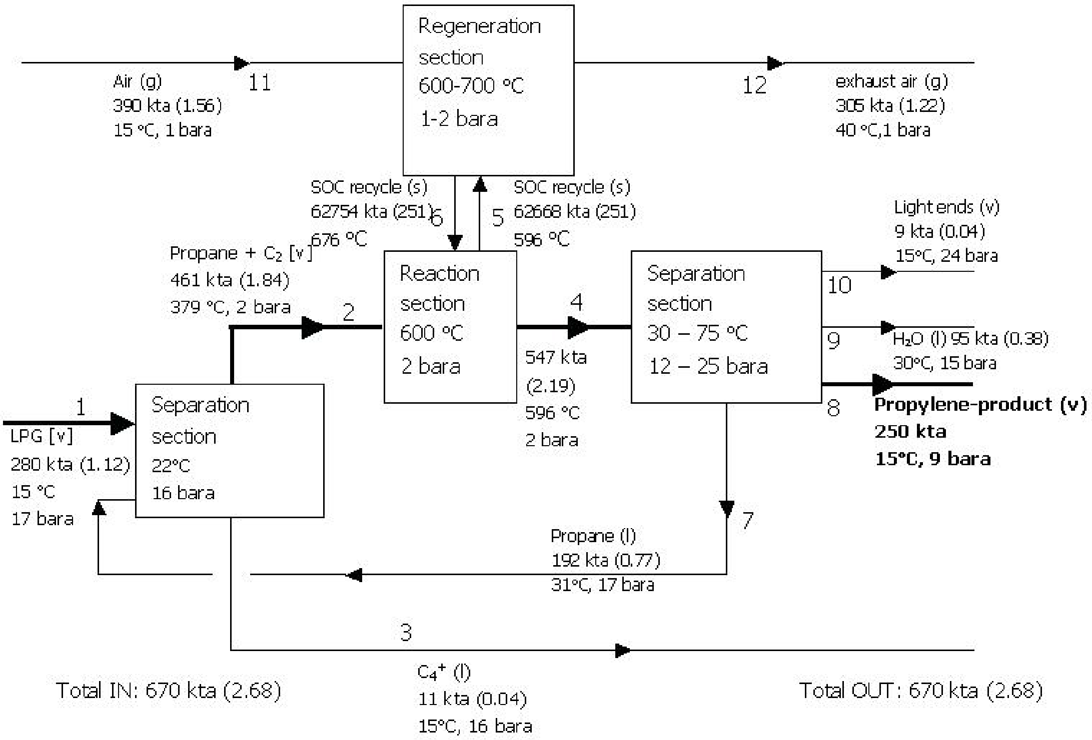


Figure 3.4 Block scheme of the Hipphox process

As shown in figure 3.4 the block scheme consists of 4 main sections: A first separation section, a reactor section, a regeneration section and finally a second separation section. In

the first separation section all components heavier than propane are separated. After the C_4^+ (stream 3) have been removed, the stream is expanded from 16 bara to 2 bara and sequentially heated to 379 degrees Celsius (stream 2). At these conditions the propane stream enters the reactor together with a SOC stream (stream 6). In the reactor 57% of available propane will be converted to propylene at high selectivity (± 99% selective). The total gas mass flow is increased due to oxygen transfer from the solid SOC stream to the gaseous hydrocarbon stream (stream 4) to form water. The spent SOC is recycled to the regeneration section. After reaction the hydrocarbon stream is immediately cooled to prevent further product loss (through thermal cracking).
In order to allow efficient separation the hydrocarbons are pressurized up to 12 bara, and the water is removed by flash and adsorption (stream 9). The light ends are removed by means of cryogenic distillation at 25 bara (stream 10). A final distillation column removes the propylene (stream 8) and recycles the liquid propane back to the initial separation section (stream 7). The total mass balances are checked and obeyed. For more detailed design review chapter 5 and chapter 8. A detailed process flow scheme (PFS) is presented in Appendix 5.3.

One important factor of basis reactor and regenerator design is the amount of SOC fed to reactor and regenerator. If the SOC and air are fed to the regenerator stoichiometricly an adiabatic temperature change of 921 K is expected. In order to keep the SOC temperatures after regeneration within bounds, an excess of SOC is used as a heat carrier material. The amount of SOC fed to the reactor and regenerator is set to an acceptable value to allow good reaction kinetics and allow proper heat integration. This value is estimated by use of a Matlab simulation, as explained in chapter 4.

3.2.3 Thermodynamic properties

Propane will be dehydrogenated to propylene. This process is a gas phase reaction. The reactions of interest for the process are:

Dehydrogenation reaction (DH):

$$C_3H_8(g) \rightleftarrows C_3H_6(g) + H_2(g) \qquad (3.1)$$

Selective Hydrogen Combustion (SHC) reaction:

$$5\,Ce_{0.9}W_{0.1}O_y(s) + H_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + H_2O(g) \qquad (3.2)$$

where y is approximately 2.

Both reactions are endothermic. The enthalpy change over both reactions is given in table 3.1.

Table 3.1 Reaction enthalpy changes

Reaction	ΔH [kJ/mole]
3.1	+129
3.2	+108

Enthalpy and entropy estimates have led to the calculation of an equilibrium constant. Reaction 3.1 is very dependent on pressure. Reaction 3.2 is not a function of pressure since the total amount of molecules remains constant. Equilibrium constants have been derived as function of pressure and temperature, as shown in equation 3.3 and 3.4.

$$K_{DH} = \frac{y_{C_3H_6} y_{H_2} \frac{p}{p^0}}{y_{C_3H_8}} \tag{3.3}$$

$$K_{SHC} = \frac{y_{H_2O}}{y_{H_2}} \tag{3.4}$$

At the chosen reactor temperature and pressure (873 K and 2 bara) the equilibrium constants are equal to 0.148 for the DH and 7.53 for the SHC.
Several combinations of DH and SHC steps are analyzed for dehydrogenation performance. Mixed DH and SHC in a single reactor proved to obtain the highest conversion, 62% at equilibrium.

Unfortunately both DH and SHC reactions are not completely selective. At reactor temperature hydrocarbons are thermally cracked to olefins, lower alkanes and alkenes. These cracking reactions have a lower reaction rate compared to the catalytic dehydrogenation. Therefore a small residence time will be required (approximately 3.65 second). Furthermore the SHC reaction is about 97% selective. Besides hydrogen also propane and propylene are assumed to be combusted with SOC. These side reactions are also endothermic.

Fortunately the SOC can be regenerated after use. The SOC can easily be regenerated with plain air, resulting in an exothermal reaction as shown in equation 3.5.

$$5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + 0.5O_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_y(s) \tag{3.5}$$

The enthalpy change of this reaction equals –355 kJ per 0.5 mole oxygen. The net effect of dehydrogenation, hydrogen combustion and SOC regeneration yields –188 kJ per mole converted hydrogen. From literature kinetic equations about the dehydrogenation and selective hydrogen combustion have been found. Although actual literature on doped cerium-tungsten oxides are not available, an estimate for reaction kinetics is obtained. Fortunately both dehydrogenation and selective combustion are relatively fast reaction. Also the regeneration of the SOC is assumed to be almost instant.
This entire system of rate equations has been modelled in Matlab, in order to predict a conversion and to estimate a reactor volume. A conversion of 57% can be achieved in a 51 m^3 (gas volume) reactor.

3.2.4 Pure component properties

All pure component properties can be found in Appendix 3.2.

3.3 Basic Assumptions

In this paragraph the basic assumptions are treated. The plant capacity, location, battery limit and the economic margin will be treated.

3.3.1 Plant capacity

The production rate of propylene is 250 kilotons per annum (kta). The propylene product has a purity of 99.5 wt%, which can be used in the polymerization to form polypropylene.
The plant is assumed to be operating 8000 hours per annum. The economical plant life is 20 years because of the stable market for propylene and a sustainable design.

Feedstocks
Liquefied Petroleum Gas (LPG) will be used as the main feed stream, as this is also used in the Oleflex process. For regeneration of the SOC oxygen is needed. This oxygen is provided from regular air.

Outgoing streams
The main outgoing stream is the product stream of 250 kta, with 99.5 wt% propylene. The other main outgoing stream is water. Hydrogen will end up in the light ends stream. The heavy ends (C_4^+) are separated in the first separation section. Air that is used for the regeneration will leave the plant with a little amount of oxygen.

3.3.2 Location

Propylene is mainly produced as a by-product of processes in the petrochemical industry like steam cracking and Fluid Catalytic Cracking. For locations, which are short of propylene, propylene production via catalytic dehydrogenation of propane can be a viable alternative. In Thailand for example, no naphtha-based steam cracker and only a small catalytic cracker were present and the discovery of natural gas in the Gulf of Thailand provided the country with ethane and propane. While the demand for ethylene and propylene was rapidly increasing, a gas-based olefin plant was a nice alternative. The first Oleflex plant was therefore built to satisfy the demand for propylene.

For the Hipphox process an environment with less refinery facilities is preferable. In such an environment not enough propylene is produced and the Hipphox process can fulfil the demand of propylene. The reactor inlet stream consists mainly of propane that can be distilled from the LPG stream. Therefore still an LPG feed stream is required for the process. Because LPG is easily transported and available at a large scale, LPG is not a constraint for the plant location. The most important factor for the decision is the amount of propylene produced as a by-product from refineries.

To implement safety in the Hipphox process the European legislation rules for acceptable risk are used. The plant will be built in an environment so that there will be no direct risk to the people in the surroundings.

Summarizing, the requirements for location are:

- A relatively high demand for propylene. This means that there is not a large production of propylene by steam cracking and petroleum refining.
- LPG available or natural gas
- No strict legislative constraints
- Industrial area available, employees etc.

3.3.3 Battery limits

UOP's Oleflex process can be divided in three different sections, namely the reaction section, catalyst regeneration and product recovery. These sections are all within the battery limits. Also all separation units for feed, between units and for product recovery are within the battery limits. The LPG recovery from refinery, H_2S removal from LPG feed, upgrading the bottom stream of depropanizer (C_4^+) and auxiliary buildings are considered to be outside the battery limits.

The battery limits for the Hipphox process are chosen almost the same as for the Oleflex process in order to compare both processes. This includes reactor and separation systems. As feed for the process LPG is chosen. Additional also air is fed into the process to regenerate the SOC. The outgoing streams are propylene, water, spent air, light ends and C_4^+.
Also hydrogen sulfide removal from LPG, auxiliary buildings (like power supply station) and the recovery of LPG is considered outside the battery limit. Also the wastewater treatment section for the produced water is outside the battery limit.
In table 3.2 a summary of the in- and outside battery limits is given.

Table 3.2 Summary of in- and outside battery limits for Hipphox

Inside battery limits	**Outside battery limits**	**Streams crossing boundary**
Reaction section	LPG recovery	LPG
SOC regeneration	H_2S removal from LPG	Air (oxygen)
Product recovery	Upgrading bottom stream of depropanizer	Propylene (product stream)
Separation units	Auxiliary buildings	Water
Pumps, compressors, heat exchangers, valves, etc.	Wastewater treatment	By-products (Light ends and C_4^+)
Basic instrumentation and control		

With the battery limits the input-output structure for the Hipphox process is defined, see also paragraph 3.2.2 and figure 3.2.

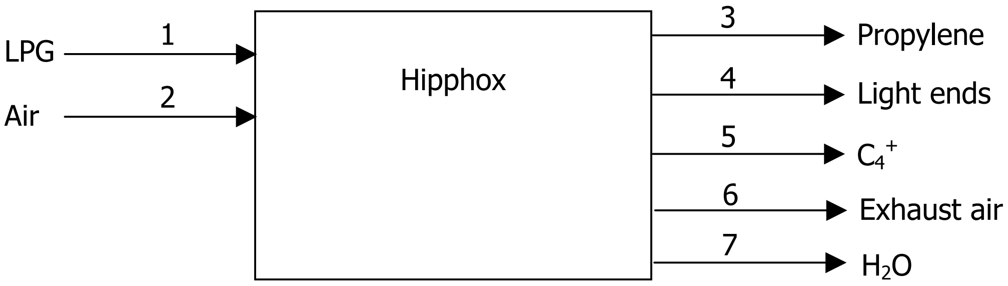


Figure 3.5 Input-output structure of the Hipphox process

3.3.4 Definition of in- and outgoing streams

In this paragraph all in- and outgoing streams will be defined. Properties like price, composition, temperature and pressure will be determined.

LPG (Table 3.3)

LPG is predominantly a mixture of C3 and C4 hydrocarbons with other hydrocarbons in the C1-C7 range. These are gases at normal ambient temperatures and pressures. Liquefaction of these gases by application of pressures of a few atmospheres to produce Liquefied Petroleum Gases (LPG) enables them to be conveniently and efficiently stored and transported in light pressure vessels. Refrigeration to below their boiling point is an economic method of liquefying large quantities of LPG for bulk storage and transport. LPG is produced in petroleum refineries as the light end fractions of distillation and cracking processes, production of crude oil or purification of natural gas. The LPG needed in Hipphox will be provided by high-pressure pipeline, from natural gas purification. On site storage can be done as pressurized (17 bara) storage at ambient temperature; refrigerated storage at ambient pressure; and semi refrigerated, partially pressurized (3 bar) product storage [22, 51].

Table 3.3 LPG stream

Stream Name :		**LPG**				
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
Propane	%mol	80-100	95.0	(1)	(1)	Values taken in consultation.
Ethane	%mol		3.0	(1), (2)		
Butane	%mol		2.0	(1), (2)	(2)	light ends and heavy ends are taken as
Sulfur compounds	ppm wt	< 120		(3)		ethane and butane respectively.
					(3)	H2S removal outside battery limitis,
						Compounds not included in mass balance.
					(4)	Price of propane [2]
Total			100.0			
Process Conditions and Price					(5)	From Ullmann's Encyclopedia [51]
Temp.	oC	5-30	15	(5)		
Press.	Bara	3-17	17	(5)		
Phase	V/L/S	L	L			
Price	$/ton	190	190	(4)		

Air (Table 3.4)

Air is freely available. It is used to regenerate the SOC, so after the regeneration section it has a different composition (spent air).

Table 3.4 Air stream

Stream Name :	Air							
Comp.	Units	Specification			Additional Information			
		Available	Design	Notes				
Nitrogen	% v	78	79.0					
Oxygen	% v	20	21.0					
Argon	% v	1	0.0					
CO2	% v	0.03	0.0					
H2O	% v	0.97	0.0					
Total			100.0					
Process Conditions and Price								
Temp.	oC	5-30	15					
Press.	Bara	1	1					
Phase	V/L/S	V	V					
Price	$/ton	0	0					

Propylene (Table 3.5)

As most of the propylene is used for polypropylene production, propylene with 99.5 wt% is produced.

Table 3.5 Propylene stream

Stream Name :	Propylene product							
Comp.	Units	Specification			Additional Information			
		Available	Design	Notes				
Propylene	%wt	80-99.5	99.5	(1)	(1)	polymer grade propylene (99.5 wt%)		
Light ends (C_3^-)	%wt	20-0.5	0.5	(1)		for production of polypropylene		
					(2)	price fluctuates between 250 and		
						500 $/ton in two years [2]		
Total			100.0		(3)	Hoekloos [53]		
Process Conditions and Price								
Temp.	oC		15	(3)				
Press.	Bara		9	(3)				
Phase	V/L/S		V					
Price	$/ton		375	(2)				

Specifications for commercial polymer grade propylene are given by Teppco [76]. An overview is given in table 3.6.

Table 3.6 Polymer grade propylene specification [76]

Specification	**Amount**
Propylene, wt%, min.	99.5
Propane, wt% max.	0.5
Acetylene, ppm by wt., max.	1
Butadiene, ppm by wt., max.	1
C4's total, ppm by wt., max.	15
C5's and heavier, ppm by wt., max.	10
Carbon dioxide, ppm by wt., max.	1
Carbon monoxide, ppm by wt., max.	0.03
Ethane, ppm by wt., max.	300
Ethylene, ppm by wt., max.	10
Hydrogen, ppm by wt., max.	1
Propadiene, ppm by wt., max.	1
Water, ppm by wt., max.	1
Sulfur, ppm by wt., max.	0.5

Water (Table 3.7)

Water is produced in the reaction of hydrogen with SOC.

Table 3.7 Water stream

Stream Name :	**H_2O**					
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
H2O	% wt	100	100.0		(1)	Price depends on the usage of the water.
Total			100.0			
Process Conditions and Price						
Temp.	oC		30			
Press.	Bara		1			
Phase	V/L/S		L			
Price	$/ton		0	(1)		

Spent air

Spent air is discharged (at 40 degrees Celsius at atmospheric pressure) into open air and contains little amounts of oxygen.

Pt Catalyst (Table 3.8) on monolith

Pt catalysts are widely used in chemical industry. The catalyst will be coated on a monolith. For more information on catalyst specification, see chapter 2.1.3.

Table 3.8 Pt catalyst stream

Stream Name :		**Pt catalyst on monolith**				
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
Pt/Sn/K on γ Al_2O_3		Pt/Sn on γ Al_2O_3	Pt/Sn/K on γ Al_2O_3	(1)	(1)	Preferable with alkali metals
					(2)	Estimated [46], catalyst contains 1 wt% Pt,
Total						when coated on monolith, price
Process Conditions and Price						determined by costs for Pt
Temp.	oC		15			monolith contains Al_2O_3
Press.	Bara		-			
Phase	V/L/S		S			
Price	$/kg		16880	(2)		

SOC (Table 3.9)

The SOC reacts with the hydrogen and can be regenerated with oxygen. For thermodynamic calculations, ceriumdioxide is used. The SOC, represented as $Ce_{0.9}W_{0.1}O_x$ has a surface area of 35.7 m^2/g, a pore volume of 0.14 mL/g and a pore diameter of 14 nm [9]. The particles have a diameter of 60 μm.

Table 3.9 SOC stream

Stream Name :		**Solid Oxygen Carrier**				
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
$Ce_{0.9}W_{0.1}O_y$		$Ce_{0.9}W_{0.1}O_y$	$Ce_{0.9}W_{0.1}O_y$	(1)	(1)	In the SHC reaction, about 0.2 mol oxygen
			CeO_2	(2)		per mol SOC reacts with water
					(2)	For the thermodynamic calculations and
Total						kinetics literature on CeO2 is used.
Process Conditions and Price					(3)	It is assumed that the SOC is much cheaper
Temp.	oC		15			than the Pt catalyst.
Press.	Bara		-			
Phase	V/L/S		S			
Price	$/kg		4	(3)		

Light ends (Table 3.10)

The light ends stream consists mainly of ethane, carbon monoxide and hydrogen. It can be burned and therefore it has a fuel value.

Table 3.10 Light ends stream

Stream Name :		**Light ends**				
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
Ethane	%mol		54.0		(1)	From Coulson&Richardson Ch. 6: [21],
Carbonmonoxide	%mol		22.0			fuel value
Hydrogen	%mol		16.0		(2)	Design
Methane	%mol		5.0			
Ethylene	%mol		3.0			
Total			100.0			
Process Conditions and Price						
Temp.	oC		15			
Press.	Bara		24	(2)		
Phase	V/L/S		V			
Price	$/GJ		4	(1)		

C_4^+ (Table 3.11)

In the first separation section the butane from the LPG and the heavier components formed in the reaction section are separated.

Table 3.11 C_4^+ stream

Stream Name :	**C4+**					
Comp.	Units	Specification			Additional Information	
		Available	Design	Notes		
Butane	%mol		71.0		(1)	From Coulson&Richardson [21] - fuel value
Propane	%mol		20.0		(2)	Hoekloos [53]
1-Butene	%mol		9.0			
Total			100.0			
Process Conditions and Price						
Temp.	oC		15	(2)		
Press.	Bara		16.8			
Phase	V/L/S		L			
Price	$/GJ		4	(1)		

3.3.5 Utility conditions and costs

Several utilities will be required in the Hipphox process. An overview of specifications is given in this paragraph.

a. Steam

In chapter 5 utility requirements are calculated from pinch technology. Only low-pressure steam is needed; the conditions are shown below in table 3.12.

Table 3.12 Low pressure steam properties

Conditions	Low pressure steam	Reference
P [bara]	3	[23, appendix 3]
T (superheated) [°C]	190	[23, appendix 3]
T (condensation) [°C]	133.5	[23, appendix 3]
Price [euro/ton]	10	[54]

b. Electricity

Electricity is needed for the compressors among other things. Details of the electricity can be found in table 3.13.

Table 3.13 Electricity properties

Power	**Voltage [V]**	**Current**	**Reference**
Low	220	AC	[23, appendix 3]
Medium	380	Three-phase AC	[23, appendix 3]
High	3000 - 10000	Three-phase AC	[23, appendix 3]
Price	0.023 [$/MJ]	0.085 [$/kWh]	[21]

c. Cooling water

Cooling water is needed in a number of coolers. The properties of cooling water can be found in table 3.14.

Table 3.14 Properties for cooling water

Water	T [°C]		p [bara]	h [kW/m^2°C]	Fouling factor	Price [$\$/m^3$]
	In	Out				
	20(1)	40(2)	3(3)	2.0	0.5	0.03
Remarks: (1) design value (2) maximum allowed (3) at ground level						

d. Refrigerant

For the cryogenic distillation (de-ethanizer) liquid nitrogen is needed. The information of the refrigerant can be found in the following table.

Table 3.15 Refrigerant properties

Liquid nitrogen	**T [°C]**		**p [bara]**	**Price [euro/GJ]**
	In	**Out**		
	<-80(1)	?(2)	?(3)	15

e. Nitrogen

Nitrogen gas is needed to purge the SOC stream in case the seal of the hopper fails. This is to prevent that oxygen enters the reactor.
Nitrogen gas as utility is available for 0.08 $\$/m^3$ [21].

3.4 Margin

The margin is calculated as the difference between income from sales minus costs for feedstock and waste streams.
Propylene is sold for 375 \$/ton. The margin is calculated in the following table.
For the production of 250 kta propylene, 280 kta of propane is needed (see chapter 5). The margin is calculated as the difference between the sales from propylene and the costs for propane. It is assumed that LPG has about the same price as propane, probably even somewhat lower.

Table 3.16 Calculation of the margin

	\$/ton	**kta**	**Million \$/a**	**Million €/a**
Propylene	375	250	93.73	75.64
Propane	190	280	53.17	42.91
Margin			40.56	32.73

For calculation of the margin the costs for waste streams and income for by-products are neglected. For example hydrogen is a valuable by-product, however a large part of the hydrogen is converted to water. By-products like the light ends will have a fuel value. The only major waste stream will be the water, however the water can be recovered with low concentration impurities. It is expected that the costs of treating the water will not be high. Air can be used for regeneration of SOC, so this will lead to no extra costs.

The margin of 40.56 million \$ per year is taken as a first start.
With this margin the maximum allowable investment for the design can be calculated at a Discount Cash Flow Rate of Return (DCFRR, r′) of 10%.
The plant life is 20 years. For each year the Net Present Worth (NPW) of cash flow can be calculated using the following formula [21].

$$\mathrm{NPW} = \frac{\text{Estimated net cash flow in year n (NFW)}}{(1+r')^n} \qquad (3.6)$$

The maximum allowable investment for the design is the sum of all the NPW for each year.

$$\sum_{n=1}^{n=t} \frac{\mathrm{NFW}}{(1+r')^n} = \text{max. allowable investment} \qquad (3.7)$$

In table 3.17 the net present worth for each year is calculated. The maximum allowable investment for the design is 345.29 million \$ (278.65 million €).

Table 3.17 Calculation of the maximum allowable investment

Year	Net cash flow (million $)	NFW/(1+r)^n (million $)
1	40.56	36.87
2	40.56	33.52
3	40.56	30.47
4	40.56	27.70
5	40.56	25.18
6	40.56	22.89
7	40.56	20.81
8	40.56	18.92
9	40.56	17.20
10	40.56	15.64
11	40.56	14.22
12	40.56	12.92
13	40.56	11.75
14	40.56	10.68
15	40.56	9.71
16	40.56	8.83
17	40.56	8.02
18	40.56	7.29
19	40.56	6.63
20	40.56	6.03
Total		345.29

In chapter 11 the economic evaluation for the Hipphox process is done.
From this evaluation a net cash flow of 6.85 million euro per year is calculated. This is a lot lower than the margin between propylene and propane (32.73 million euro). The utilities account for a large part (about 10 million euro per year). Furthermore the margin is decreased by cost factors like operating labour, maintenance, capital charges and indirect production costs (research and development among other things). There are no high costs for the waste streams and the by-products do not yield a lot, as expected.
The total investment costs for the Hipphox process are 36.4 million euro, which is less than the maximum allowable investment.

4 Thermodynamic Properties & Reaction Kinetics

In this chapter equations and values are given, required for property estimation of the component's mixtures. Three possible scenarios have been thermodynamically assessed: Combined dehydrogenation and selective oxidation (DH & SHC), Staged dehydrogenation followed by selective oxidation (DH -> SHC -> DH) and finally the Oleflex process (DH diluted in hydrogen). In the last part the reaction kinetics are described in detail.

4.1 Thermodynamic calculations

First the reactions of interest are given, together with the important thermodynamic values and VLE data. From this information the equilibrium constants and reaction equilibria are calculated. Calculations were done for DH, DH+SHC in series and DH&SHC combined in one reactor. The SOC can be regenerated in two different ways: Regeneration with oxygen or with water. For this also calculations are made. For a detailed description of the properties of the pure components the reader is referred to the list of pure component properties (chapter 3.2.4).

4.1.1 Equilibrium constants

The reactions of interest for the process are:
DH reaction:

$$C_3H_8(g) \rightleftarrows C_3H_6(g) + H_2(g) \tag{4.1}$$

SHC reaction:

$$5\,Ce_{0.9}W_{0.1}O_y(s) + H_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + H_2O(g) \tag{4.2}$$

The SHC reaction can also be written in defect-chemistry notation as:

$$O_o^x + 2Ce_{Ce}^x \rightleftarrows 0.5O_2(g) + V_o^{\cdot\cdot} + 2Ce_{Ce}^{'} \tag{4.3}$$

$$0.5O_2(g) + H_2(g) \rightleftarrows H_2O(g) \tag{4.4}$$

X (in 4.3) means net zero charge, ' (in 4.3) a charge of –1 and ¨ (in 4.3) a charge of +2.

The enthalpy and entropy of formation for reaction 4.3 are based on literature about non-stoichiometric defect models for CeO_2 and $Ce_{0.9}W_{0.1}O_{1.95-x}$ [47]. In reaction 4.3 oxygen is freed from the lattice. Oxygen vacancies are formed. In reaction 4.4 the freed oxygen reacts with hydrogen.
From literature [43, 47] it can be seen that the enthalpy and entropy changes as a function of the amount of freed oxygen. Therefore estimates have to be made for the enthalpy and entropy of reaction 4.3. The influence of the oxygen content in $Ce_{0.9}W_{0.1}O_{1.95-x}$ on the equilibrium enthalpy and entropy is shown in appendix 4.1.

In order to obtain the equilibrium composition y_i and x_i at a certain pressure and temperature, first the equilibrium constant for each reaction K_j is calculated. The procedure for this is described in appendix 4.2. The results of these calculations are shown in table 4.1.

Table 4.1 Thermodynamic properties of the reactions at 873K and 2 bara.

Reaction	**$\Delta_r Cp_{873}$ (kJ/(moleK))**	**$\Delta_r H_{873}$ (kJ/mole)**	**$\Delta_r S_{873}$ (kJ/mole)**	**$\Delta_r G_{873}$ (kJ/mole)**	**K_j**
4.1	1.81	129.81	132.79	13.89	1.48E-01
4.3	-	355*	200*	180.4	1.61E-11
4.4	-6.94	-246.62	-59.06	-195.06	4.69E+11

* Chosen value from [47], see appendix 4.2

From table 4.1 it can be concluded that both the dehydrogenation reaction and selective hydrogen combustion are endothermic reactions. The total enthalpy change of the selective hydrogen combustion reaction is equal to the sum of the reaction enthalpy of 4.3 and 4.4: 108 kJ per mole. The overall equilibrium constant for this combined reaction is equal to 7.53.

4.1.2 Vapour Liquid Equilibrium data of main components

In the Hipphox process polar as well as non-polar components are used. The role of non-polar is more important than polar components, since in quantity they are present in a much larger extent. In Dimian [54, ch. 5] it can be found that for non-polar properties it is best to use cubic equations of state like for example Soave-Redlich-Kwong and Peng-Robinson. However these models do not incorporate polar behaviour. In the PR-BM model adjustments are made in order to be able to describe polar properties, of e.g. water, so this seems to be the best model to use in our simulations, when water is present.

T,x,y-diagrams are calculated using Aspen Plus version 11.1. T,x,y-diagrams have been constructed for the relevant components for each column. For example in a deethaniser the most difficult separation will be the ethane-propylene separation. The SRK property method proved to be suitable for such T,x,y-diagrams. Since water-hydrocarbons are immiscible at higher pressures, no suitable T,x,y-diagram could be produced. However the PR-BM property model is suitable for AspenPlus simulation at lower concentrations.

The reaction section will be at a temperature of 500 to 800 °C and pressure of about 2 bara, all components are in the vapour phase during reaction, except off course the solid oxygen carrier, which is in a solid phase. The T,x,y-diagrams can be found in appendix 4.3.

4.1.3 Equilibrium composition

In order to calculate the equilibrium composition expressions for the equilibrium constants have to be derived. This is done in appendix 4.4. The results are presented in this paragraph.

The expressions for the DH and SHC reaction equilibrium constants are:

$$K_{DH} = \frac{y_{C_3H_6} y_{H_2} \frac{p}{p^0}}{y_{C_3H_8}} \tag{4.5}$$

$$K_{SHC} = \frac{y_{H_2O}}{y_{H_2}} \tag{4.6}$$

DH & SHC

In appendix 4.4 the relations for the fraction of component i (y_i) are given. With these expressions, expressions 4.5 and 4.6 can be solved to get an equilibrium conversion. With the chosen enthalpy and entropy value for reaction 4.3, an equilibrium conversion of 62% for the DH reaction can be achieved and 88% conversion for the SHC reaction at a temperature of 873 K and a pressure of 2 bara.

DH + SHC + DH (option 4)

Also the equilibrium conversion for option 4 has been calculated. The relations are given in appendix 4.4. First the equilibrium for DH is calculated. The conversion of DH is 26%. This is used as input for the SHC. This gives a conversion of 88%. This is again used for DH and results in a final conversion of 48%. In order to compare the equilibrium conversions for various options the following table is made.

Table 4.2 Equilibrium conversions of various options

	Conversion of propane
DH (Oleflex)	26%
DH + SHC + DH	48%
DH & SHC	62%

From this table it is clear that the combined DH & SHC (option 3) has the highest possible equilibrium conversion (mol propylene produced per mol propane fed).

The temperature dependence of this equilibrium is reviewed by repeating the procedure of Appendix 4.4, a selection of the results is given in the following table:

Table 4.3 Temperature dependence of the equilibrium conversion

T [K]	$K_{4.1}$ [-]	$K_{4.3}$ [-]	$K_{4.4}$ [-]	Conversion DH	Conversion SHC
700	1.97E-03	9.04E-17	1.98E+15	0.03	0.15
800	3.00E-02	1.85E-13	1.02E+13	0.20	0.65
873	1.48E-01	1.61E-11	4.69E+11	0.62	0.88
900	2.49E-01	6.97E-11	1.70E+11	0.78	0.92

From the results of the equilibrium conversion of the DH a well-founded choice can be made about the temperature at which the reactions should best take place. In Grasselli's experimental work [44] an equilibrium conversion was obtained of 65%. This is best comparable with the conversion of 62% in table 4.3. Therefore in the Hipphox process the reaction section will have a temperature of 873 K. This choice also seems to be a viable temperature since the Oleflex process operates at the same temperature.

4.1.4 Side reactions

DH – Thermal cracking

Thermal cracking consists of a series of cracking reactions, which are summarized in reaction equations 4.7 to 4.15 [19]. The main reaction is the cracking of propane to ethylene and methane. The thermal cracking reactions are very temperature dependent and are expected to decrease as the temperature drops.

$$C_3H_8(g) \rightarrow C_2H_4(g) + CH_4(g) \qquad (4.7)$$

$$C_3H_8(g) \rightleftharpoons C_3H_6(g) + H_2(g) \qquad \text{(Similar to catalytic dehydrogenation)} \qquad (4.8)$$

$$C_3H_8(g) + C_2H_4(g) \rightarrow C_2H_6(g) + C_3H_6(g) \qquad (4.9)$$

$$2C_3H_6(g) \rightarrow 3C_2H_4(g) \qquad (4.10)$$

$$2C_3H_6(g) \rightarrow 0.5C_6 + 3CH_4(g) \qquad (4.11)$$

$$C_3H_6(g) \rightleftharpoons C_2H_2(g) + CH_4(g) \qquad (4.12)$$

$$C_3H_6(g) + C_2H_6(g) \rightarrow C_4H_8(g) + CH_4(g) \qquad (4.13)$$

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \qquad (4.14)$$

$$C_2H_4(g) + C_2H_2(g) \rightarrow C_4H_6(g) \qquad (4.15)$$

As only two side reactions are reversible, the equilibrium constants are calculated for reaction 4.12 and 4.14 (see appendix 4.2). The results are shown in the table 4.4. Reaction 4.8 is the dehydrogenation of propane and is therefore neglected as a side reaction.

Table 4.4 Properties of DH side reactions at 873 K and 2 bara.

Reaction	**$\Delta_r Cp_{873}$ (kJ/(moleK))**	**$\Delta_r H_{873}$ (kJ/mole)**	**$\Delta_r S_{873}$ (kJ/mole)**	**$\Delta_r G_{873}$ (kJ/mole)**	**K_j**
4.12	-4.50	138.95	126.1	28.98	1.87E-02
4.14	-4.54	143.48	128.3	31.49	1.30E-02

Both side reactions from table 4.3 have rather low equilibrium constants, as is expected.

SHC – side reactions

The selectivity of the SOC is 97% [42]. This means that 3% of the SOC reacts with hydrocarbons. The main side reactions are the combustion of propane and propylene to carbon monoxide.

$$C_3H_8(g) + 3.5O_2(g) \rightleftharpoons 3CO(g) + 4H_2O(g) \qquad (4.16)$$

$$C_3H_6(g) + 3O_2(g) \rightleftharpoons 3CO(g) + 3H_2O(g) \qquad (4.17)$$

The selectivity of the SOC is 97%, so these reactions take place, but in a small amount. The heat effects of these reactions are calculated, as this is needed for the reactor design. As the oxygen has to be freed from the lattice, this is also a part of the side reactions. The results are shown in table 4.5. All the details can be found in appendix 4.2.

Table 4.5 Enthalpy calculations of SHC side reactions

Reaction	**ΔH [kJ]**	**ΔH per mol SOC [kJ]**	**Total [kJ]**
4.16	-1192 (per mol hydrocarbon)	-34.06 (-1192/(5*3.5/0.5))	36.94 (-34.06+71)
4.17	-1075 (per mol hydrocarbon)	-35.83 (-1075/(5*3/0.5))	35.17 (-35.83+71)
4.3	355 (per 0.5 mol O_2)	71 (355/5)	

As shown in table 4.4 the SHC side reactions are endothermic due to the highly endothermic reaction 4.3 (oxygen freed from Cerium-Tungsten lattice).

4.1.5 Regeneration of the SOC

For the regeneration of the SOC two different options are possible. It can be done with water or with oxygen. The regeneration reaction with water is the opposite of the reaction in the reaction section (eq. 4.2):

$$5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + H_2O(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_y(s) + H_2(g) \qquad (4.18)$$

This again can be split up in:

$$H_2O(g) \rightleftarrows 0.5O_2(g) + H_2(g) \qquad (4.19)$$

$$0.5O_2(g) + V_o^{\cdot\cdot} + 2Ce_{Ce}^{'} \rightleftarrows O_o^x + 2Ce_{Ce}^x \qquad (4.20)$$

The regeneration reaction with oxygen is:

$$5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + 0.5O_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_y(s) \qquad (4.21)$$

Also written as:

$$0.5O_2(g) + V_o^{\cdot\cdot} + 2Ce_{Ce}^{'} \rightleftarrows O_o^x + 2Ce_{Ce}^x \qquad (4.20)$$

In appendix 4.4 it was determined that it costs 355 kJ to free 0.5 moles of oxygen from the lattice of SOC. For 0.5 moles of oxygen 5 moles of SOC are needed, because only 10% the available oxygen in the SOC can react. For the regeneration with oxygen the opposite is valid. This means that 0.5 moles of oxygen is needed to regenerate five moles of SOC. To regenerate one mole of SOC 1/5 of 355 kJ is released. The heat of reaction of the regeneration of the SOC with oxygen is therefore –71 kJ/mole SOC. An overview of the thermodynamic data is given in table 4.6.

Table 4.6 Overview of thermodynamic data for regeneration

Reaction	Δ_r **Cp$_{873}$ [J/(mole K)]**	Δ_r **H$_{873}$ [kJ/ 0.5 mole O$_2$]**	Δ_r **H$_{873}$ [kJ/ mole SOC]**	Δ_r **S$_{873}$ [kJ/0.5 mole O$_2$]**	Δ_r **G$_{873}$ [kJ/0.5 mole O$_2$]**	**K$_j$ [-]**
Regeneration with Oxygen 4.20	-	-355	-71	-0.200	-180.40	6.23E+10
4.19	6.94	247	49.4	0.048	205.12	5.33E-13
Regeneration with water 4.19+4.20	6.94	-138	-27.6	-0.152	-5.28	2.07E+00

From table 4.6 it can clearly be seen that regeneration with water is thermodynamically unfavourable. The equilibrium conversion of the regeneration with water is about 60%. To get a higher conversion the temperature has to be lowered. At lower temperature however the energy integration with the reaction section is difficult.

From thermodynamic point of view regeneration with oxygen is favoured. However hydrogen is a valuable by product. Economic calculations have been made to make the decision between regeneration with oxygen and water.

Economics calculation for regeneration of the SOC

Hydrogen is produced during the regeneration of the SOC. As this is a valuable by-product, the value of this should be taken into account. However the regeneration with oxygen will provide more heat than the regeneration with water, which can be used in the reaction section.

In the following table (4.7) calculations are made to compare the two options economically. The calculations are based on a production of 250 kta of propylene. First the amount of hydrogen formed by regeneration of the SOC with water is calculated. Next all the energy values needed for the reactions and produced by the regeneration of the SOC are calculated. The price of the energy is based on the fuel value. From these values the profits and costs are calculated.

Table 4.7 Economic calculations for the comparison of regeneration with oxygen or with water

	[t/hr]	[$/hr]
H_2 formed	0.79	511
	[GJ/hr]	Costs [$/hr] on basis of fuel value
Energy needed for DH	96	-672
Energy needed for SHC	70	-492
Total	166	
Energy by reg. with H_20	-42	295
Energy by reg. with 0_2	-237	1666
Total profit oxygen		**502**
Total profit water		**-358**

The economic calculations are based on the values mentioned in table 4.8.

Table 4.8 Prices of Energy and hydrogen

	Price
Energy (fuel value)	7 $/GJ [21]
Hydrogen	650 $/ton [8]

From table 4.8 it can be seen that the profit of producing hydrogen is not so high, only 511 $/hr. A lot of energy is produced by the regeneration of the SOC with oxygen, namely 237 GJ/h. This is enough to supply the energy needed for the DH and SHC reaction. When the regeneration of the SOC is done with water, not enough energy is produced to supply both the reactions. If most of the heat produced by the regeneration with oxygen can be integrated in the reaction section, then a lot of money can be saved, even more than that is earned with the production of hydrogen. From economic point of view it is better to regenerate with oxygen. It is noted that the values of total profits are not real profits, but merely a way to compare the two methods.

4.2 Reactions Kinetics

The kinetics of the three most important reaction frameworks will be discussed. Since kinetics finally determine the reactor size, it is of great importance. Since not all kinetics are exactly known, some assumptions will have to be made.

4.2.1 DH reaction

The dehydrogenation of propane leads to our product propylene and is given by the reaction equation 4.1. Several models concerning propane reaction rates are proposed in literature, ranging from power-law equations like equation 4.21 to more complicated Langmuir-Hinshelwood type equations. The power-law equation [15] is a first order equation dependent amongst others of the propane partial pressure, temperature and time on-stream. The Langmuir-Hinshelwood type equation also accounts for propylene absorption, deactivating the catalyst. For simplicity reasons however a basic power law equation, describing the dehydrogenation reaction rate, will be used. Reaction kinetics are based on the usage of a Pt-Sn-K/γ-Al_2O_3 catalyst. The power law equation will now be further explained.

$$-r_{C_3H_8} = k_{app} * \left(p_{C_3H_8} - \frac{p_{C_3H_6} * p_{H_2}}{K} \right) \tag{4.21}$$

$$K = 1.76^{12} * \exp\left(\frac{-15521}{T} \right) \tag{4.22}$$

The reaction rate is dependent on the partial pressures of both products and reactants. The equilibrium composition is both temperature and pressure dependent. The reaction rate constant is dependent on the number of active sites on the platinum catalyst and the reaction temperature as shown in equation 4.23.

$$k_{app} = k_{site} * N_{sites} = N_{sites} * 6.14 * 10^{-24} * \exp\left(\frac{-7545}{T} \right) \tag{4.23}$$

The number of actives sites decreases during dehydrogenation due to coke formation on the catalyst. The amount of coke formation is a function of the time on-stream of the catalyst as shown in table 4.9.

Table 4.9 Coke formation effects

On-stream time [minutes]	**Active sites /10^{21} [sites/kg]**	**k_{site} *10^{28} [mol/site*s*Pa]**	**$k_{site,average}$ *10^{28} [mol/site*s*Pa]**
0.00	5.24	-	-
3.00	3.60	3.09	-
120	0.67	2.86	-
Averaged	-	-	2.98

For simulation purposes, the average k_{app} value will be used. As briefly explained in chapter 2 coke deposition on the catalyst is negligible. The dehydrogenation catalyst is assumed to be self-regenerating. The assumption of a self-regenerating catalyst has some major consequences. The regeneration of the Pt catalyst will be neglected in further design.

4.2.2 SOC reaction

The reaction of the SOC is given by equation 4.2.

$$5Ce_{0.9}W_{0.1}O_y(s) + H_2(g) \rightleftarrows 5Ce_{0.9}W_{0.1}O_{y-0.2}(s) + H_2O(g) \qquad (4.2)$$

The hydrogen is selectively oxidized using the oxygen of the SOC. In a number of literature references [16, 32, 41] a mechanism for this process is proposed and will be explained here. The mechanism is developed for CeO_2 as well as for doped ceria. It is assumed here that the model also describes the behaviour of hydrogen on $Ce_{0.9}W_{0.1}O_{y-0.2}$. A schematic representation of the process is shown below.

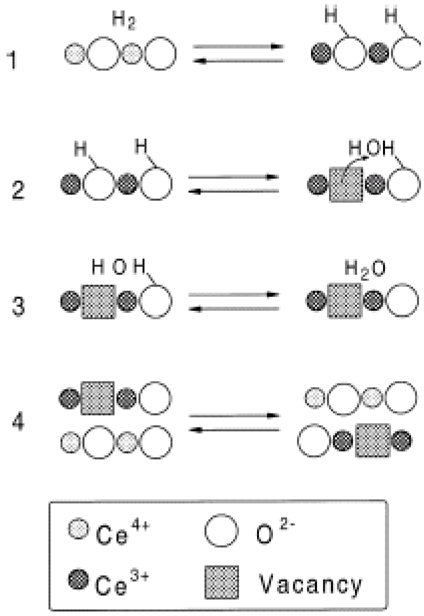


Figure 4.1 mechanism of selective hydrogen oxidation with the SOC. 1 = dissociative chemisorption of hydrogen, 2 = anionic vacancy formation with reduction of the neighbouring cations, 3 = water desorption, 4 = diffusion of the surface anionic vacancies into the bulk.

In this scheme, surface steps include step 1, step 2 and step 3, followed by bulk step 4. Since all the experiments that were done in order to obtain this mechanism were conducted with an excess of hydrogen in the bulk, the diffusion of hydrogen to the SOC was left out. The first step therefore is the adsorption of hydrogen onto the surface of the SOC to form hydroxyl groups. Next anionic vacancies are formed with the reduction of the neighbouring cations. The third step is desorption of water from the surface, followed by the final step, which is the diffusion of surface anionic vacancies into the SOC. In the Hipphox process no excess hydrogen is present in the bulk, however in chapter 8.2.1, mass transfer this assumption will be explained to be valid.

In chapter 4.1 the thermodynamics of the SOC reaction were treated, using among others the findings of Bevan and Kordis [48], values are given for the enthalpy and entropy of the SOC reaction. From these figures (figure 4.2), which are shown below, a conclusion can be drawn as to in what amount the SOC will be reduced.

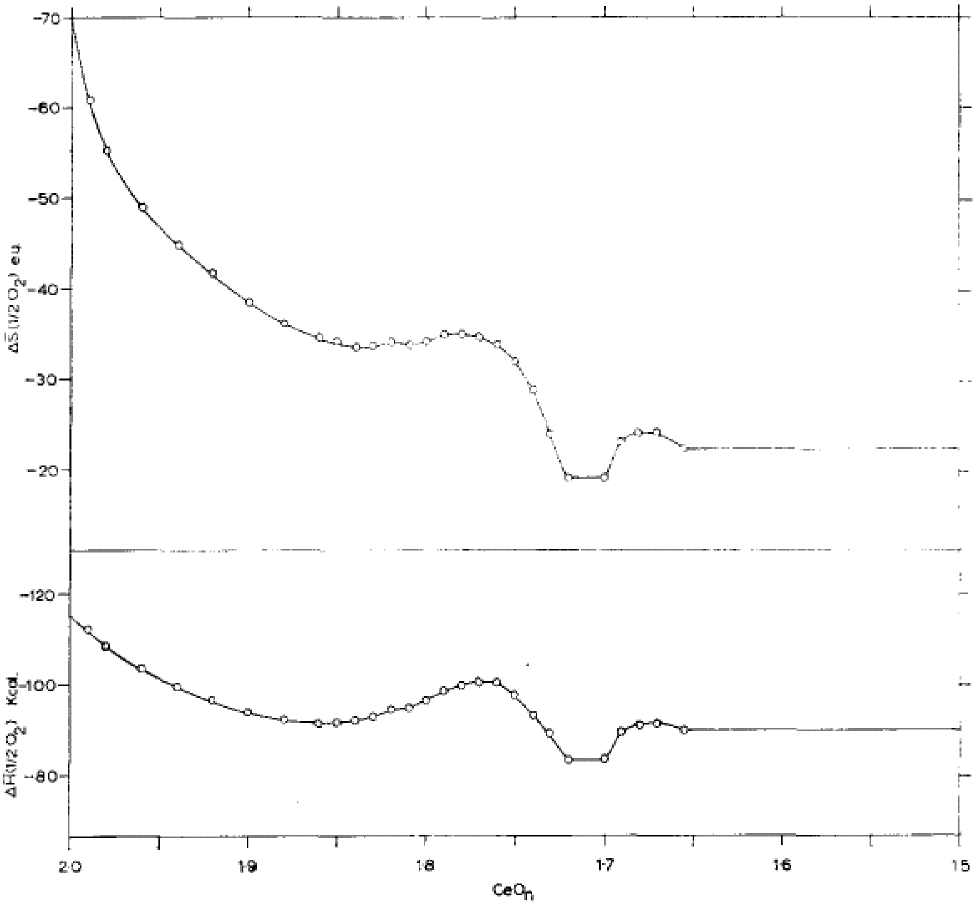


Figure 4.2. Bevan & Kordis figures

As can be seen in figure 4.2 the values of the enthalpy and especially the entropy of reaction 4.3 change drastically when the value of x in CeO_x decreases below a value of 1.77. This value corresponds with an amount of reacted oxygen of (2-1.77)/2=0.115, which is 11.5 %.

J. El Fallah [16] et.al. have determined a kinetic model for the separate steps of the reduction process (as shown in figure 4.1) and have found values for the reaction rate constant for each of these steps at two temperatures, namely 593 and 673 K. From these kinetic studies it becomes obvious that the first three steps have a high rate constant, which means that they develop quickly. Once the surface oxygen has reacted however, the diffusion of the anionic vacancies into the SOC becomes the rate-determining step. This step however is much slower compared to the first three, as can be seen in figure 4.3.

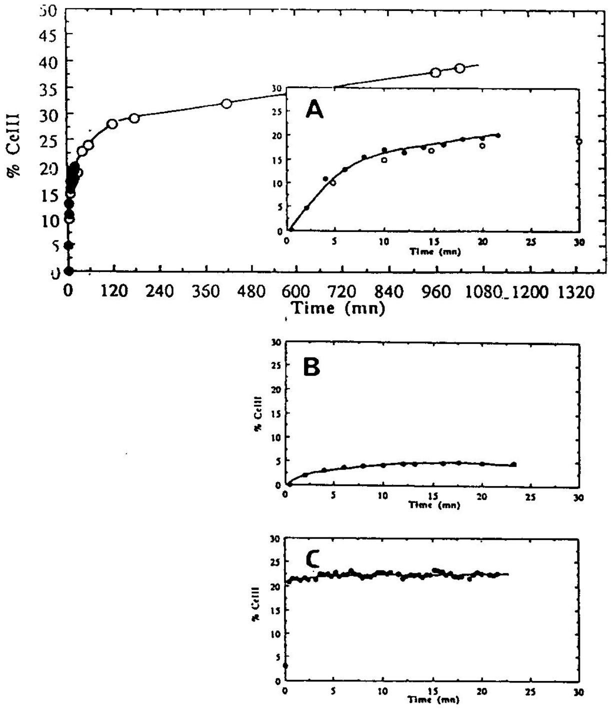


Figure 4.3. Reduction kinetics expressed as % CeIII on (A) CeO_2 sample A_1; (B) CeO_2 sample A_2 and (C) Rh/ CeO_2 sample.

In this figure it can clearly be seen that the first part up to about 25% of cerium reduction, which is presumably steps 1, 2 and 3 of the SOC-reaction, is very fast compared to the remainder. When 25% of the cerium is reduced the amount of oxygen reduction is 6.25%. This can be seen from the rate equation for the reduction of CeO_2.

$$10CeO_2 + 1.25H_2 \rightleftarrows 1.25Ce_2O_3 + 7.5CeO_2 + 1.25H_2O$$

When 25% of the cerium is reduced 1.25 of 20 of the oxygen, which is 6.25%, has formed water.

These findings and the decrease of the enthalpy and entropy found by Bevan and Kordis lead to a conclusion that a maximum of 10% of the oxygen-content of the SOC will be used in our reaction, since otherwise when the y in $Ce_{0.9}W_{0.1}O_y$ becomes too small the kinetics become too slow. The fact that 10% is taken instead of 6% is substantiated by figures 4.2 and 4.3 and by the fact that the presence of Tungsten in ceriumoxide favours the reaction kinetics.

The value of the reaction rate constant will have to be estimated, since no data is available for the temperature dependence. The estimation will be done on basis of the values found in El Fallah's article [16]. Here there were several reaction rate constants found, but all of them were from ceriumoxide without doping. Doping the ceriumoxide with the transition state metal Rh enhances the adsorption of hydrogen [16], it is assumed here that this also holds for W. Furthermore the first 3 steps in the reaction mechanism of figure 1 are very fast. This was also found by G. Rothenberg et al.[9]. The reaction rate constant that was found in the article of El Fallah for Rh/CeO$_2$ was 0.167 mole/s*kg$_{cat}$. This value will also be used in this project.

In order to obtain a proper kinetic model for reaction 4.2 the effect of the hydrogen concentration in the reactor has to be taken into account. All experiments found in literature work with an excess of hydrogen. Therefore a first order dependence on hydrogen is assumed. This gives us the following rate-equation for reaction 4.3:

$$R_{soc} = -k\left[x_{H_2} - \frac{x_{H_2O}}{K}\right] \tag{4.3}$$

where k is the reaction rate constant (0.167 mol per s per kg SOC), x_{H2} the hydrogen fraction, x_{H2O} the water fraction, and K is the equilibrium constant of reaction 4.2.

4.2.3 DH side reactions

In paragraph 4.1.4 the dehydrogenation side reactions are given. The corresponding reaction rate equations have been found in literature [19] to be:

$$-r_{4.7} = k_{4.7}\left[\frac{F_{C_3H_8}}{F_t}\left(\frac{P_t}{RT}\right)\right] \tag{4.4}$$

$$-r_{4.8} = k_{4.8}\left[\frac{F_{C_3H_8}}{F_t}\left(\frac{P_t}{RT}\right) - \frac{F_{C_3H_6} * F_{H_2}}{F^2{}_t * K_2}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.5}$$

$$-r_{4.9} = k_{4.9}\left[\frac{F_{C_3H_8} * F_{C_2H_4}}{F^2{}_t}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.6}$$

$$-r_{4.10} = k_{4.10}\left[\frac{F_{C_3H_6}}{F_t}\left(\frac{P_t}{RT}\right)\right] \tag{4.7}$$

$$-r_{4.11} = k_{4.11}\left[\frac{F_{C_3H_6}}{F_t}\left(\frac{P_t}{RT}\right)\right] \tag{4.8}$$

$$-r_{4.12} = k_{4.12}\left[\frac{F_{C_3H_6}}{F_t}\left(\frac{P_t}{RT}\right) - \frac{F_{C_2H_2} * F_{CH_4}}{F_t^2 * K_6}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.9}$$

$$-r_{4.13} = k_{4.13}\left[\frac{F_{C_3H_6} * F_{C_2H_6}}{F^2{}_t}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.10}$$

$$-r_{4.14} = k_{4.14}\left[\frac{F_{C_2H_6}}{F_t}\left(\frac{P_t}{RT}\right) - \frac{F_{C_2H_4} * F_{H_2}}{F^2{}_t * K_8}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.11}$$

$$-r_{4.15} = k_{4.15}\left[\frac{F_{C_2H_4} * F_{C_2H_2}}{F^2{}_t}\left(\frac{P_t}{RT}\right)^2\right] \tag{4.12}$$

In these reaction rates the k values are temperature dependent. The equilibrium constants (K) are dependent on both pressure and temperature. F_i indicates the molar flow rate of component i. Adding up all component flows results in the total mole flow F_t. Temperature dependency can be calculated using the turnover frequency ($k_{0,x}$) and activation energy from the Arrhenius equation (4.13). Results are presented in table 4.10.

$$k_x = k_{0,x} * \exp\left(\frac{-E_a}{R*T}\right) \tag{4.13}$$

Table 4.10 Arrhenius coefficients of cracking reactions. Source: Sundaram et al [19]

Rate coefficient	**Turnover frequency [sec^{-1} or *mole^{-1} sec^{-1}]**	**Activation energy [kJ/mole]**
k_1	4692 *10^{10}	21171
k_2	5888 *10^{10}	8908
k_3	2539 *10^{13} *	24711
k_4	1514 *10^{11}	23347
k_5	1423 *10^{9}	19037
k_6	3794 *10^{11}	24849
k_7	5553 *10^{14} *	25108
k_8	4652 *10^{13}	27278
k_9	1026 *10^{12} *	17263

4.2.4 SHC side reactions

The SOC side reaction kinetics are largely unknown. However the selectivity of the hydrogen combustion reaction with SOC is known, and therefore the reaction rate of the side reactions is therefore assumed to be equal to 1 minus this selectivity times the hydrogen combustion rate.

$$-r_{side} = \left(1-0.97\right) * r_h = -(1-0.97) * k\left[x_{H_2} - \frac{x_{H_2O}}{K}\right] \tag{4.14}$$

4.2.5 SOC regeneration with oxygen

In El Fallah [16], the reoxidation of pure Ceria and of Rh-doped Ceria with dry air is investigated. The experiments were carried out at a temperature of 673 K. It is found there that the regeneration rate for pure Ceria is much faster than the reduction rate. The reoxidation is also complete. For Rh-doped Ceria, the reoxidation is also very fast, but it needs some induction time. Moreover, the reoxidation is not complete, about 3-5% of the cerium remains at the Ce^{3+}-state.

There are different explanations possible for these two effects, given in El Fallah [16]. One possible explanation is the occupation by Rh-atoms of oxygen vacancy sites. During the reducing phase (reaction) Rh-atoms occupy oxygen vacancies in the fluorite crystal, which stabilizes the structure and "loosens" the oxygen atoms. In the reoxidation phase (regeneration) the gaseous oxygen has to expel the Rh-atoms from the anionic sites before filling them with oxygen, the first being rate-determining. This causes the induction time.
Doping the ceria with rhodium therefore causes an incomplete reoxidation, but the advantage is that the rate of reoxidation and reduction are in a similar time range: the reduction is extremely accelerated and reoxidation is slowed down a little. The reoxidation behaviour of Tungsten doped ceria is not known. Also the value of the induction time is not

known. It is therefore not possible to do educated guesses on the amount of the induction time without further research. Therefore it is not taken into account.

Pure ceria can be reoxidated even at room temperature [16, 45]. The influence of doping is not known in this matter, but it can be assumed that regeneration can be carried out at a wide temperature range. Because the reaction is carried out at 873 K, the regeneration should be carried out at a higher temperature to optimize the heat integration.

In Rothenberg [9] several doped cerium oxide compounds were evaluated on their hydrogen oxidation performance. The $Ce_{0.9}W_{0.1}O_x$ compound has an average activity of 23%, measured as mol% fraction of lattice oxygen atoms available for oxidation, compared to the theoretical limit when all the cerium ions are reduced to Ce^{3+}, after 19 repeated reduction and reoxidation experiments. In these experiments the temperature of reaction and regeneration is 873 K.

4.2.6 SOC regeneration with water

In order to regenerate the SOC with water, the temperature has to be lowered to approximately 573 K. As found in literature [45], typical regeneration rates are 10^{-6} moles of H_2 per second per gram of reduced SOC (at 573 K in figure 4.5). Regeneration times range from 50 up to 150 minutes, as shown in figure 4.6, for complete regeneration.

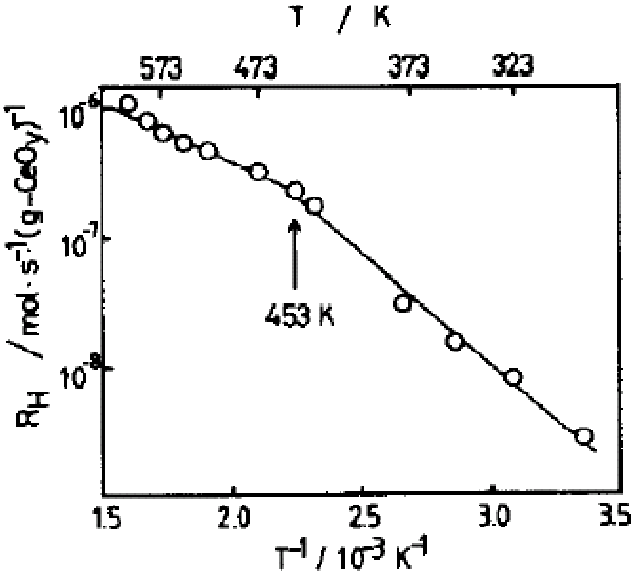


Figure 4.5 Rate of hydrogen formation (R_H) as function of temperature: Starting composition $CeO_{1.900}$. [45]

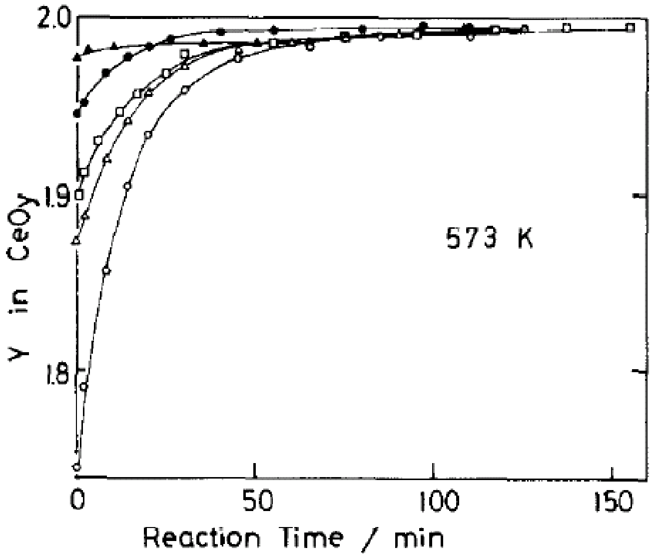


Figure 4.6 Kinetic curves of oxidation of various starting compositions of CeO$_y$: at 573 K. [45]

Typical regeneration times of 50 to 150 minutes result from figure 4.6. This is however very slow compared to the hydrogen combustion reaction and the regeneration with oxygen. Both the low regeneration temperature and the relatively small regeneration rate agree with the fact that water regeneration is not favourable.

4.2.7 Matlab simulation

In order to estimate the required reactor size and volume and estimate selectivity's of occurring reactions a Matlab simulation model has been written (Appendix 4.5). For details on programming and assumptions see chapter 8. The Matlab script results in a conversion-selectivity vs. reactor volume plot, as shown in figure 4.7. In the left figure the conversion and selectivity have been plotted. The conversion of propane appeared to be heavily dependent on the SOC concentration in the reactor, because the SHC reaction rate is increased. The SHC reaction rate constant is expressed as moles per second per kg SOC. Therefore as the SOC concentration in the reactor increases, the reaction rate increases. The SOC flow has been varied in large steps over a range of 1 up to 20,000 moles per second. A SOC flow of 10,000 moles per second proved to be a good quantity of SOC. At this amount of SOC the conversion was found to be about 62%. At higher SOC flows the conversion was higher, however it was found to be an unrealistic value for two reasons, firstly because a conversion of 62% was found to be practically achievable by Grasselli (see below) and secondly because the SOC flow becomes too unrealistically high. The volumetric load of 10,000 moles of SOC in the gaseous reactor feed does not exceed 2 vol%. The reaction rate proved to be sufficiently fast. Besides the increased reaction rate also heat integration favours a high SOC flow, since the SOC flow is also used as a heat carrier to transport heat from the regenerator to the reactor. The heat supplied from 10,000 moles of SOC per second is sufficient to ensure a reactor temperature drop of approximately 60 degrees Celsius, as shown in the right figure of figure 4.7. This temperature drop ensures almost constant reactivity over the complete reactor.

The optimal propylene yield is found at approximately 100 m^3. However a reactor volume of 51 m^3 is chosen, since the propylene conversion is practically the same at this volume.

Besides the advantage of a smaller reactor, also the selectivity of propylene is slightly higher. At this reactor volume the residence time is approximately 3.65 seconds, which is high enough to allow a conversion of approximately 57%. This conversion is comparable with literature by Grasselli on mixed DH+SHC reactors [44]. At higher residence times (and volumes) the selectivity decreases as shown in figure 4.8. This effect is caused by thermal cracking side reactions. Since most thermal cracking reactions have very low reaction rates (10^{-5} moles per m^3 per second), these side reactions have been neglected in Aspen simulation. Only reactions 4.7 and 4.13 proved to be more influential. From the Matlab model, fractional conversions of all relevant reactions have been calculated, as shown in table 4.11. These fractional conversions will be used in AspenPlus simulation.

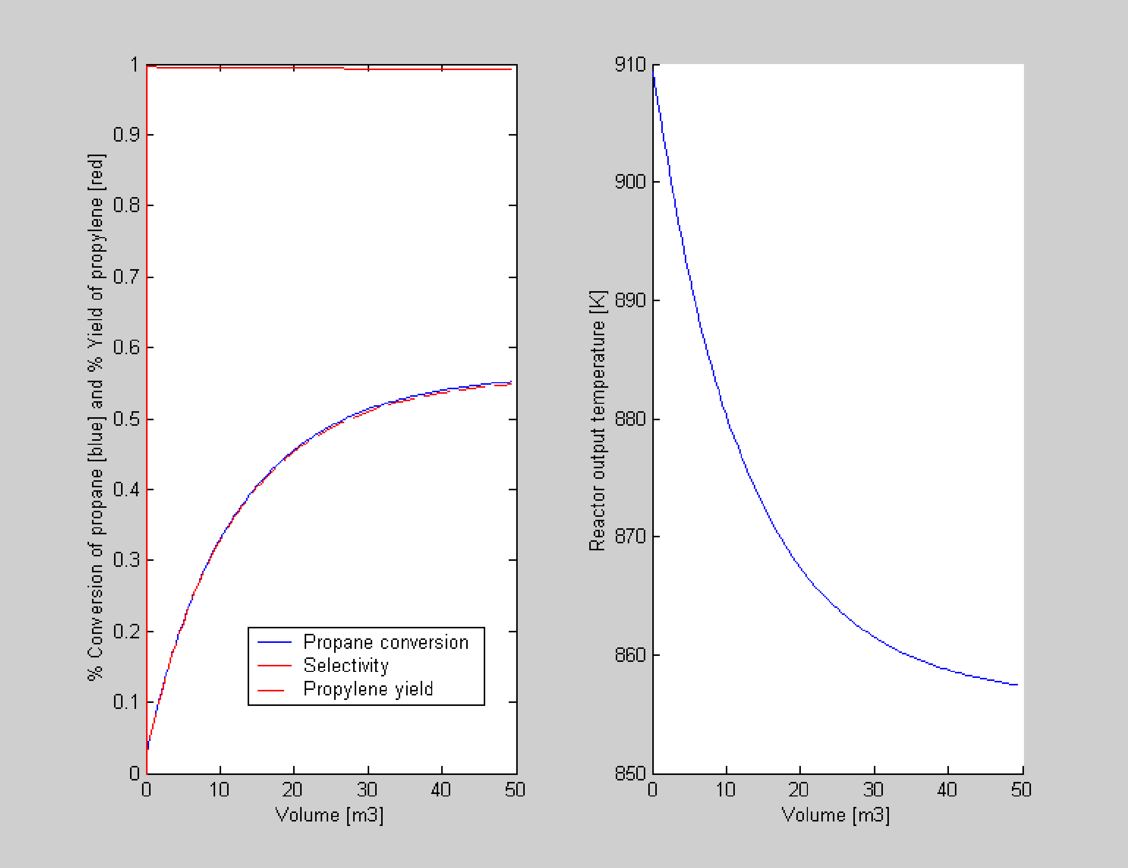


Figure 4.7 Matlab results

Table 4.11 Fractional conversions

Reaction:	**Fractional conversion:**	**Of component:**
Dehydrogenation reaction	0.58	Propane
SHC reaction	0.877	Hydrogen
SHC side reaction	0.002	Propane
SHC side reaction	0.0025	Propylene
Thermal cracking (4.7)	0.0025	Propane
Thermal cracking (4.13)	0.003	Propylene
Spent SOC regeneration	1.00	Spent SOC

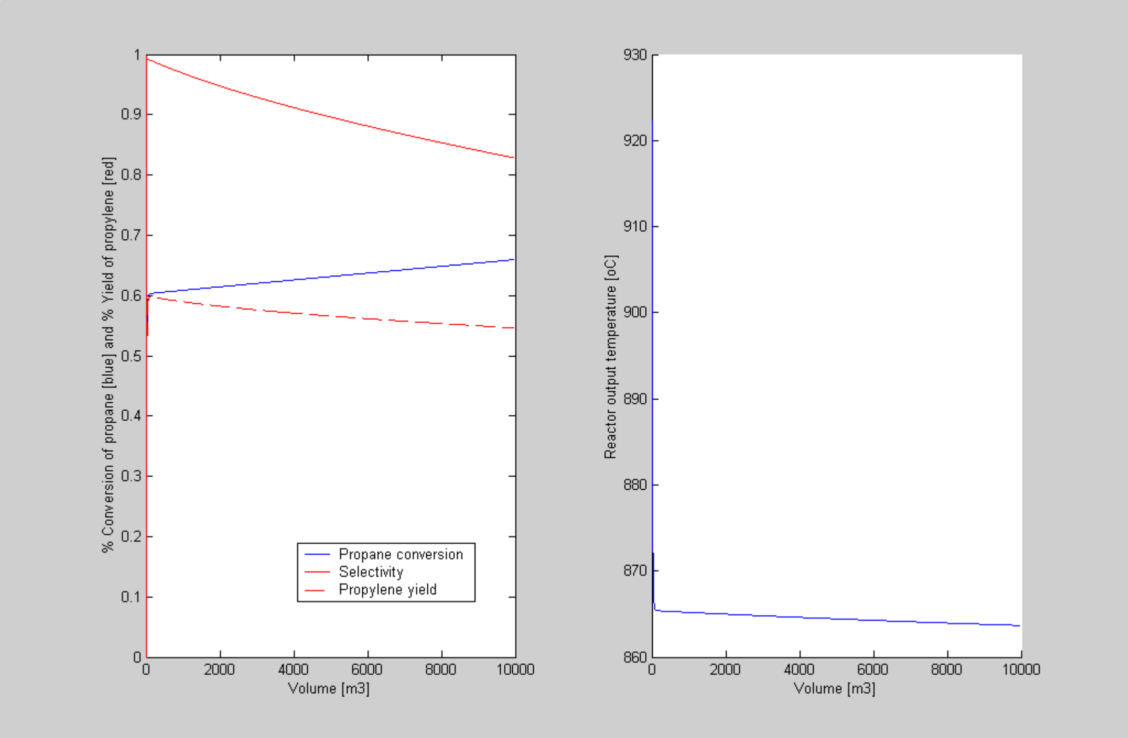


Figure 4.8 Matlab results for higher residence times

Because of the highly exothermal regeneration of spent SOC to fresh SOC the reactor temperature initially is 955 K. A higher SOC temperature is not allowed because of sintering of the SOC at higher temperatures. In order to obtain reasonable reactor temperatures, the gaseous feed will be fed to the reactor at 651 K. This results in average reactor temperatures of around 873 K. At this temperature the dehydrogenation rate is sufficient. A temperature decrease appears to have a very negative impact on conversion as shown in figure 4.9, where the temperature is approximately 773 K.

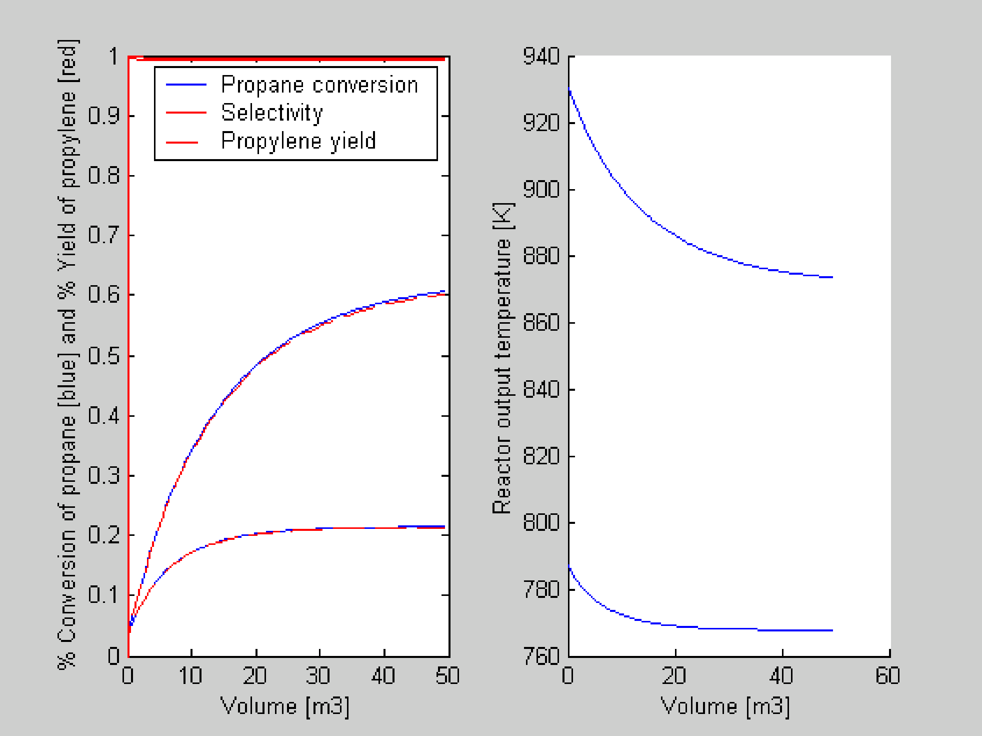


Figure 4.9 Matlab results for lowered temperatures

5 Process structure and description

In this chapter the tasks from the block scheme of Appendix 3.1 will be translated into unit operations and equipment. First the mass balances of the preliminary block scheme will be described. Then the recycle structure will be determined and thereafter the structure of the separation system will be determined. Subsequently the heat exchanger network is designed. From these structures, a process flow scheme (PFS) is developed and described, along with the process stream summary (PSS). The process stream summary (PSS) forms a unity with the process flow scheme. An overview of the utilities is given and the process yields are determined.

5.1 Mass balances of preliminary block scheme (Appendix 5.5)

Simple mass balance calculations were done to get a first idea of the amounts of various components and streams. In this way a preliminary the block scheme of Appendix 5.5 could be produced. The conversion of the DH reaction is set on the conversion calculated from the thermodynamic equilibrium, namely 62 mole%. For the dehydrogenation a selectivity of 90 mole% is assumed (this is the selectivity of the Pt-catalyst used in the Oleflex process). The conversion of the SHC reaction is set on 88 mole%; this is also the equilibrium conversion. The selectivity of the selective hydrogen combustion is 97 mole%. This means that 97 mole% of the SOC is used to convert the hydrogen to water. The other 3 mole% of the SOC is used to oxidize hydrocarbons. Other assumptions are:

- The product stream contains 99.5 wt% propylene
- The impurity in the product stream will be mostly propane (0.5 wt%)
- The feed stream is LPG, which consists of 95 wt% propane, 3 wt% butane and 2 wt% ethane.
- Per year there are 8000 operating hours

With these assumptions the streams in the block scheme can be calculated and this is shown in the next table.

Table 5.1 Results from mass balances calculation of block scheme

	Stream	**kta**	**t/h**	**kmol/hr**	**t/t**
Product stream (99,5wt% propane)	OUT 8	**250.00**	31.25		1.00
Propylene out	8	248.75	31.09	738.92	1.00
Propane in reactor	2	467.08	58.39	1324.23	1.87
Propane out reactor	4	177.49	22.19	503.21	0.71
Propane in product	8	1.25	0.16	3.54	0.01
Propane recycle	7	176.24	22.03	499.66	0.70
Propane in feed	1	290.84	36.36	824.57	1.16
LPG (95wt% propane) feed	IN 1	**306.15**			1.22
C4 in LPG (3wt%)	3	9.18	1.15	19.75	0.04
C2 in LPG (2wt%)	2	6.12	0.77	25.45	0.02
Propane + C2 reactor in	2	473.21	59.15		1.89
H2 reactor uit	4 = OUT 11	**1.43**	0.18	88.67	0.01
H2 formed by DH propane		11.92	1.49	738.92	
H2O formed by SOC	OUT 9	**93.71**	11.71	650.25	0.37
O2 (0.5 mol O2 --> 1 mol H2O)	IN 12	**83.23**	10.40	325.12	0.33
Total 4 (2+12)	4	556.43			2.23
Total 4 (7+8+9+10+11)	4	556.43			
By-product	OUT 10	**35.05**			0.14
Mass balance check		kta			t/t
IN = LPG + O2		389.38			1.56
OUT = product + H2O + by-product + H2		389.38			1.56

5.2 Recycle structure

To design the recycle structure of the Hipphox process the method described in chapter 6 of Douglas [24] is used.

5.2.1 Recycle structure decisions

First the number of reactor systems is determined. One reactor system is required for the DH and SHC (R1). Furthermore a reactor system is needed for the regeneration of the SOC (R2).

A solid-gas separation is necessary between R1 and R2 and between R2 and R1. Then the number of recycle streams is determined. There are two recycle streams: the propane recycle and the SOC recycle. The propane recycle is the bottom stream of the P/P-splitter, which will be liquid, therefore no compressor is required. The SOC recycle is a solid stream and has to be lifted with a lift system.

In table 5.2 all components and their destinations are given.

Table 5.2 Components and their destination

Component	**NBP* (°C)**	**Destination**
H_2	-253	By-product
C_{2-}	~-95	By-product
Propylene	-47.6	Primary product
Propane	-42.1	Recycle – liquid
C_4^+	~-5	By-product
SOC		Reactant – Recycle to R1 – solid
SpentSOC		By-product – stream to R2 – solid
Pt catalyst		Catalyst in reactor

*NBP = normal boiling point

In order to obtain a high conversion of the propane an excess of SOC is used, see chapter 4.2.7. The amount is calculated from kinetics. With the mass balances it can be calculated how much SOC is required to convert the formed hydrogen to water. However with this flow of SOC in the reactor the reaction will not take place, as the kinetics are then too slow. Therefore an excess of SOC is needed in the reaction section.

These decisions lead to the recycle structure of the Hipphox process given in figure 5.1.

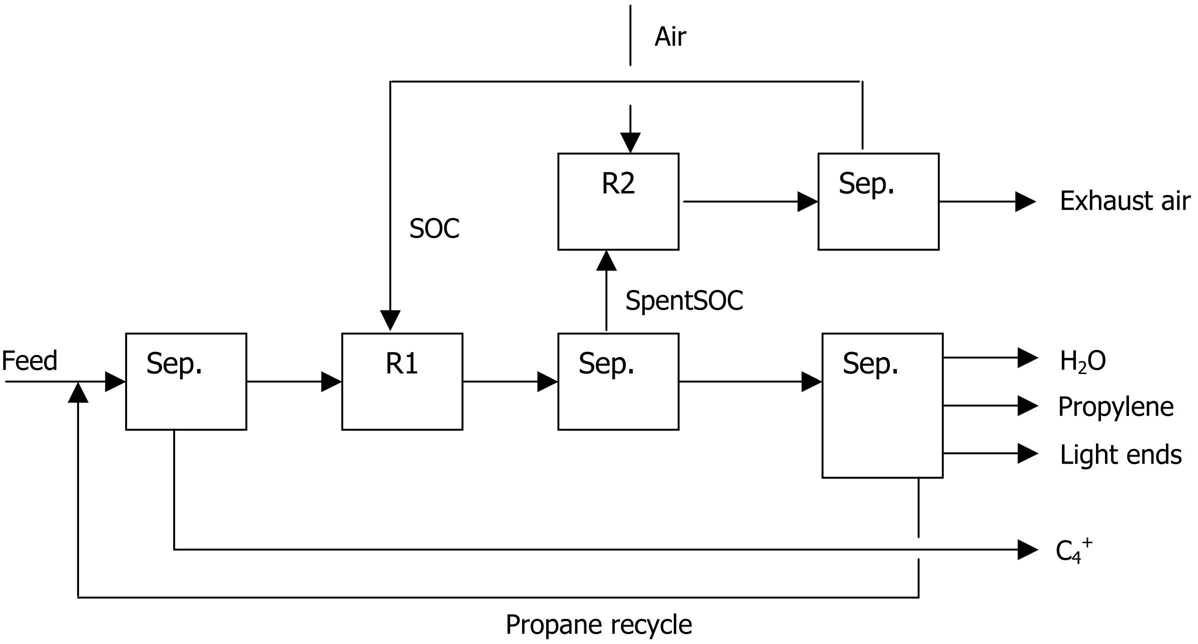


Figure 5.1 Recycle structure Hipphox process; R1 and R2 are reaction systems, Sep. are separation systems.

5.2.2 Recycle material balances

First a material balance is made for the component propane. The conversion of propane is first calculated base on equilibrium conversion, it is 62 mole%. Later more accurate calculations based on the kinetic model were simulated and resulted in a lower conversion of 57 mole%. The amount of propane required in the reactor system can be calculated from the production rate of propylene, which is 250 kta (99.5 wt% purity; 739 kmol/h). This means that 43 mole% of the propane will not be converted and has to be recycled.

In an early stage of the design the selectivity of the DH reaction was based on literature [10]. Therefore first selectivity is set to 90 mole%. The final selectivty was based on the kinetic model for the dehydrogenation. This resulted in a selectivity of 99 mole%, which is not used in these calculations, since these calculations are first estimates.
The amount of propane required in the reactor is therefore:

$$F_{propane} = \frac{F_{propylene}}{\xi \cdot S} = \frac{739}{0.62 \cdot 0.9} = 1324\,\text{kmol/hr}$$

In the product stream there will be 0.5 wt% of propane present. The recycle stream will therefore contain the following amount of propane:

$$F_{R,propane} = F_{\text{propane}} - F_{\text{propane\_converted}} - F_{\text{propane\_in Product}}$$

$$= 1324 - 0.62 \cdot 1324 - \frac{0.005 \cdot 250 \cdot 10^3}{M_{propane} \cdot 8000} = 500\,\text{kmol/hr}$$

The recycle stream of SOC

For every mole of hydrogen converted, 5 moles of SOC are needed. From the mass balances it is calculated that 650 kmol/hr hydrogen will be converted to water. This means that 5•650=3251 kmol/hr of SOC is needed for the SHC. However the selectivity of the SOC is 97%; this means that 97% of the SOC is used to convert hydrogen into water and 3% of the SOC is used to convert the hydrocarbons into CO and CO_2. Mostly CO will be formed due to the very low oxygen concentrations. This also resulted from the kinetic modelling. Therefore in the calculations and the simulations the formation of CO_2 is not taken into account. So the amount of SOC needed in the reactor is 3251/0.97=3352 kmol/hr. This amount of SOC will be regenerated in reactor system R2. An excess of SOC is needed to satisfy the kinetics and the heat balances.

5.2.3 Reactor heat effects

From the thermodynamic calculations the enthalpy values for the reactions are calculated. This is shown in table 5.3. The combined reaction of DH and SHC is endothermal. The heat load of the reactor (R1) can be calculated.

Table 5.3 Reaction enthalpy values for all reactions

R1:	**Reaction enthalpy ΔH_R**	
DH	130	[kJ/mole propylene]
SHC	355 + -247	[kJ/mole H_2O formed]
Side reactions DH	-26	[kJ/mole by-product]
Side reactions SHC	36	[kJ/mole SOC]
R2:		
Regeneration exhaust SOC	-71	[kJ/mole exhaust SOC]

The conversion of the hydrogen by the SHC reaction is 88% (see chapter 4.1.3). The reactor heat load is mainly determined by the DH and SHC reaction. From the production rate of propylene, the amount of hydrogen formed can be calculated and therefore also the amount of water formed.

$$F_{H_2O} = F_{propylene} \cdot \xi_{SHC} = 739 \cdot 0.88 = 650\,\text{kmol/hr}$$

$$\text{Reactor heat load}_{\text{main reactions}} = \Delta H_{R,DH} \cdot F_{propane} \cdot \xi_{DH} \cdot S_{DH} + \Delta H_{R,SHC} \cdot F_{H_2O}$$

$$= 9.61 \cdot 10^7 + 7.02 \cdot 10^7 = 1.66 \cdot 10^8 \text{ kJ/hr}$$

5.2.4 *Heat effects of side-reactions*

Side reactions DH

As the selectivity of the DH reaction is in the first calculation 90 mole%, 10 mole% of the propane is converted by thermal cracking. The enthalpy of the side reactions is determined by the mean value of the enthalpy of the most important thermal cracking reactions.

$$\text{Reactor heat load}_{\text{side reactions DH}} = \Delta H_{side\_DH} \cdot F_{propane} \cdot \xi \cdot (1 - S)$$

$$= -26 \cdot 1324 \cdot 10^3 \cdot 0.62 \cdot 0.1 = -2.13 \cdot 10^6 \text{ kJ/hr}$$

Side reactions SHC

The side reactions of the SHC are the oxidation of the hydrocarbons to carbonmonooxide. In the thermodynamic calculations the reaction enthalpy of the main side reactions is determined, see table 5.3. The heat effect of the side reactions of SHC is therefore:

$$\text{Reactor heat load}_{\text{side reactions SHC}} = \Delta H_{side\_SHC} \cdot (1 - S) \cdot F_{SOC}$$

$$= 36 \cdot 0.03 \cdot 3352 \cdot 10^3 = 3.62 \cdot 10^6 \text{ kJ/hr}$$

Regeneration SOC

In reactor R2 the exhaust SOC will be regenerated using oxygen. The heat of reaction of the regeneration is –71 kJ/mole. This value is obtained from the thermodynamic calculations, see chapter 4.1.5. All the SOC will be regenerated, as the equilibrium constant is high enough.

The reactor heat load for R2 is therefore:

$$\text{Reactorheatload}_{\text{R2}} = F_{SOC} \cdot \Delta H_{regenerationSOC} = 3352 \cdot -71 = -2.38 \cdot 10^8 \text{ kJ/hr}$$

Adiabatic temperature change in the reactor

With the values in table 5.4 the adiabatic temperature change can be calculated.

Table 5.4 Data of the reaction section feed

Stream	**kmol/hr**	**Cp (kJ/kmolK)**
Propane feed	825	160
Propane recycle	500	160
C_2	25	110
SOC recycle	3352	62

This value is calculated using the amounts needed stoichiometrically.

$$\Delta T_{ad} = T_{R,out} - T_{R,in} = \frac{\text{-Reactor heat load}}{F \cdot Cp}$$

$$\Delta T_{ad} = \frac{-1.86 \cdot 10^8}{(825 + 500) \cdot 160 + 25 \cdot 110 + 3352 \cdot 60} = -398$$

From these calculations it shows that the temperature effect from the endothermal reactions is very large.

However, the amount of SOC can be increased, as the SOC can act as a heat carrier (see chapter 4.2.7). Furthermore the kinetics require a larger load of SOC in the reactor as otherwise the reaction will not take place. If more solids are present in the reactor the adiabatic temperature rise will be smaller. This will be calculated in the following paragraph.

Adiabatic temperature change from SOC regeneration

All the SOC that is being used in R1 has to be regenerated. The adiabatic heat change can be calculated. First the amount of air needed for the regeneration has to be calculated. For every mole of exhaust SOC 0.1 mole of oxygen is needed. In air 21v% oxygen is present. From these values the air flow at 1 bara needed for the regeneration can be calculated.

$$F_{air} = \frac{0.1 \cdot F_{exhaustSOC} \cdot M_{O_2}}{\rho_{O_2} \cdot 0.21} = \frac{0.1 \cdot 3352 \cdot 32}{1.35 \cdot 0.21} = 3.78 \cdot 10^4 \, \text{m}^3/\text{hr}$$

Table 5.5 Data of the regeneration feed

Stream		Cp
SOC exhaust	3352 [kmol/h]	60 [kJ/kmolK]
Air feed	$3.78*10^4$ [m^3/h]	1.38 [kJ/m^3K]

$$\Delta T_{ad} = T_{R,out} - T_{R,in} = \frac{\text{-Reactor heat load}}{F \cdot Cp}$$

$$\Delta T_{ad} = \frac{2.38 \cdot 10^8}{3352 \cdot 60 + 3.78 \cdot 10^4 \cdot 1.38} = 921 \text{ K}$$

The adiabatic temperature change of the regeneration section is very high. To make optimal use of the heat produced an excess of SOC will be used as an heat carrier.

Adiabatic temperature change using solid heat carriers

As the adiabatic temperature changes calculated in the previous paragraph are too high, the adiabatic temperature change is calculated when more solid are present in the reactor systems. The amount of solids is set to a value, which will satisfy the kinetics and the heat balances. This is done using Matlab and described in chapter 4.

5.2.5 Equilibrium limitations

The conversion of the DH and SHC reactions were set on 62% and 88% respectively. These values are based on the equilibrium composition calculated in chapter 4. Higher conversions are therefore not possible. The aim is to achieve a conversion with a value near the equilibrium value. This optimilization is done designing the reactor simulation in Matlab, also described in chapter 4.

Diluents

In the Oleflex process hydrogen is used to dilute the feed stream, in order to prevent coke formation. A disadvantage of dilution in the Hipphox process would be the poor heat integration; the diluent would carry a lot of heat out of the reactor. Since heat is required for the DH and SHC reaction, dilution is not desirable. In the Hipphox process dilution is less necessary than in Oleflex, as water is formed during the reaction. Water is known to prevent coke formation [17]. Furthermore dilution with hydrogen will influence the equilibrium conversion and this is not desirable. Another option is to dilute with water. The dilution with water will indirectly influence the equilibrium conversion of DH, since it will influence the conversion of reaction 2.5. Dilution with inert components, like CO_2, is also not desirable because of environmental issues. As water will be formed during the reaction, this will prevent coke formation. Therefore the decision was made not to dilute the feed stream.

5.2.6 Reactor design

For the reactor there are several options available. As the SOC has to be regenerated continuously, no fixed bed can be applied. The options available are a riser reactor, fluidized bed reactor, moving bed reactor and radial flow moving bed reactor. However in a later stage of the design it became clear that the Pt catalyst does not need to be regenerated. So it is very preferable to immobilize the Pt catalyst. One very promising option is the monolith reactor [57]. This is described in chapter 8.2.1. The design criteria for the reactor are high conversion, good heat integration and an optimal amount of SOC in the reactor.

5.3 Separation system

The reactor effluent steam is all vapour. It is cooled to 30 ^{0}C to acquire a phase split. The condensed liquid is then sent to the liquid separation system and the vapour to the vapour separation system. It is chosen not to feed the reactor effluent directly to a distillation column, since the water needs to be removed first. This has as a disadvantage that some traces of light ends and product will leave with the liquid stream. But when the vapour is sent directly to the distillation column which separates the light ends from the product stream, the water will damage the system, since it is a cryogenic distillation.

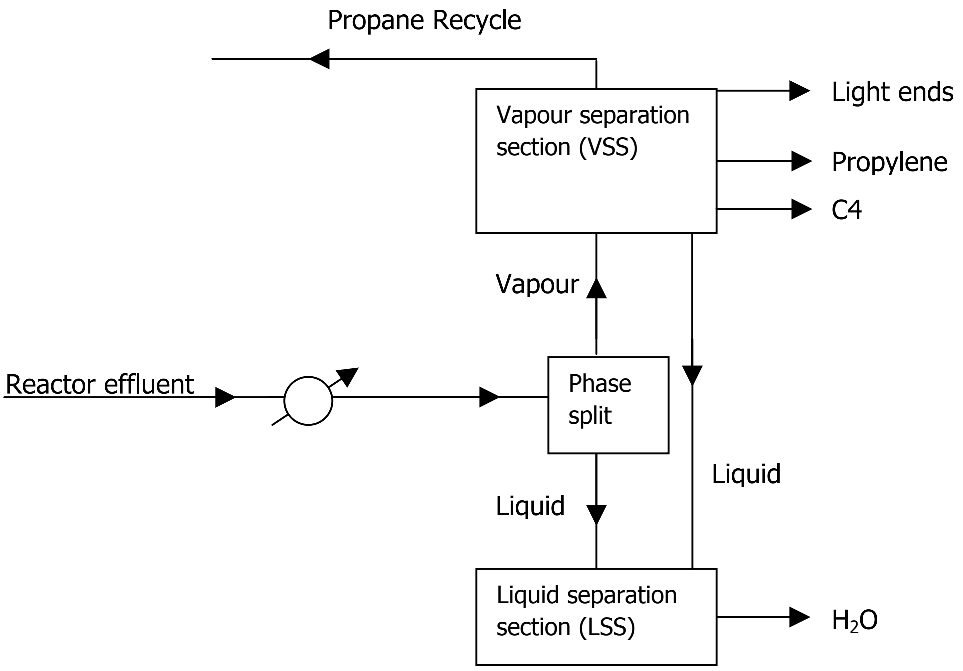


Figure 5.2 Flow scheme reactor section

The vapour separation section (VSS) is the product recovery section and is called "vapour separation section" because it treats the vapour phase after the phase split. In the VSS also liquid streams are present, because of the distillation columns that are required. The liquid separation section (LSS) is just the water removal from the hydrocarbon stream.

5.3.1 Vapour separation section

The product stream has to be refined to a 99.5 wt% pure propylene stream. The first step in the design of the VSS is the lumping of the different components present into groups with boiling points in the same temperature range. The results are presented in table 5.6.

Table 5.6 Lumping of components in vapour separation system

Component	**Formula**	**Boiling point [°C]**	**Mass flow [kg/hr]**	**Lump group**
Hydrogen	H_2	-252.87	184	A
Carbon monoxide	CO	-191.50	248	A
Methane	CH_4	-161.48	58	A
Ethylene	C_2H_4	-103.77	38	A
Ethane	C_2H_6	-88.60	632	A
Propylene	C_3H_6	-47.60	31475	B
Propane	C_3H_8	-42.20	23637	C
Butane	C_4H_{10}	-11.70	10	D
1-Butene	C_4H_8	-6.20	131	D
Water	H_2O	100.00	11927	E

The next step is the design of the column sequence. This is done based on the heuristics given in [24, page 177].

Most plentiful first

The most plentiful component in the reactor effluent that has to be separated from the product, measured in kg/hr, is propane and then water; see Appendix 5.1, stream <108> and table 5.6. The mole flow of water in the reactor effluent is even larger. Therefore the water separation needs to be done first.

Lightest first

The lightest lump is group A, see table 5.6, therefore group A needs to be separated first.

High recovery separation last

The product stream needs to be 99.5wt% pure, therefore the propane - propylene separation should be done last.

Difficult separation last

The propane – propylene separation is the most difficult, the relative volatility is about 0.9. This separation should be done last.

Favour equimolar splits

Group B, C and E are in the same molar range. The optimal configuration is the removal of water first, and then the separation of A+B and C+D.

Next separation should be cheapest

The separation of light ends from the reactor effluent is expensive because of the cryogenic cooling that is required, and the propane - propylene separation is expensive because the relative volatility is low; a lot of trays are required.

These heuristics lead to contradictions, for example the most plentiful is also the heaviest (water). The propane – propylene separation is difficult and needs a high recovery, therefore the placement of this separation will highly influence the design of VSS. It is also very important to remove water first from the system, as mentioned before. Therefore it is

not an option to remove hydrogen first, even though it is the lightest component and present in considerable amounts.
This results in two feasible column sequences, as shown in figure 5.3.

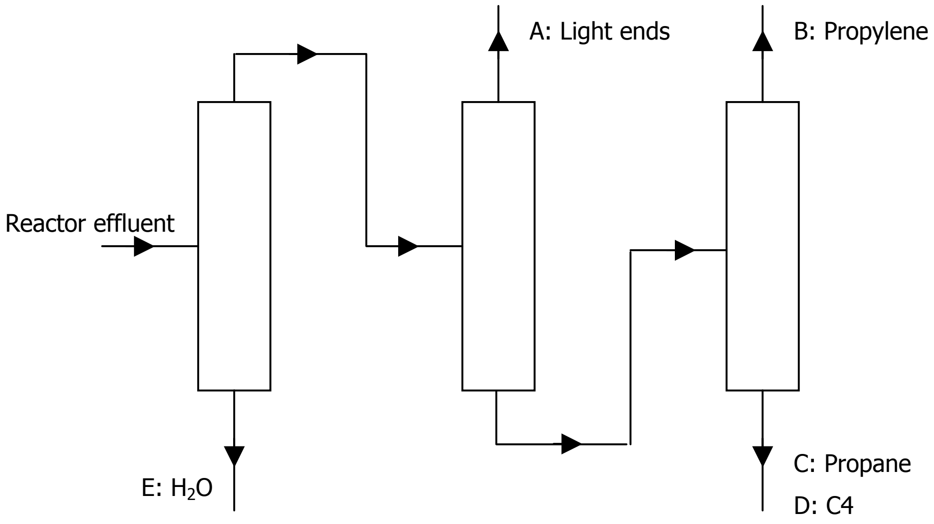


Figure 5.3 Column sequencing options, with lumped groups destination. Scheme 1: light ends removal before propane – propylene separation

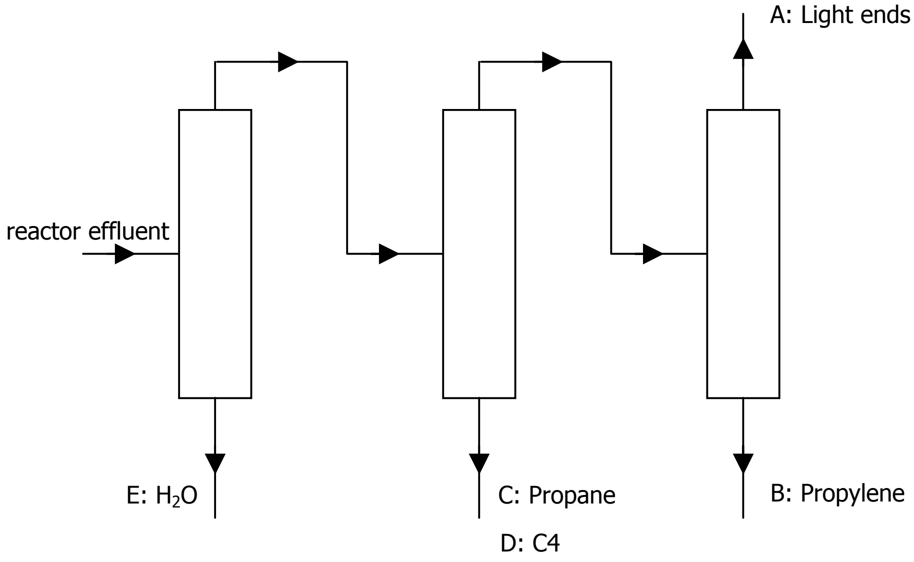


Figure 5.3 Column sequencing options, with lumped groups destination. Scheme 2: light ends removal after propane – propylene separation

The second option is a promising scheme, but the throughput through the propane-propylene separating column is higher, and probably too large to satisfy the product specifications. Therefore scheme 1 is chosen.
The propane and C4 are recycled to the separation section before the reaction section, see figure 5.1. For this separation a distillation column is used, because the separation of C4 from C3 is difficult and no alternatives are available on large-scale. A stabilizer column is chosen for the separation.
The separation of the light ends from the propane-propylene stream is not possible on large scale with alternatives like adsorption or membranes; therefore a distillation column is used.

The same holds for the separation of propane and propylene. Since the light ends removal is a difficult separation, a stabilizer column is chosen, with cryogenic cooling. The propane – propylene separation is even more difficult, therefore here a stabilizer column is used as well.

5.3.2 Liquid separation section

The phase split results in an aqueous stream containing traces of light ends and product and a vapour stream containing small amounts of steam. The aqueous stream is directly sent to the wastewater treatment, which is outside the battery limits of Hipphox. In chapter 9 this stream will be discussed in more detail. From the vapour stream the steam needs to be removed, this can be done in several ways. Most commonly applied are molecular sieve zeolites and absorption. An example of a molecular sieve zeolite is zeolite 3A. This zeolite only absorbs water and does not absorb any larger molecules. However, as there is also hydrogen present in the gas stream, this will also be absorbed and this is not desirable.

Absorption can for example be done with triethyleneglycol (TEG) as absorbent. This is widely applied in the petrochemical industry. The water is removed from the wet gas by counter current absorption in a liquid with a high boiling point. TEG has a high boiling point and a high selectivity for water. The TEG is recovered in a stripping column, where the water leaves the top and the TEG is recycled to the absorber. This system is well suitable for the water removal from the hydrocarbon stream in Hipphox. Because this system is already commercially available, this unit is not designed in detail nor simulated in the conceptual process design. An estimate is made to determine the investment costs of removing the water from the gas stream, see chapter 11.1.

Design criteria for distillation columns

As is described above, in the Hipphox process five columns are used. The first column is the depropanizer C101 for purification of the reactor feed. For this column two criteria are important. The amount of C4 in the reactor has to be low because this stimulates side reactions. Also the amount of propane in the bottom stream has to be low because this is inefficient use of raw materials.

The water is absorbed in C102 with glycol. All the water has to be removed because of the cryogenic cooling in the next column. The goal for C103, the stripping column for glycol is to recover as much as glycol as possible.

The column for light ends removal, column C104, is operating with cryogenic cooling. Therefore the economic aspects of this column influence the design. As cryogenic cooling is expensive the cooling duty has to be as low as possible to meet the product specifications. The light ends have to be completely removed, at least as far as possible, for the last column to operate well. Therefore a small loss of propylene and propane is accepted in the top stream.

In the last column, the PP splitter, C105, the most important overall specification is the product stream of 99.5 wt% propylene. Because this separation is difficult one of the goals in the design is to prevent cryogenic cooling because of economic aspects. Also, the recycle stream should not be too large, to minimize the recycling costs.

Table 5.7 Summary of design criteria for columns

Column	**Name**	**Design Criteria**	
C101	Depropanizer	Traces of butane in top stream	Less raw material loss in bottom stream
C102	Contactor (Absorber)	All water is absorbed	
C103	Reconcentrator		Recovery of glycol
C104	De-ethanizer	Low cooling duty	
C105	PP-Splitter	99.5 wt% propylene in top	No cryogenic cooling

5.4 Heat integration

Heat integration is a very important aspect of process integration. Two important factors in the Hipphox design are the heat integration by heat exchangers and the use of a heat pump in the propane-propylene splitter.

Heat pump

A heat pump is an energy saving optimalization. Besides heat savings also the required amount of cooling water is reduced, which are the main design criteria. When a heat pump is used, the overhead vapours of column C105 are mechanically compressed and fed to the column reboiler as shown in figure 5.4 [54].

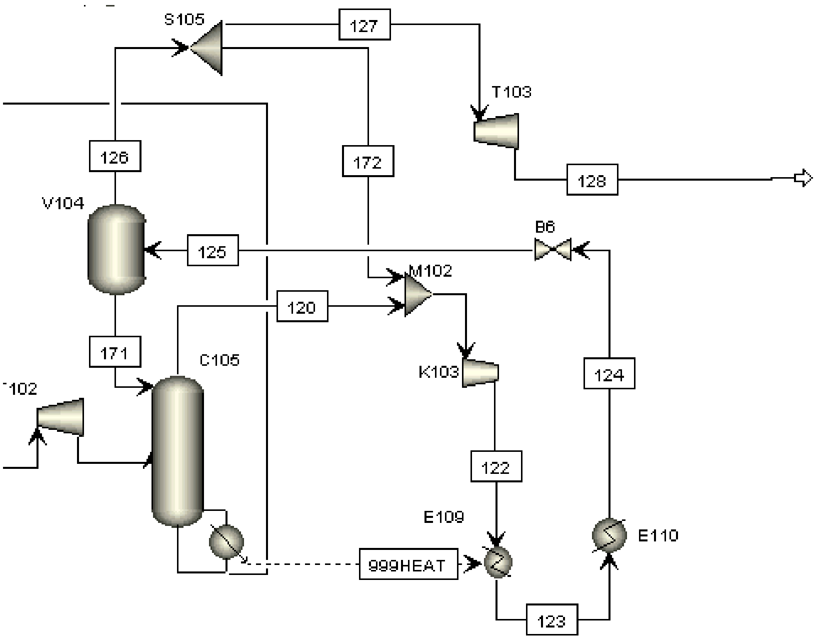


Figure 5.4 Heat pump design

The vapour stream is compressed from column pressure (10 bara) up to 18 bara. After compression to 18 bara the gaseous top stream is fed to the column reboiler. In the reboiler the top stream transfers heat to the reboiler and condenses. After transferring heat from the compressed top stream, the top stream is fed to a trim heat exchanger. This heat exchanger ensures sufficient condensate after decompression to column pressure. The heat exchangers cool the distillate to 302.6 K. After decompression and an adiabatic flash, this results in sufficient liquid distillate. At S105 (SP101 in PFS) a part of the propylene product is recycled to the compressor to allow sufficient reflux and product quality.

Recompression of the distillate renders the condenser obsolete. This allows a lower column operating pressure without using costly cryogenic cooling. A lower column pressure allows a smaller column since the separation factor increases as pressure drops. A total of 119 actual stages are required to obtain sufficient distillate purity.
The total energy consumption of a heat pump driven distillation column is compared to a conventional distillation column.

Table 5.8 Overview of propane-propylene distillation column duties

	Conventional distillation	**Heat pump distillation**
Condenser duty [kW]	-45479	0
Reboiler duty [kW]	41944	0 (39702)
Total compressor duty [kW]	0	5300
Trim heat exchanger duty [kW]	0	-8868

As shown in table 5.8, a heat pump distillation column is more energy efficient and does not require expensive cryogenic cooling. However a heat pump distillation column does require mechanical energy to compress the overhead vapour. The economics of a heat pump distillation column heavily depends on the price of mechanical energy (electricity). Besides the higher electricity cost, also the investment cost are considerably higher due to a expensive gas compressor. Documentation of industrially applied heat pump systems [66] indicates a payback time of approximately 2 years. This is relatively small compared to the plant lifetime.

Heat exchanger network

All heat exchangers, reboilers and condensers have been integrated. Also reboilers and condensers have been taken into account since this equipment has a mayor impact on heat integration in the Hipphox process. The first step is to make an overview of all streams, reboilers and condensers as found in Appendix 5.2. In order to obtain a Temperature-Enthalpy graph a temperature change of 1 degree has been chosen for phase transitions in reboilers and condensers. A minimum temperature difference of 10 degrees has been chosen in order to design robust heat exchangers. From the overview of streams cold and hot composite curves have been constructed, as shown in figure 5.5.

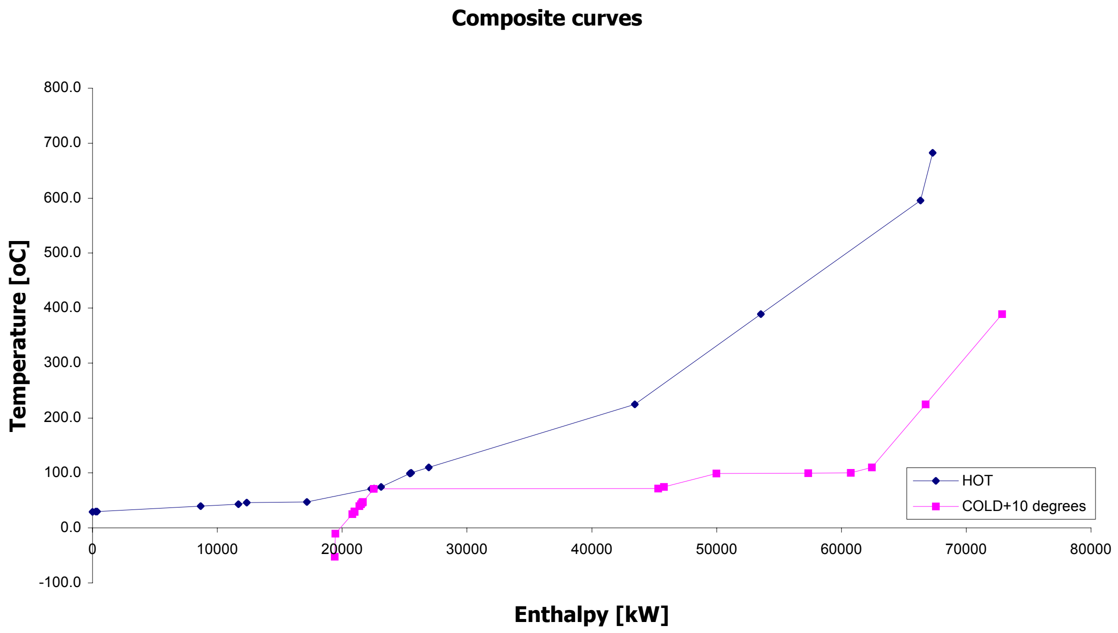


Figure 5.5 Hot and cold composite curves.

A pinch temperature of 70.9 degrees Celsius is calculated. A minimum of 5349 kW of hot utilities and 19188 kW of cold utilities are calculated from this graph. The second step is the construction of a grand composite curve in order to estimate the type of required utilities.

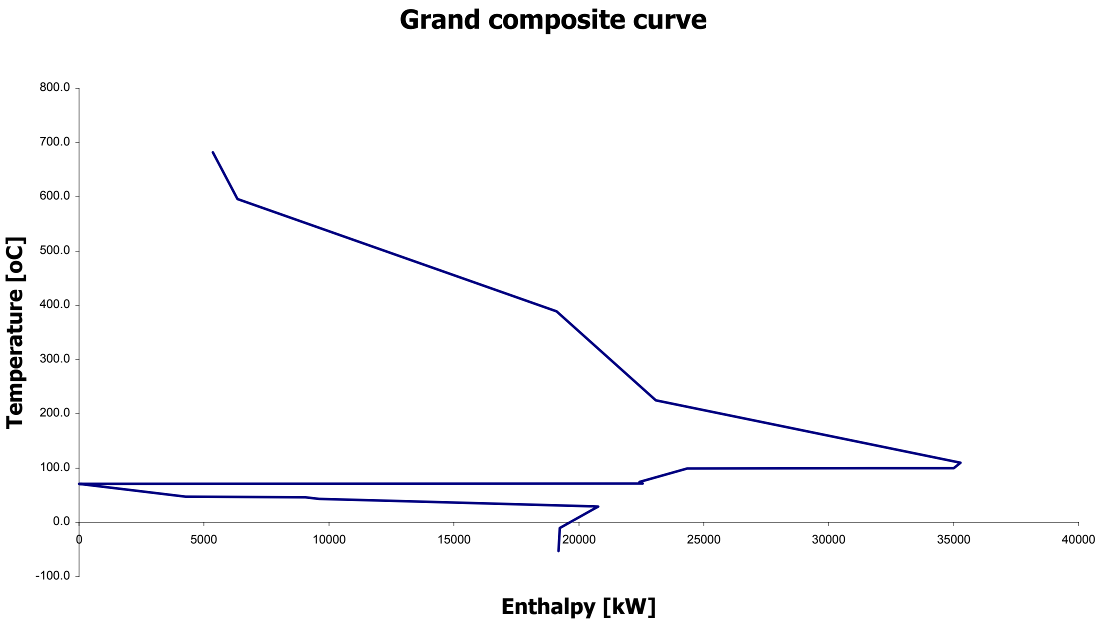


Figure 5.6 Grand composite curve.

From the grand composite curve can be found that hot utilities can be supplied at a temperature as low as 70.9 degrees Celsius. A low-pressure steam heater would be sufficient. Cooling water can be used for all cooling purposes, except for cryogenic cooling. Since the pinch temperature and utilities are now known, a theoretical heat exchanger network can be set up. A heat exchanger network (HEN) is set up by coupling hot streams to cold streams above and below the pinch temperature.

Table 5.9 Overview of Heat Exchangers

IN	OUT	PFS equipment:	IN	OUT
106	107	E102	158	159
106	107	E103	109	110
117	118	E106	109	110
C101 reboiler		E105	109	110
C104 reboiler		E107	109	110
C104 reboiler		E108	111	112
C104 reboiler		E111	115	116
Heater		E118	C104 reboiler	
185=168	175	E109	111	112
106	107	E104	115	116
Cooler		E110	111	112
Cooler		E112	115	116
Cooler		E116	158	159
Cooler		E115	123	124
Cooler		E101	C101 Condenser	
Cooler		E113	C104 Condenser	
Cooler		E117	154	170
122	123	E114	C105 Reboiler	

A systematic approach of coupling the hottest hot stream to the hottest cold stream has been used, in order to minimize additional utilities. The HEN as shown in table 5.9 integrates column reboilers, condensers and all process heat exchangers. One drawback of this proposed HEN is the controllability of the process. By heat integration several degrees of freedom in controlling the distillation columns are lost. To counter this effect in practice additional heaters or coolers will be placed in order to allow proper controllability of column temperatures. In order to account for additional cost of these extra heaters and coolers a very rough margin of 20 % extra cost will be assumed. For detailed cost design data see chapter 11.

Unfortunately the HEN exchanger network was developed before tuning the C104 reboiler column (de-ethanizer). The column was optimized in order to reduce cryogenic cooling cost as described in chapter 8.1.5. However changing the reflux ratio of a column has a large impact on the column reboiler capacity. The reboiler had already been integrated in the heat exchanger network. The reboiler duty is reduced to 5134 kW instead of 21582 kW. From figure 5.5 can be observed that the pinch temperature will probably not be changed by the decreased reboiler duty. However the amount of hot utilities required will be different since the cold composite curve will be "shifted" to the left side of figure 5.5. Due to lack of time the HEN is not adjusted to the new and correct values. Instead the known error is included in the design error. Since required utilities will be slightly decreased and moved towards cooling utilities instead of heating utilities, no dramatic impact on total cost is expected.

5.5 Process Flow Scheme (PFS)

In Appendix 5.3 the process flow scheme (PFS) is given. In this paragraph a step-by-step process review will be given.

The feed stream LPG <129> contains propane, ethane and butane. It enters the flow scheme from storage and is pumped by pump (P109) to be mixed with the propane recycle <151> into the feedstream <102> for the depropanizer (C101). The propane recycle contains also heavy components, which are formed in the monolith reactor (R101). In the depropanizer these heavy components (C_4^+) will be separated from the propane and light ends. The top stream <103> is cooled by a condensor (E101) and is sent to the reflux accumulator of C101 (V101). A part <178> is refluxed to the column by the reflux pump of C101 (P101). The depropanizer (C101) operates at a top pressure of 16.7 bara. The overhead of C101 <105> is expanded by expander (T101) to 2 bara, since this is the operating pressure of the monolith reactor (R101). Furthermore this stream is heated by heat exchangers (E102, E103 and E104) as the operating temperature of the reactor is higher than the overhead stream of C101. Heat exchanger (E105) is the reboiler of C101. Stream <107> is the gas feed stream for the monolith reactor (R101). In this reactor the propane is converted to propylene and the hydrogen formed by the dehydrogenation is combusted to water. The other feed stream of the monolith reactor is the SOC stream <157> supplied by hopper H102.

The effluent of R101 is a mixed gas and solid stream <108>. The solids are separated from the gas stream by cyclones (S101). This unit consists of three cyclones in parallel, shown as one unit in the PFS. The solid stream <155> contains spent SOC that will be regenerated in the riser reactor (R102). The solids are transported by gravity force in a hopper (H101) to the entrance of the riser reactor. An air stream <174> will lift the solids and regenerates the spent SOC. This air stream is first compressed by a compressor (K104) since the inlet pressure of the riser is 2.35 bara. Due to the compression the air stream is also heated. The effluent of R102 is sent to cyclones (S102) to separate the solids from the gas stream. This cyclones unit consists of five cyclones in parallel. The air stream is almost completely removed from the solids stream, as the air with a small amount of oxygen is not allowed to enter the reactor for safety reasons. The solids are then transported by gravity back to the monolith reactor. The exhausted air stream <158> is sent to heat exchanger (E102 and E116) to be cooled.

Returning to the first cyclones unit (S101) the gas stream containing the product <109> is cooled by heat exchangers (E103, E105, E106 and E107) and compressed by a compressor (K101). The compression is done because vessel V102 operates at 12 bara to achieve a good separation of the water from the hydrocarbons. This stream <111> is further cooled by a heat exchanger (E108, E109 and E110) to condense the water and sent to a vessel (V102). In this vessel the water is condensed to stream <160> and separated from the gas stream.

The water stream is sent to a wastewater treatment unit outside the battery limits. It contains traces of dissolved hydrocarbons. The gas stream <113> still contains some water. This is removed in the glycol unit. This glycol unit consists of a glycol contacter (C102) and a glycol reconcentrator (C103). The water is absorbed by the glycol and leaves the glycol contacter with stream <164>. In the glycol reconcentrator the water is removed from the glycol and leaves the column (C103) by stream <164> and is also sent to a wastewater treatment unit outside the battery limits. The reconcentrated glycol <163> is sent back to the glycol contacter.

The gas stream containing the propylene leaves the glycol unit by stream <114>. This stream is compressed by a compressor (K102) and cooled by a heat exchanger (E105). The compression is done to reach the operating pressure of the de-ethanizer (C104). This stream <116> is sent to the de-ethanizer (C104). The light ends stream (top stream <165>) leaves the de-ethanizer and is cooled by a condenser (E113). This stream <166> is sent to the reflux accumulator of C104 (V103). A part <167> is refluxed to the column by the reflux pump of C104 (P106). The overhead of C104 <168> is heated by a heat exchanger (E109) to leave the PFS as stream <185>. The bottom stream of C104 <117> partly reboiled by heat exchanger (E107, E108, E111 and E118) and sent to a heat exchanger (E106) to be heated. This stream <118> is expanded in expander (T102) to become the feed stream <119> of the P/P-splitter (C105).

In the P/P-splitter the propane is separated from the propylene. The propane leaves the column at the bottom as stream <169> and is recycled by a pump (P104) as stream <151> to be mixed with the LPG feed stream <101>. Heat exchanger (E114) is the reboiler of C105. The top stream of C105 <120> is sent to a compressor (K103) and is cooled by heat exchanger E114. The cooled stream <123> is sent to a heat exchanger (E115) and sent through a valve. This stream is then sent to the reflux accumulator (V104) of C105. A part <171> is refluxed to the column by the reflux pump of C105 (P107). The overhead of C105 <126> is the product stream. A part of stream <126> is sent back to stream <120> to allow sufficient reflux and product quality. Stream <126> is then expanded by a turbine (T103) to deliver the propylene product at 9 bara and 15°C. The whole system of C105, E114, K103, E115 and V104 works like a heat pump to minimize the costs and to save energy.

5.6 Process Stream Summary (PSS)

The process stream summary (PSS) is given in Appendix 5.1. The mass flows are tabulated for all components separately and the stream numbers are the same as in the process flow scheme. The mass and heat balances are checked (see chapter 7).

The composition of a few streams is not known. The reason for this is that these streams were not simulated in Aspen, as for columns C101 and C104 a RadFrac was used. This applies for the top streams of C101 and C104, the feed streams and discharge streams of V101 and V103 and the reflux streams of C101 and C104.

The product quality is met; the product should be 99.5 wt% propylene. However if polymer grade propylene is desired, the amount of ethane is too large. The product quantity is met, since the plant should produce 250 kta. This is shown in table 5.10.

Table 5.10 Propylene product specifications, stream <128>

	kta	**wt%**	**ppm by weight**	**wt% or ppm by weight allowed**
Propylene	248.9	99.6	-	99.5 wt% min.
Propane	0.9	0.3	-	0.5 wt% max.
Ethane	0.2	0.1	602.2	300
Ethylene	0.0	trace	1.9	10
Methane	0.0	trace	0.0	-
CO	0.0	trace	0.00	0.03
Total	250.0	100		

In the simulation the formation of carbon dioxide is neglected. It is however likely that some carbon dioxide will be formed. The specification requires that the maximal amount is 1 ppm by weight.
It is also assumed that no sulphur is present in the LPG feed. The amount of sulphur in the product stream can only be originating from the LPG feed, if any is present. The specification requires that the maximal amount is 0.5 ppm by weight.
Water removal is essential in the design, since the cryogenic cooling of column C104 causes problems when water is present. In the design the water removal is complete, but in practice some traces will be left. The maximal amount is 1 ppm by weight, required by the specification.
Finally in the design it is assumed that no dienes will be formed. The specification requires that the maximal amount is 2 ppm by weight for butadiene and propadiene together.

5.7 Utilities

From the heat exchange network the cold utilities and hot utilities have been calculated. Also it was determined that cooling water can be used a cold utility and low pressure steam as hot utility. With the heat duties the amount of cooling water and amount of low pressure steam can be calculated. This is done in table 5.11.

Table 5.11 Amounts of cooling water and low pressure steam

Coolers	**kW**	**Utility**	**Specific heat [kJ/kg/K]**	**Amount [t/a]**	**[t/h]**
E110	3271	CW	4	1118463	139.81
E112	2073	CW	4	862996	107.87
E116	357	CW	4	122885	15.36
E115	8871	CW	4	4510503	563.81
E101	4617	CW	4	1832319	229.04
Heater					
E118	5349	LP steam	2	154063	19.26

The top stream of column C104 has to be cooled with refrigerant (5135 kW). As the temperature is about -60 °C, liquid nitrogen is needed. By decreasing the reflux rate the amount of refrigerant can be decreased. This was done and described in chapter 8.2.2. This utility stream contributes for about 20% to the total costs of the utilities.

The duties of the pumps were calculated by simulation in Aspen. One pump (P109, the LPG feed pump) was designed by a method described in chapter 8. The duties are given in the utility summary in Appendix 5.4. Pump 105 does not exist, and is therefore not given in the Appendix. The duties are not very high.

The duties of the compressors and turbines were also calculated by simulation in Aspen and the values are summarized in the Appendix 5.4.
The compressors require a lot of energy. The compressor of the reactor effluent (K101) and the compressor of the top stream of C105 (K103) are very large. The separation section however requires a high pressure of at least 12 bara. Optimalization was done by looking at the pressure of the separation section and the costs for the compressors and the columns.

This means that the duty is minimized and that there are no other options or possibilities for reduction.

5.8 Process Yields

In the following table an overview of the process yields are given. Consumption per ton of propylene is given for the in- and outgoing streams, defined by the input-output structure in chapter 3. Also the costs and profits per dollar of propylene are given. This gives an indication of the costs that have to be made or the profits that are gained per one dollar, earned by selling the propylene. In the figure below, the input-output structure is given together with the flow rate, t/t propylene and the price per $ of propylene.

Table 5.12 Process yields

Process Streams										
Name	Ref.	kg/s		t/h		t/t C3=		costs	profits	
	Stream	IN	OUT	IN	OUT	IN	OUT	$/h	$/h	$/ $ propylene
Feed (LPG)	<101>	9.72		35.0		1.12		6646.89		0.57
Air	<173>	13.55		48.8		1.56		-		
Propylene	<128>		8.68		31.2		**1.00**		11716.63	
Light ends	<185>		0.32		1.1		0.04		259.20	0.022
C4	<170>		0.39		1.4		0.04		276.34	0.024
Water	<176>		3.29		11.8		0.38		-	
Water	<164>		0.03		0.1		0.00		-	
Exhaust Air	<159>		10.57		38.1		1.22		-	
Total		23.27	23.27	83.77	83.77	2.68	2.68	6646.89	12252.16	

Utilities										
Name	Ref.	kg/s	kW	t/h	kW h/h	t/t C3=	kW h/			
	Stream						t C3=	$/h		$/$ propylene
LP Steam	-	5.35		19.25		0.62		238.64		0.020
CW	-	293.31		1055.90		33.79		16.89		0.001
Electricity	-		10704		10704		342.59	888.43		0.076

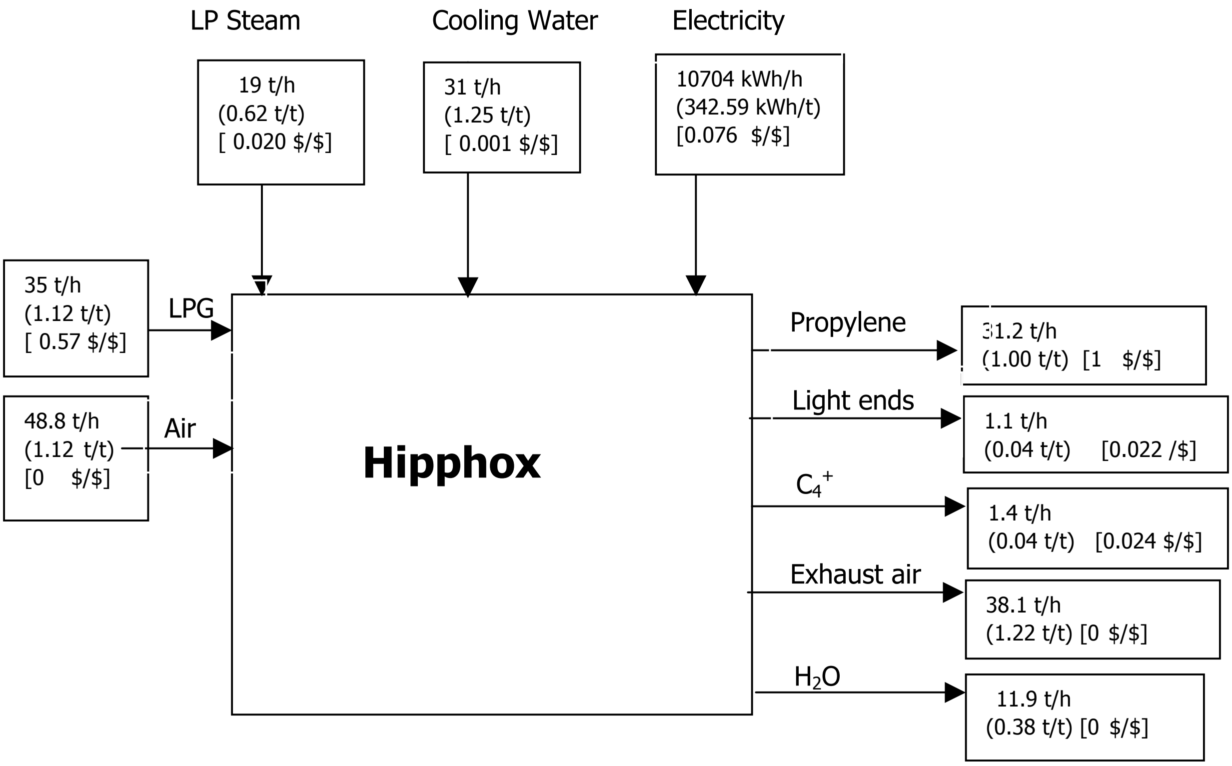


Figure 5.7 Input-output structure with process yields

From this figure it can be seen that the costs for the utilities are not very high. When all the $/$ values are added up, this comes to 0.71 $/$ propylene. This means that for every dollar of propylene earned, 0.71 $ has to be spent.
For a more detailed presentation of the Hipphox process, the reader is referred to Appendix 3.1 for the final block scheme.

6 Process control

6.1 Introduction

In this chapter the process control of the plant will be treated. First the procedure of designing the control system will be discussed and then the controllability of the individual processing units will be treated more in detail.
In literature several heuristics can be found for developing a control system, for example in Douglas [24, pg. 414/415] and in Stephanopoulos [66, pg. 470/471]. The latter method consists essentially of following steps.
First the process is divided into separate blocks, which consist of a processing unit and some equipment like heat exchangers.
Secondly the degrees of freedom and the number of controlled and manipulated variables are determined for each block.
Thirdly all feasible loop configurations are determined for the block. Finally the blocks are recombined and the best configuration for each block is chosen keeping an eye on key variables and control objectives.

Considering the scope of this course a full analysis of the degrees of freedom is too extensive. In order to do this properly all equations relating all the variables have to be written down and this takes too large amount of work. Alternatively the following procedure was followed based on Stephanopoulos' heuristic. First all variables were listed and the control objective of the processing unit was determined. The variables were considered one by one and the dependence on other variables was determined. When this was the case one of the variables was removed from the control variables. Next the remainder of Stephanopoulos' method was followed.

In the next paragraph the method of developing a control system for a single unit will be explained in detail for distillation column C101, which separates propane from butane and heavier hydrocarbons. This procedure has been done for each individual processing unit, however here it is only explained in more detail for column C101. The control system of the other processing units is also explained in consecutive paragraphs. Finally the remaining unexplained controllers and the influence of the control system on the design are treated.

6.2 Column C101

In figure 6.1 the distillation column C01 is drawn together with all the in- and outgoing streams.

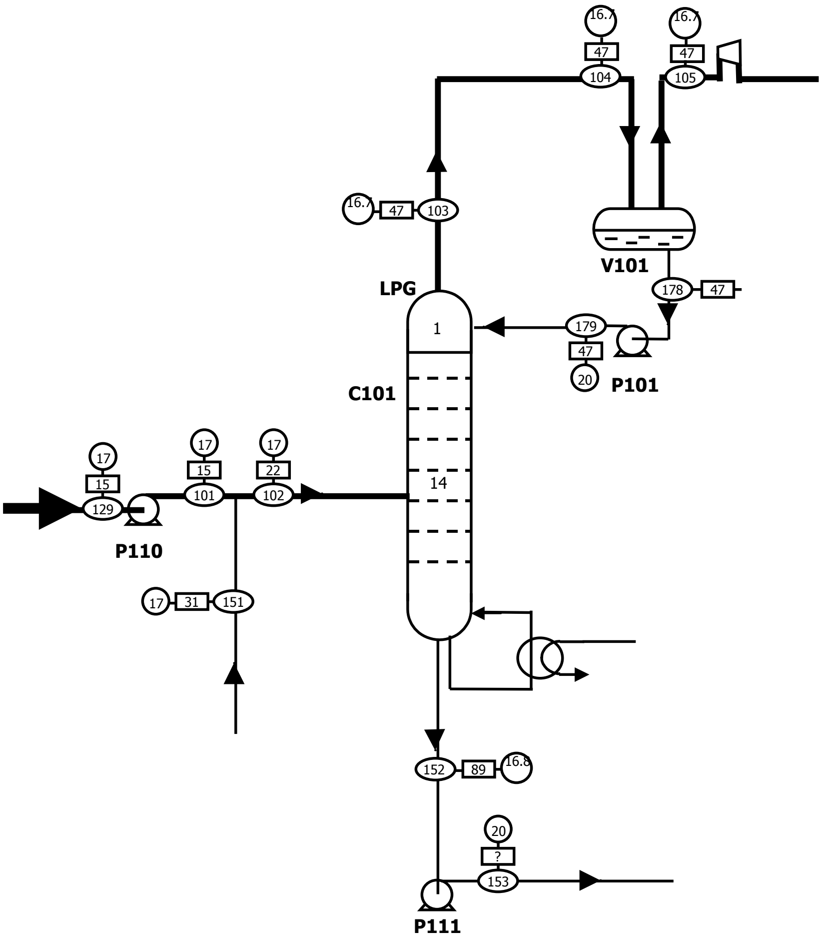


Figure 6.1 Distillation column C101

The control objective for this unit is to deliver a qualitatively good distillate stream. The variables that are disturbances for the column are listed in the following table.

Table 6.1: Disturbance variables for column C101.

Mass Flow	**Composition**	**Temperature**	**Pressure**	**Other**
151	151	151		
	101			

The variables that have to be controlled ("degrees of freedom") for this column are mentioned in the table below.

Table 6.2 Relevant variables for column C101.

Mass Flow	**Composition**	**Temperature**	**Pressure**	**Other**
101		top	top	level bottom
		bottom		level condenser

In order comply with the control objective and to correspond properly to disturbances the control system of figure 6.2 was designed.

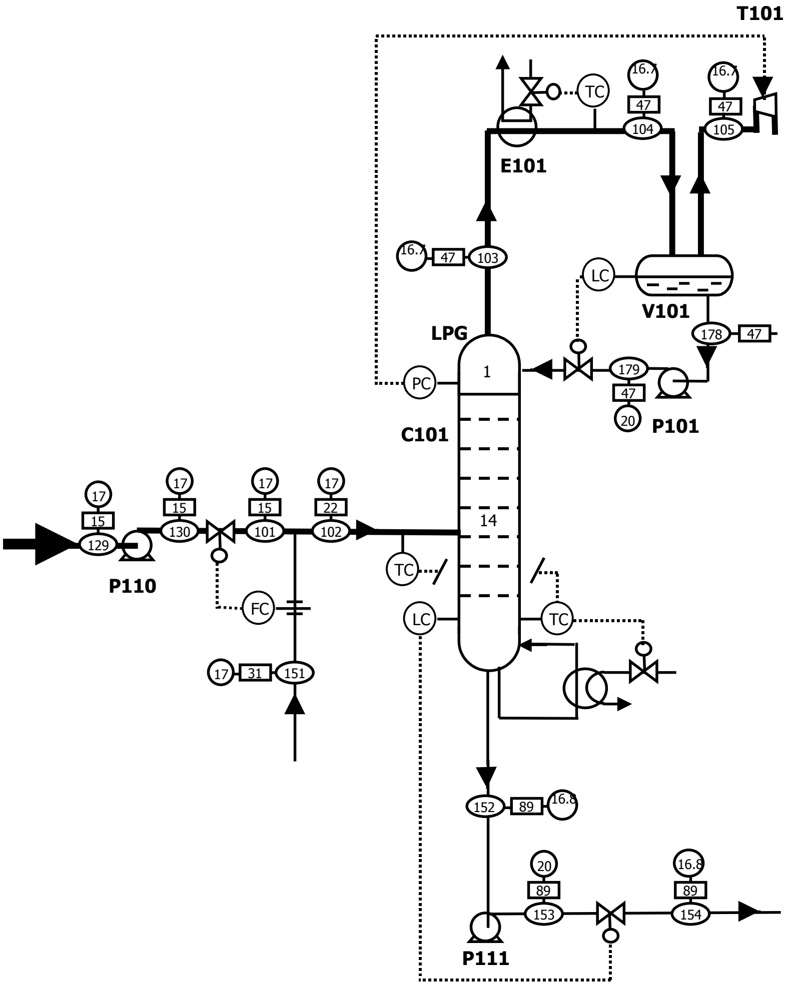


Figure 6.2 Control system for column C101.

Flow controller (stream 130)

The mass flow of stream 129 is assumed to be constant, since it is delivered on the plant. The recycle stream however is not constant, the reason for this is that in order to control column C105 properly, the reboiler level has to be kept constant. A consequence of this is that this acts as a disturbance for this column. The mass feed stream of column C101 is therefore kept constant (102) irrespective of changes in composition of streams 101 and 151, by adjusting the inflow of LPG on the inflow of recycle.

Level controller reboiler

A general remark can be made at this point on the controllability of distillation columns that in order for a column to work properly, it is required that it has a constant level in the reboiler. This enables a good steady-state behaviour of the column, since the temperature of the reboiler can more easy be kept constant. This again is important because the separation of the components is done based on a difference in boiling point (and consequently volatility). The level in the reboiler can be controlled using a valve behind pump 111.

Cascade temperature controller reboiler
The temperature of the reboiler can be kept constant using a temperature measurement on the bottom of the column. However, since the temperature of the feed possibly has large changes due to the changes in the origin of the flow (101 or 151) a cascade temperature controller is used. This controller works as follows: the temperature of the feed is measured and this gives the controller at the reboiler a set point according to the change in temperature of the feed. The controller at the reboiler now will control the valve accordingly while more or less fluid reaches the reboiler. The temperature controller at the reboiler therefore reacts in a feedforward manner to changes in temperature of the feed.

Changes in composition are also accounted for however only in a feedback manner. When more heavy components enter the column, the temperature of the reboiler decreases and the temperature controller acts according to this.

Temperature controller topstream (104)
Since the control objective of the column is to deliver a qualitatively good distillate stream it is essential for the condenser to have the correct pressure and temperature. The temperature can be controlled by measuring the temperature of stream 104 and controlling the heat exchanger (E101) accordingly. The measurement is done behind the heat exchanger, which is done for every standard temperature controller throughout the process, since in this way the working of the heat exchanger is made sure.

Pressure controller top
The pressure at the top of the column can be controlled by adjusting the amount of work of turbine T101. A consequence of this is that the pressure of stream 106 is not constant. This will be discussed later at the reactor control section.

Level controller condenser
In order to obtain a good separation in the condenser the level has to be controlled. It is believed that the column corresponds properly to the disturbances and all “degrees of freedom” are eliminated.

6.3 Reactor (R101)

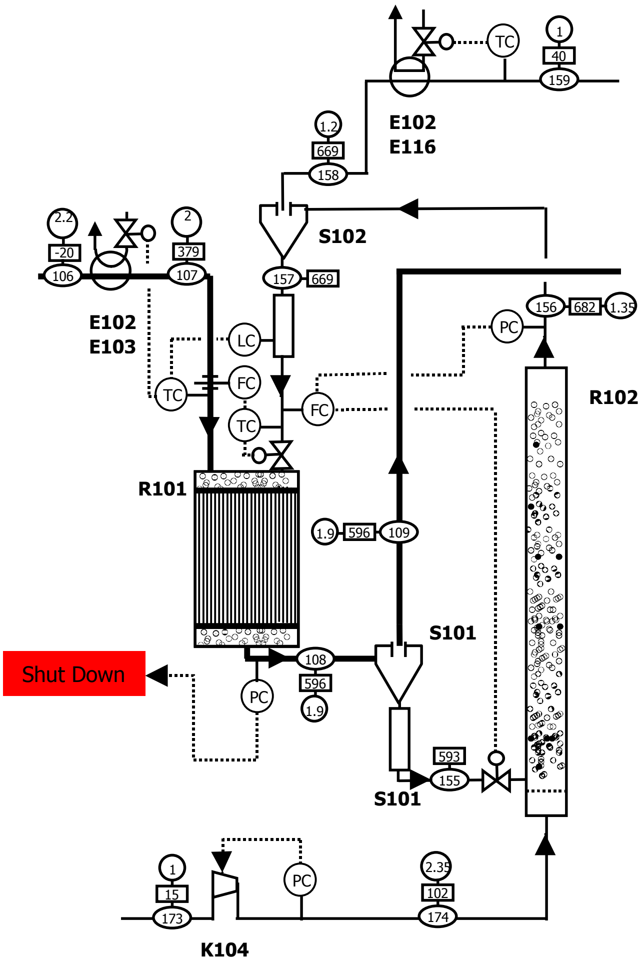


Figure 6.3 Reactor and riser control system.

The control objective of the reactor is to quantitatively and qualitatively convert propane into propylene. The reactor is one of the most important processing units of the plant. The control system of the entire process is designed in such a way that disturbances in de reactant and the product mass flow stream, within reasonable limits, do not have to be controlled. The reason for this decision is that the process is much more flexible in this way and the control system does not take on a too dominant role. However many variables still have to be controlled. The control system of the reactor and the riser is treated simultaneously due to the high interdependence caused by the circulating SOC stream.

Cascade temperature (107) and level controller (157) reactor inlet.

Due to the heat integration of the SOC with the reactant stream into the reactor these two streams will be mixed just before entering the reactor. Since the SOC acts as a heat carrier absence of the SOC stream will cause the reaction nearly not to take place. In order to circumvent this problem an extra heater is placed between stream 106 and 107, so that this heater can heat the reactant stream when the SOC stream is blocked. This is a very costly way of producing propylene, it was however preferred over the alternative of shutting down the entire plant with all it's equipment and columns. The regulation of this system is as follows. A regular temperature controller is placed at stream 107 to control the heat exchanger (E102/E103/E104). The level controller at the SOC hopper (157) measures whether or not there is SOC present inside the hopper. When this is not the case it gives a new set point to the temperature controller causing it to heat up the reactant stream much higher.

Pressure controller exit reactor (108).

A possible problem at which special attention has to be paid is the possible occurrence of plugging of monolith pores due to SOC accumulation. In order to correspond properly to this problem a pressure sensor has been placed at the exit of the reactor. When plugging occurs to an unacceptable extent the reactor will have to be shut down. Since disturbances occur in the inlet pressure of the reactor this controller should not be adjusted too accurately, merely because plugging to a lesser extent still enables the reactor to run in an acceptable way.

Cascade heat integration controllers (107,157).

Next to these extreme scenarios controllers were placed for more regular control. In order to integrate the heat of the SOC properly with the reactor inlet stream a temperature controller was placed at stream 157 and a flow controller at stream 107. The flow controller measures the mass flow stream of 107 and gives a corresponding set point to the temperature controller, which controls the amount of SOC that is let into the reactor.

6.4 Riser (R102)

The riser has two control objectives which are firstly to regenerate the SOC and secondly to transport the SOC upward. The control system is shown in figure 6.3.

The riser is designed in such a way that the air stream flows with a constant flow into the riser. The airflow chosen corresponds with a maximum amount of SOC that has to be pumped around. When the valve in solid stream 155 is completely open the amount of SOC that enters the riser corresponds to this value. The amount of oxygen present in this air stream corresponds with 1.1 times the amount of spent SOC that has to be regenerated. In this way the SOC normally always is transported upwards and the amount of SOC that normally reacts is also regenerated.

Pressure controller (173,174)

The pressure at the inlet is controlled by a pressure controller, which measures the pressure behind compressor K104, and controls this compressor.

Flow controller (157)

The amount of SOC that is transported upward should be adjusted to the amount of SOC that is fed into the reactor. In this way the SOC mass balance is always accounted for and no accumulation or absence of the SOC takes place in one of the two hoppers (H101/H102). The flow controller at stream 157 measures the SOC flow into the reactor and accordingly controls the valve at the riser inlet (155).

Pressure controller (156)

Since it is possible that plugging occurs in the riser the pressure at the top of the riser is measured and when this becomes too low the pressure controller gives a set point to the flow controller, which makes it close the SOC inlet valve. In this way the riser is cleaned by blowing out the remaining SOC.

6.5 Flash vessel (V102)

In figure 6.4 the flash vessel control system is shown.

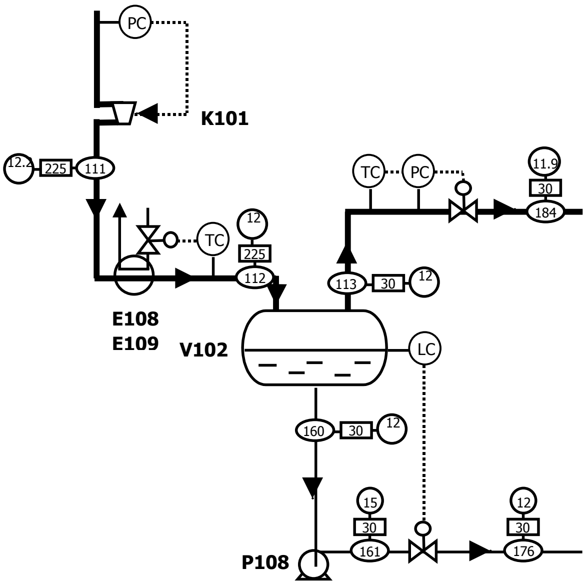


Figure 6.4 Flash vessel control system.

Pressure controller (110)
The pressure at the inlet of the flash vessel is disturbed, since the compressor is used for keeping the pressure in stream 110 constant. The reason for this is that otherwise the flow out of the reactor jeopardised and consequently cyclone S101 will not work properly.

Temperature controller (112), cascade temperature and pressure controller (184)
For the same reasons as at a distillation column, as mentioned at column C101, a constant pressure and temperature is essential for a flash vessel to work properly. The temperature of the stream into the flash vessel is controlled by a standard temperature controller. Since the boiling point is dependent on both the temperature and the pressure a cascade controller is used, where the temperature controller gives a set point to the pressure controller.

Level controller (161)
The level in the flash vessel is controlled in the standard way.

6.6 Glycol processing unit (C102, C103), Distillation column C104

Since the glycol unit is a commercially available processing unit also a control system for this column can be found. Therefore a control system has not been designed here. An example of a control system can be found in [64].

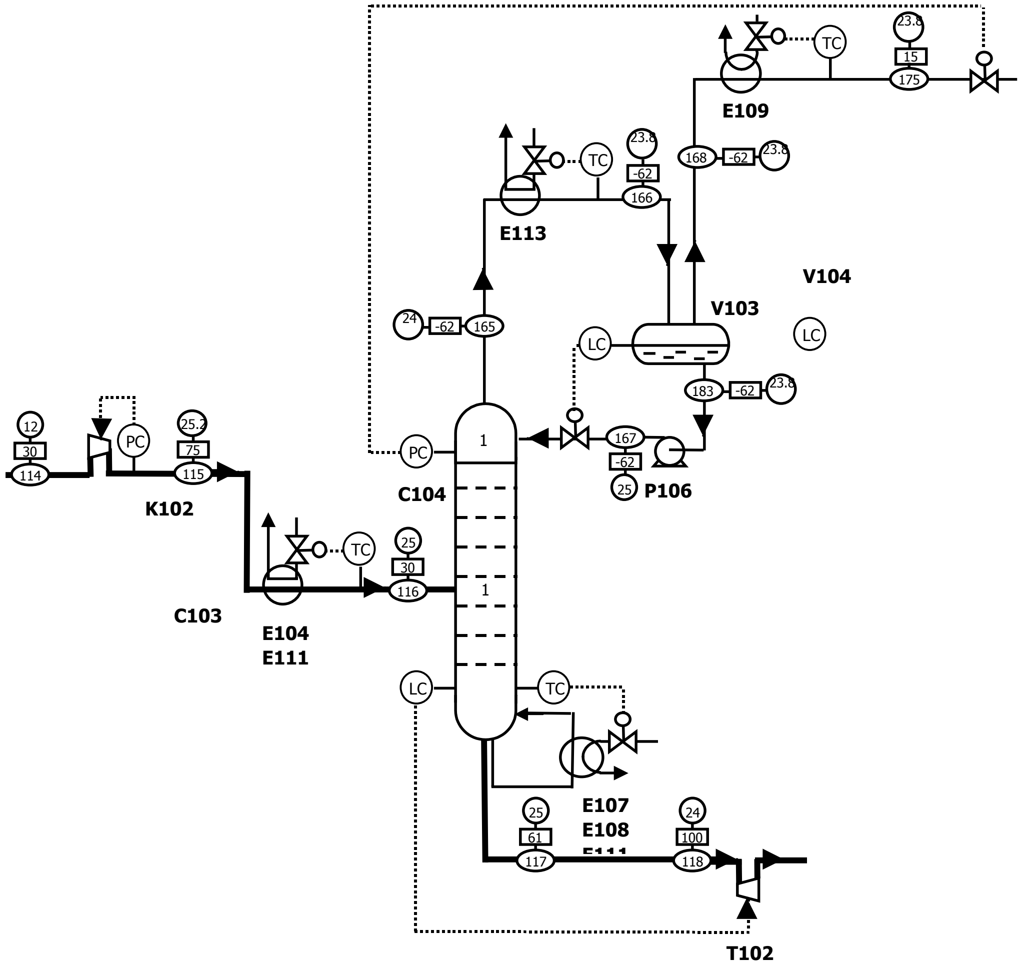


Figure 6.5 Distillation column C104 control system.

The control system of distillation column C104 (see figure 6.5) is design almost identically as the control system of distillation column C101. This column however is less complex, since the feed stream is not subject to disturbances, except mass flow. The temperature and pressure can be controlled in a standard way.

6.7 Distillation column C105

In figure 6.6 the propane-propylene splitter is shown with a heat pump. This column has two control objectives firstly it has to deliver a qualitatively good top stream and secondly it has to deliver a quantitatively minimal bottom stream. The bottom level, the vessel level, the bottom temperature, the column top pressure, and the condenser pressure are controlled in the same way as in the other distillation columns. The splitter SP101 is set at a constant value, therefore this does not have to be controlled.

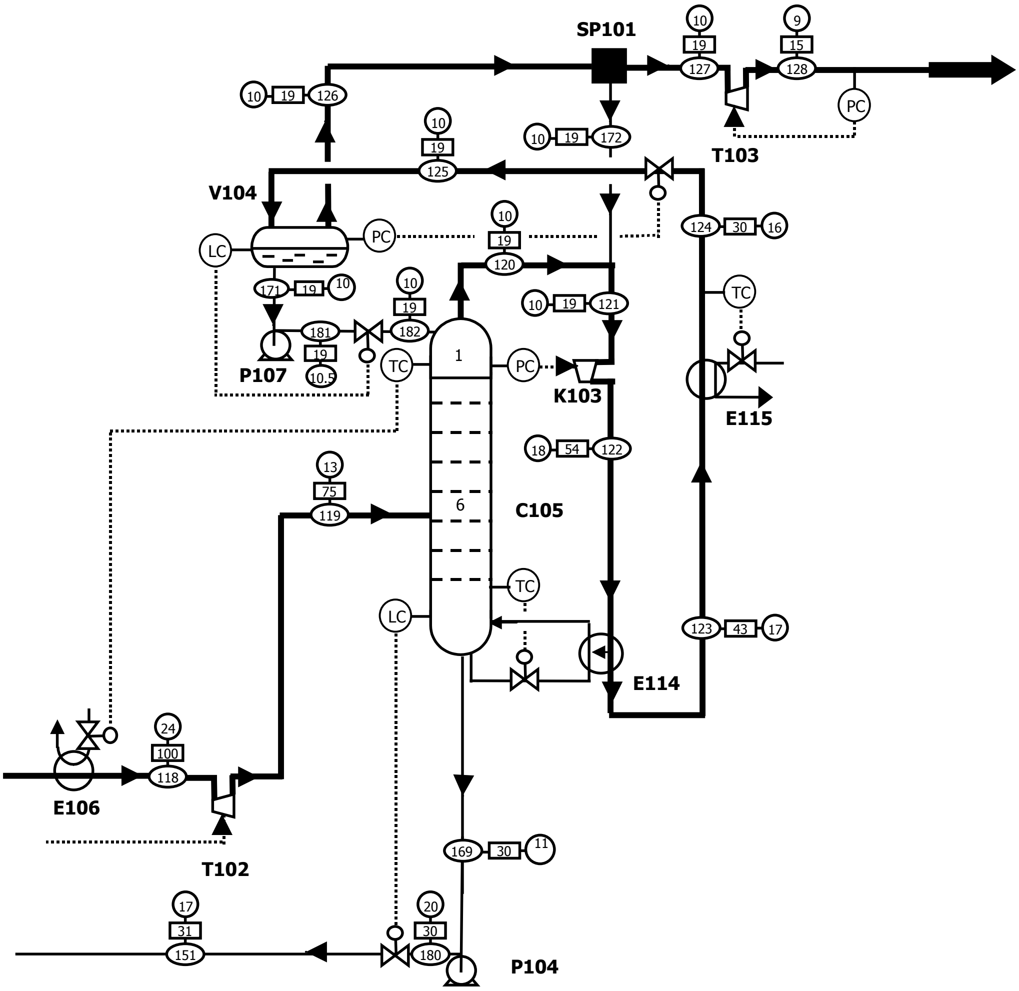


Figure 6.6 Distillation column C105 control system.

Pressure controller (124)
The pressure in streams 122, 123 and 124 suffer from possible disturbances, since the compressor K103 is used for keeping the pressure of the column constant. This problem is overcome by controlling the valve in stream 124.

Temperature controller (123)
In order to obtain sufficient liquid throughput in vessel V104, which causes a high enough reflux ratio, the heat exchanger E115 is added. It is controlled by a temperature controller.

Temperature controller (117, top column)
The temperature in the top of the distillation column is controlled by heat exchanger E106. Since the temperature of the stream entering the top from the vessel is controlled this should be sufficient.

6.8 Overall process control

As has been explained before the controllers of the mass flow should not conflict with each other. This is essential for the control system because when this does happen one of the two controllers will not be able to function properly. Therefore the choice was made to make all processing units capable of coping with disturbances in either the incoming mass flow or disturbances in the incoming composition. A first example of this is that the controller of compressor K101 reacts on disturbances in the pressure in the incoming stream in stead of keeping the outgoing stream constant. Keeping the level in the bottom of column C105 constant is another example, since this causes a composition disturbance in the incoming flow of column C101.

Other controllers that have not been treated yet are the following:

- Temperature controller in stream 158. This controls the temperature of the outgoing stream in order to meet the product specifications.
- The same holds for the heat exchanger E109.
- The same holds also for the pressure controller in stream 127.

Review of control design

From the HAZOP study one problem came to light on which the control system of the riser and reactor does not respond well. This problem is when the incoming air for regeneration and transportation does not have a high enough oxygen content. The occurrence of this is not very likely, also because the amount of air is taken in excess, however it cannot be ruled out. The control system will respond to this problem in the following manner: first not all the SpentSOC will be regenerated, the SOC in hopper H102 does not have a sufficient high temperature and the control valve will be opened. The opening of the valve will continue until it is opened to it's maximum (so will the valve in stream 155). The problem now is that the temperature still will not be high enough and therefore the conversion in the reactor will be lower. In the actual process control operators have to be alert to this problem, they will be able to recognise this problem when the SOC stream is at it's maximum, and for example oxygen tanks have to be kept stand-by to add oxygen to the air.

When reactor R101 for a certain reason doesn't produce propylene a large propane stream will be sent into the separation system. The result will be an amount of propane in the water stream (160) and column C105 will not be able to work properly, the product stream 128 will contain more propane than allowed. A way to prevent this problem is to somehow measure the composition of the reactor effluent and when this is too low the plant has to be shut down. Note that the composition measurement should allow the composition that is reached when no hydrogen is combusted, since this is probably caused by a riser failure, which is accounted for by the control system.

6.9 Heat exchanger network

Nearly all heat exchangers are used to control variables of the processing units. In the heat exchanger network however the exchangers have been coupled. This makes the controllability more complex, since it removes a degree of freedom per coupling. Considering the scope of this course no extra work has been put in developing a control system for this system. However the amount of heating and cooling utilities almost certain will increase. In the control system design it is treated as if each heat exchanger still is controllable as if it were a utility.

6.10 Controllability influences on the design

In order to obtain good controllability two adjustments have been made on the processing equipment.

Reactor and riser hopper
The use of SOC in two units which are interconnected via heat integration have caused the need for hoppers H101 and H102 to store the SOC temporarily. These units solely serve a controllability cause, since only in this way buildup or lacking of soc in a certain place can be prohibited. The valves that control the soc inlet stream are designed in such a way that if opened 100% both valves let through the same amount.

Heat exchanger E115
This has been added in order to add a degree of freedom of the heat pump.

6.11 Process flow scheme

For an overall process flow scheme the reader is referred to appendix 5.3.

7 Mass & Heat balances

7.1 Balance for total streams

An overview of the results of the mass an heat balances is given in appendix 7.1. Per unit of equipment the in- and outgoing stream are listed and the mass balances checked. For the reactor design the heat integration is an important design criterion. The heat balances were made based on the results for the enthalpy from thermodynamic calculations.

The mass and heat balances for the different units are in balance except for both the reactors. Therefore the heat balances for R101 and R102 are described in more detail below.

The heat balances for the glycol unit (C102 and C103) are not in balance. This can be explained by the fact that the glycol unit is not fully designed.

7.1.1 Heat balance for the R101

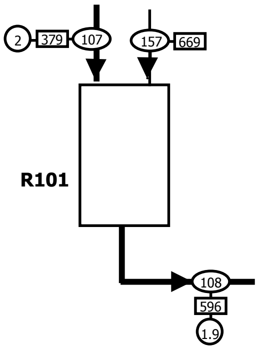


Figure 7.1 Flow scheme R101

The heat balance for the reactor R101 is:
Acc. = In – Out + Conversion.

$$0= F_{107}*c_{p,107}*T_{107}+ F_{157}*c_{p,157}*T_{157} - F_{108}*c_{p,108}*T_{out} + \Delta H_r*F_{mol,r} \qquad (7.1)$$

Table 7.2 Data for heat balance over R101

	F <107> Feed gas [kmol/hr]	F <157> Feed solids [kmol/hr]	F <108> Reactor out [kmol/hr]	Cp,873 kJ/kmol*K	<107> Heat gas in [kJ/hr]	<157> Heat solids in [kJ/hr]	Heat gas out [kJ/hr]	Heat solids out [kJ/hr]
Propylene	8.4	0.0	747.9	136	747384		88384756	
Propane	1282.0	0.0	536.0	163.95	137028379		76367889	
Hydrogen	0.0	0.0	91.5	29.76	0		2365226	
Water	0.0	0.0	662.0	39.66	0		22817180	
Methane	0.0	0.0	3.6	66.35	0		207208	
Ethane	23.3	0.0	21.0	113.7	1724801		2076698	
Ethylene	0.0	0.0	1.3	88.48	0		103293	
1-butene	0.1	0.0	2.4	183.37	15382		379089	
Butane	0.2	0.0	0.2	212	33076		44087	
CO	0.0	0.0	8.9	31.77	0		244899	
SOC	0.0	44443.6	41103.7	61.6	0	2.60E+09	0	2.20E+09
SpentSOC	0.0	0.0	3279.0	61.6	0	0	0	1.76E+08
Total					**1.40E+08**	**2.60E+09**	**1.93E+08**	**2.38E+09**

The heat effect is based on the enthalpy of the main reactions, DH and SHC. The heat effect of the site reactions is not taken into account in the first calculation.
Therefore the heat effect of the reaction is calculated as:

$\Delta H_r * F_{mol,r} = \Delta H_{DH} * F_{mol,propylene} + \Delta H_{SHC} * F_{mol,water}$

ΔH_{DH}: 129810 kJ/kmol

ΔH_{SHC}: 108380 kJ/kmol

$F_{mol,propylene}$: 747.9 kmol/hr

$F_{mol,water}$: 662.0 kmol/hr

This results in $\Delta H_r * F_{mol,r} = 1.69*10^8$ kJ/hr

In this balance is assumed that the heat transfer from solids to gas is ideal, based on calculations explained in chapter 8.2.1.
The temperature of stream 157 is determined from a heat balance over R102, the riser reactor. The solids enter the reactor at T_{157} = 669 °C. From the data the temperature of the feed stream of the reactor is determined by (1). This results in T_{107}=379 °C.
The temperature in the stream to the riser is calculated with the Matlab simulation, see chapter 4 and 5.

7.1.2 Heat balance for R102

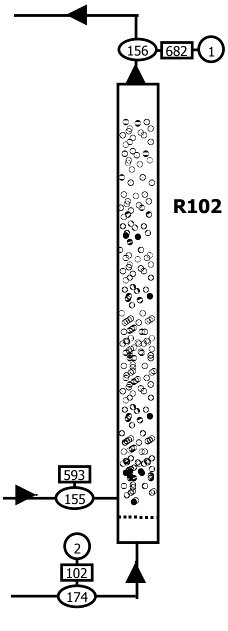


Figure 7.2 Flow scheme R102.

The heat balance for the riser R102 is:
Acc. = In – Out + Conversion.

$$0= F_{174}*c_{p,107}*T_{174}+ F_{155}*c_{p,155}*T_{155} - F_{156}*c_{p,156}*T_{out} + \Delta H_{r,SHC}*F_{mol,r} \qquad (7.2)$$

Table 7.2 Data for heat balance over R102

STREAM Nr. :	155	174	174	156	156	Heat in	Heat Out
name:	Spent SOC to riser	Air feed riser	Cp	Effluent R102	Cp		
COMP	kmol/hr	kmol/hr	kJ/kmol*K	kmol/hr	kJ/kmol*K	kJ/hr	kJ/hr
Oxygen	0	355.50	29.9	20.05	34.6	3.80E+06	6.64E+05
Nitrogen	0	1335.39	29.3	1335.39	32.4	1.40E+07	4.14E+07
SOC	41104	0	61.6	44443.57	61.6	2.20E+09	2.62E+09
SpentSOC	3279	0	61.6	0	61.6	1.76E+08	0
Total	44383	1690.89		45799.01		2.39E+09	2.66E+09
Temp [K]	869	357.2		955.35			
Phase	S	V		S+V			

The heat effect is based on the enthalpy of SOC regeneration. The heat effect of the side reactions is not taken into account in the first calculation.
Therefore the heat effect of the reaction is calculated as:

$\Delta H_r * F_{mol,r} = \Delta H_{SOC} * F_{mol,Spentsoc}$

ΔH_{SOC}: -71000 kJ/kmol

$F_{molSpentSOC}$ = 3279 kJ/kmol

This results in $\Delta H_r * F_{mol,r} = -2.33*10^8$ kJ/hr

These calculations lead to in imbalance in the heat balance. The outgoing temperature of the riser is calculated by solving the heat balance. The outgoing temperature is chosen with earlier results of the reactor. In the optimization of the Hipphox process the effluent of the reactor has slightly changed therefore the outgoing temperature is slightly different from the outgoing temperature necessary to balance the heat balance. With an outgoing temperature of the riser of 952 K the balance is in balance.

7.2 Balance for stream components

In table 7.3 the overall component mass balance & stream heat balance is given. This balance shows the mass balance per component around the battery limit. The heat balance is performed as well and shows that a lot of heat has to be removed with coolers. From the heat balance for the total streams this cannot be seen, as there is no heat balance made for each heat exchanger, but only per total unit. So the heat duties from the heat balance for total streams is the duty, which will be delivered by a number of heat exchangers. From the heat exchanger network and design of the heat exchangers the duties can be found. When all the duties of the heat exchangers are added up, a total of 19188 kW of cooling water has to be delivered. For hot utilities 5348 kW is needed. With these numbers the heat balance is almost satisfied. The difference can be explained by the fact that the heat exchanger network is not designed with the latest version of the properties of all the streams. The main difference is that the condenser duty of C104 is reduced by reducing the reflux ratio. This means that a lower reboiler duty is needed and therefore the heat exchange network will be somewhat different, which means that the cold utilities and hot utilities will be different.

Table 7.3 Overall Component Mass Balance & Stream Heat balance

	101+173 Total Plant	**IN**		**159+185+128+164+176+170 Total Plant**	**OUT**	**OUT-IN Total Plant**
COMP	MW	kg/hr	kmol/hr	kg/hr	kmol/hr	kg/hr
Propylene	42.08	0.00	0.00	31115.26	739.42	
Propane	44.10	33234.45	753.68	339.90	7.71	
Hydrogen	2.02	0.00	0.00	184.36	91.46	
Water	18.02	0.00	0.00	11926.78	662.04	
Methane	16.04	0.00	0.00	57.65	3.59	
Ethane	30.07	699.67	23.27	632.00	21.02	
Ethylene	28.05	0.00	0.00	37.69	1.34	
1-Butene	56.11	0.00	0.00	126.25	2.25	
Butane	58.12	1049.51	18.06	1049.51	18.06	
CO	28.01	0.00	0.00	248.46	8.87	
Oxygen	32.00	11375.57	355.50	641.46	20.05	
Nitrogen	28.01	37408.92	1335.39	37408.92	1335.39	
SOC	176.50	0.00	0.00	0.00	0.00	
SpentSOC	176.50	0.00	0.00	0.00	0.00	
Total		**83768.12**	**2485.89**	**83768.24**	**2911.19**	**-0.12**
Enthalpy	kW	-27092		-50790		-23698
	kW	19188	CU	5349	HU	839

8 Process and Equipment design

In this chapter the process structure and equipment of chapter 5 will be further developed into a final process design configuration. Process integration is done by simulation with AspenPlus and Matlab. The required equipment is selected and designed.

8.1 Integration by process simulation

8.1.1 Matlab simulation

In order to gain more insight in the many parallel reactions occurring in the reaction section a Matlab model has been written (appendix 4.5). All reactions occur parallel and simultaneously.
For most reactions a reaction rate expression has been found as explained in chapter 4. (kinetics). Both dehydrogenation reaction and hydrogen oxidation have been estimated at first order equilibrium reactions. In order to estimate a conversion of propane and the selectivity towards propylene a simple Euler method calculation will be used. This method uses a simple forecast algorithm as shown in equation 8.1.

$$x\left(t+\partial t\right)=x\left(t\right)+\frac{\partial x}{\partial t}*\partial t \qquad (8.1)$$

In this equation the variable x is expressed as the sum of a known value of x at time t and the derivative of x times the time step. All component calculations are mole based and therefore the derivative is simply the sum of all reaction rates concerning the component. For example the number of moles of hydrogen can be estimated by the following equation 8.2:

n_hydrogen=n_hydrogen+step*(+r2+r8+r_dh-r_SOC) (8.2)

As long as the time step (variable ‘step’) is chosen small enough (0.01-0.1 seconds) the calculation is assumed to have a relatively small error, since the calculation results are independent of the time step.

In this simulation an ideally mixed batch process is assumed. A reactor of 1 m^3 is considered. The reactor solid load (vol%) and SOC/DH catalyst ratio (vol% SOC / vol% DH cat.) are varied. Using these assumptions, a conversion and selectivity can be calculated as function of the residence time.

After modelling a batch reactor, the model has been rewritten to a continuous PFR model. Most of the reaction equations remain the same, with exception of the iteration variable. The PFR volume is the iteration variable. With this model the reactor volume can be estimated. Several details and assumptions will be explained.

Equilibrium constants

All equilibrium constants are a function of temperature and pressure. Since the temperature of the reactor is not constant (the feed is hotter compared to effluent), the equilibrium constants change. The dehydrogenation reaction equilibrium constant is a known function of temperature. Therefore this equilibrium constant will be iteratively calculated. The relation between the equilibrium constants of the cracking reactions and the reactor temperature are unknown. However the reactor temperature drop is relatively low and therefore the equilibrium constant is assumed constant over the reactor temperature span. The cracking reaction equilibrium constants were obtained from Sundaram et al [19].

Reaction kinetics

Most reactions are a function of temperature. From [19] several rate models and equations are tested at various temperatures. The temperature dependencies of these reactions are iteratively calculated in the Matlab script. Both the SOC reactions, selective combustions and regeneration, are assumed to be independent of temperature.

Stability

The stability and calculation speed of the Euler algorithm is low compared to other available algorithms. However for simplicity reasons an Euler algorithm has been chosen. The iteration step size was varied in order to estimate the calculation error. The error was found to be insignificant, over an iteration size range of 0.01-0.0001.

Coke formation

Coke formation was initially modelled with the corresponding rate equation. The results showed that almost no coke was formed. Since in a later stage of the design the Pt catalyst was assumed to be self-regenerating, coke formation is neglected in the final Matlab model. The thermal cracking reaction rate responsible for coke formation (propylene forms coke and methane) is set to zero.

Reaction heat

Several endothermic reactions occur in the reactor; therefore a temperature drop is expected. In order to calculate the local temperature, the following reactions have been taken into account:

- Dehydrogenation of propane to propylene
- Hydrogen combustion to water (with SOC)
- SOC side reactions with propane and propylene

The cracking side reactions have been neglected for temperature calculations. Furthermore, ideal gas phase mixing is assumed. Therefore the temperature can be calculated by the following equation.

$$T_2 = T_1 + \partial V * \frac{\sum_i \partial H_{r,i} * r_i}{\sum_{j,gas} f_j * c_{p,j} + \sum_{j,solid} f_j * c_{p,j}} \qquad (8.3)$$

Solid gas heat exchange

The solid SOC particles possess a higher temperature after (exothermal) regeneration. Once the SOC particles re-enter the reactor, the SOC particles contact the cooler propane feed. Because of the very small particle size, ideal mixing behaviour has been assumed. This will be explained in this chapter.

SOC concentration

The hydrogen combustion reaction is assumed to be a first order reversible reaction. Therefore the reaction rate is a first order function of the SOC concentration. Because the SOC particles fall through the monolith in a downward direction, the SOC particles will have a smaller residence time. In order to deal with the residence time difference, a correction factor of 1.24 has been applied. This correction factor is explained in detail in chapter 8.2.1.

Mass balance check

In order to check total mass streams, a total mass balances has been made. The net effect of the SOC reaction is a mass transfer of one atom of oxygen; therefore the vapour mass increase is equal to the solid mass decrease as shown in figure 8.1. The mass balances were obeyed.

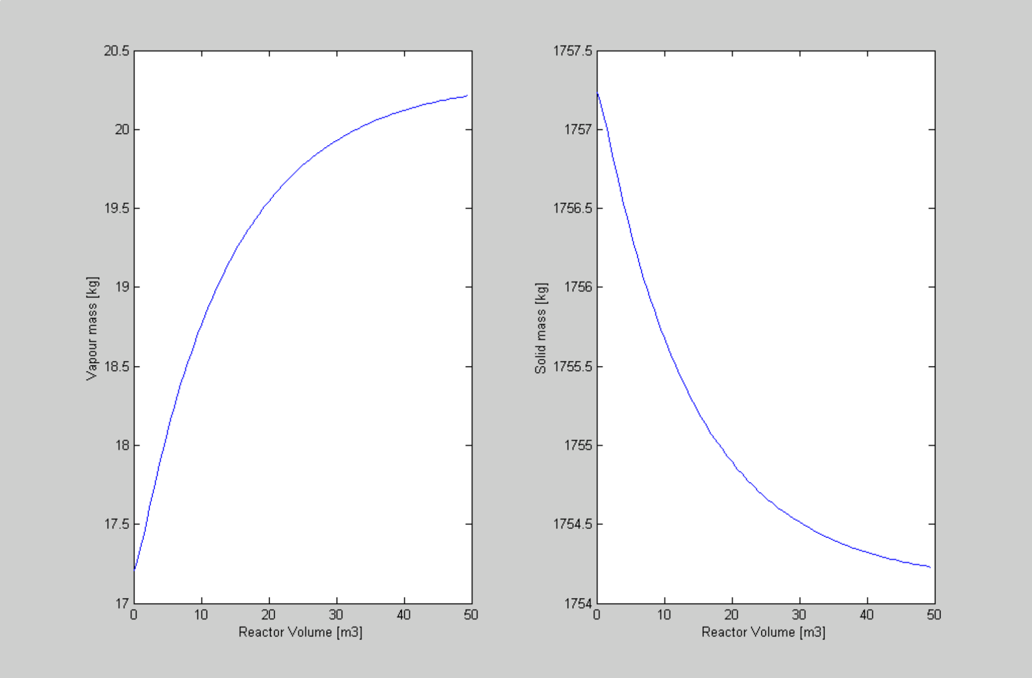


Figure 8.1 Mass balance checks

Reaction rates check

Besides a mass balance check, also the reaction rates are checked. Most reactions are considered irreversible, and the reaction rates should therefore be positive. This is shown in figure 8.2. All reaction rates proved to be positive. The cracking reactions mentioned in figure 8.2 equal reactions (4.7) to (4.15). Note that cracking reaction 2 (dehydrogenation of propane to propylene) and reaction 5 (coke formation reaction) have been set to zero.

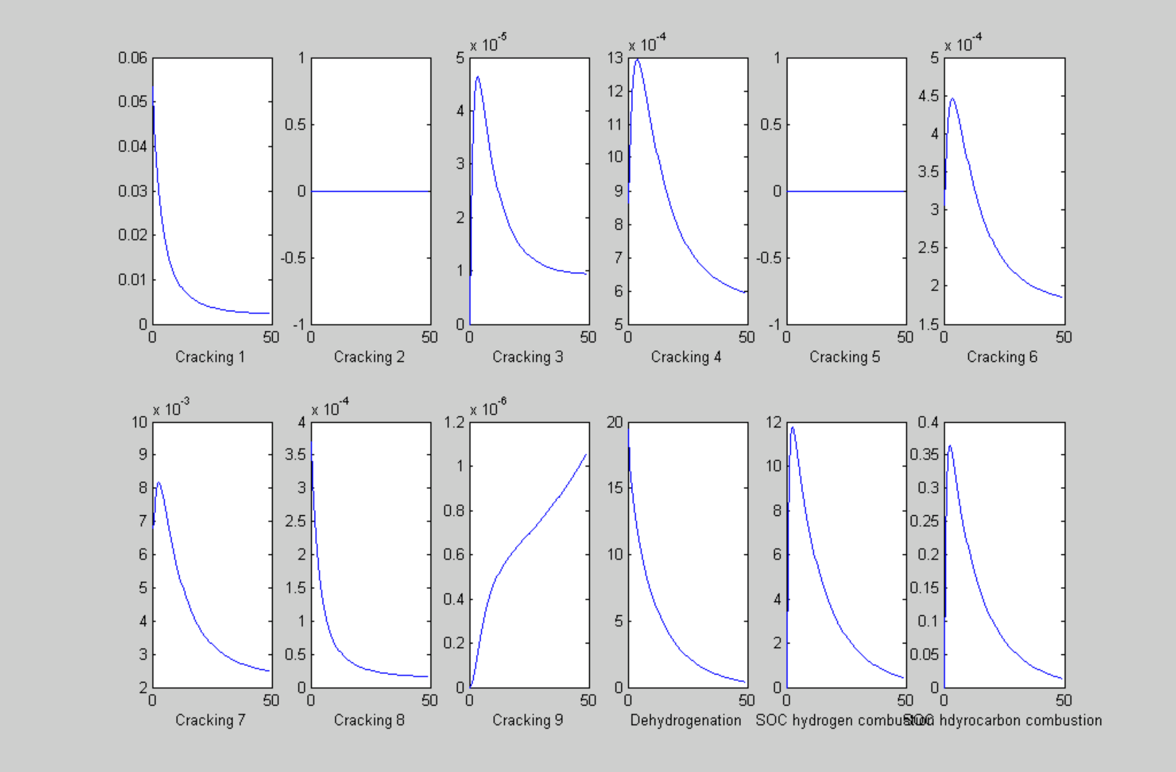


Figure 8.2 Reaction rates check

Pressure

One of the mayor drawbacks of the Matlab simulation script is the pressure assumption. In order to simplify the simulation the reactor pressure has been assumed constant at 2 bara. This resulted in pressure independency of all reaction rates and equilibrium constants. All reaction rates were written as function of partial pressures as shown in the equation below from the Matlab script.

`r1=k1*((f_propane/f_gas)*P/(R_cal*T));`

This is the first thermal cracking reaction where (f_propane/f_gas)*P equals the partial pressure of propane. A logical result of the constant pressure assumption is an increase in the volumetric flow rate. In a real world reactor constant pressure is not feasible since more molecules are formed by chemical reactions, and pressure drops should be integrated in simulation. This will probably have an impact on reactor sizing. Nevertheless a good approximation can be obtained from the Matlab model by assuming constant pressure.

8.1.2 Aspen Plus simulation

After manual setup of mass balances and process structures, an AspenPlus simulation was done using AspenPlus 11.1 from AspenTech.

The simulation sheet was built in several steps. First the reactor section was developed. The reactor and regenerator are modelled with two stoichiometric reactors with fixed fractional conversions. Fractional conversions of relevant reactions and side reactions were obtained from Matlab simulation as described in this chapter and chapter 4. The R101 monolith reactor is modelled with a stoichiometric reactor, with known fractional conversions. In order to allow reactions to take place independently the "Reactions occur in series” option has been selected. Furthermore all the reaction enthalpies were entered in the reactor specification sheet. The Solid stream is modelled using a CISOLID (Conventional Inert Solid) substream. The SOLIDS property method was used to allow calculations. In order to separate the CISOLID stream from the MIXED gas stream ideal SSplit units have been used. Ideal splitters with split fractions of 1.0 were assumed. For the SOC regenerator (R102) the second stoichiometric reactor is used. A fractional conversion of 1 is used, thus regenerating 100% of the spent SOC. The Aspen Plus reactor section is shown in the figure 8.3.

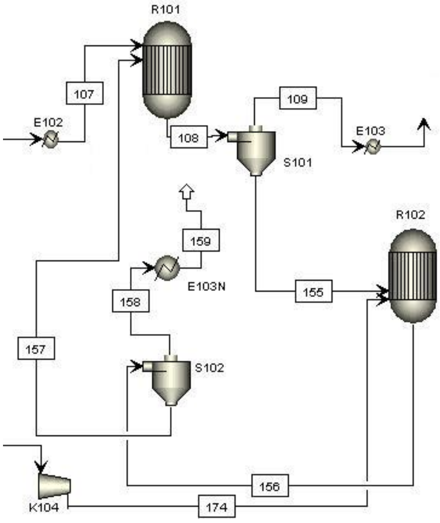


Figure 8.3 AspenPlus reactor section

After modelling the reactor section the complete recycle structure has been modelled. Using simple shortcut distillation units (using Winn-Underwood-Gilliland method) and ideal separators for water separation the recycle structure is closed. After the simulation showed fast convergence the shortcut units are replaced by rigorous 2 or 3-phase fractionators (RadFrac units) and flash vessels. As described in chapter 4 the SRK and PR-BM property methods are used for simulation. The SRK property method is used for hydrocarbon mixtures. The PR-BM property method is used to estimate hydrocarbon streams containing water. The column design method as described in chapter 8.2.2 is used to model distillation columns. After initial water removal by a simple flash column, an ideal separator models the TEG water removal column. This unit has not been simulated in AspenPlus, since commercial contactors and reconcentrators are available to remove this water efficiently.

The compressors were modelled as isentropic compressors, with a specified discharge pressure. The phase equilibrium check in the compressor specification sheet was used to check and prevent condensation in the compressors. Pumps were modelled by simple pump units as present in AspenPlus, by specifying either a pressure increase or a discharge pressure. Heat exchangers were modelled by specifying both exit temperature and pressure. Both liquid and vapour were assumed to be valid phases.

The final step in completion of the AspenPlus model is the integration of a heat pump for the propane-propylene splitter, as described in chapter 5. After tuning the propane-propylene splitter to meet product specifications, convergence of the entire flow sheet proved to be rather slow. In total 44 complete iterations were required to converge all variables. The used convergence model is the Wegstein method. The solver tolerance is set at $1*10^{-4}$. The largest relative error reported is 0.96. No errors occurred during the simulation.

In order tune the C105 column and heat pump several variables were manually tuned. Aspen could not converge if design specs were used in order to reduce heat pump duties automatically. Three objectives for tuning were assessed:

1. Obtain sufficient product quality
2. Minimize recycle rate (recycle to first separation section)
3. Minimize compression duties

The first variable used for tuning is the exit temperature of the trim heat exchanger (E115). The second variable used for tuning is the split factor of the splitter (SP105). By changing these two variables the P/P-splitter (C105) obtained a qualitatively good propylene product stream (0.9957704 wt%) and a quantitatively good recycle stream (97 wt% propane). However the ratio between the heat pump reboiler and the heat pump compressor is approximately 7.5. This is significantly lower compared to Dimian [page 453 of 453], where a reboil duty to power ratio of 11.4 is obtained. Therefore it is assumed that the heat pump system is not tuned optimal. Another possible difference between our heat pump system and the system designed in Dimian is the bottom effluent specifications. Since a minimization of the recycle rate has also influenced the two controlled variables differences in compressor duties can occur.

One important aspect has not been taken into account in the simulation of the process in AspenPlus. When gas streams or liquid streams pass a heat exchanger, there is a pressure drop. In AspenPlus however this pressure drop is neglected. The pressure drop is calculated to be around 0.2 bara for gases and 1.0 bara for liquids, see chapter 8.2.8.
An overview of the complete AspenPlus simulation is given in Appendix 8.1.

8.2 Equipment selection and design

Equipment from the PFS is selected, designed and sized according to the design performance criteria. The following equipment is reviewed: the reactors, the distillation columns, the glycol unit, the vessels, the gas-solid separators, the heat exchangers, the pumps and the compressors and turbines.

8.2.1 Reactor selection and design

In the design of the reaction section the design of the reaction unit and the regeneration unit is combined. Since the SOC has to be recycled between the reactor and the regenerator unit the integrated design is inevitable.

R101 design
In this chapter a decision is made on the reactor type and the reactor dimensions. The design criteria for the reactor are high conversion, good heat integration and an optimal amount SOC in the reactor, see chapter 5. With the help of a simulation model in Matlab (see chapter 4.2.7) the conditions of the reactor have been determined. This includes the gas flow into the reactor, the flow of SOC into the reactor, the residence times of both, and the temperatures of in and outflow of the reactor. In fixing these parameters a large part of

the reactor design has already been done. A lot of choices however still have to be made at this point on the reactor design. In an earlier stage of the project a process option was chosen (see chapter 2.3), and the choice was made to continuously regenerate the SOC.

The Pt catalyst is fixed on a monolith in the reactor. This configuration is best since the SOC catalyst reacts very fast and therefore has to be regenerated frequently and the Pt catalyst does not have to be regenerated.

Fixing the platinum catalyst in the reactor can be done in several ways; the problem however is that also a continuous SOC stream has to flow through the reactor. The option of a fixed bed of platinum and separating the SOC particles from the platinum particles with a cyclone inside the reactor does not seem to be very advantageous. Another way of keeping the platinum catalyst inside the reactor is to fix it inside the reactor. Several options come into the picture, however fixing the platinum on a monolith quickly comes out as the best option. There are two major reasons for this.

Firstly fixing the platinum on a large substance compared to SOC particles takes out the necessity of separating the two. No cyclones are needed inside the reactor and the SOC stream can be controlled much better since the residence time distribution is smaller. The second great advantage of a monolith is a very low pressure drop compared to a reactor with a catalyst bed and monoliths are readily available at low prices.

Important in the design is smooth flow through the pipes of the monolith. The size of the SOC particles is important because the particles have to be easily separated from the gas stream and easy to transport through the regeneration. This is described in detail in paragraph 8.1. The size of the particles is designed at 60 μm. Hence the size of the channels is chosen at 400 cpsi to prevent plugging in the channels of the monolith.

Technical data about the monolith are given in the table below.

Table 8.1 Technical data of the chosen monolith [74]

Specifications	400 cpsi
Width of channels	1 mm
Specific surface area	1000 m^2/m^3
Density	890 $kg_{monolith}/m^3_{reactor}$
Catalyst load	90 kg cat/$m^3_{reactor}$

The next step in the design is to decide whether to use a downer or riser reactor.

For favourable kinetics the amount of SOC that has to be present per amount of gas in the reactor should be equivalent to 10.0 mol/s when the particles do not move relative to the gas, see chapter 4.2.6. However solid particles always move relative to the gas stream, which will be further explained in Appendix 8.2. A choice for a riser or a downer depends on this relative speed, because the amount of SOC that practically is present in the reactor, in order to achieve the 10.0 mol/s is different for both types. In a downer reactor the solid particles move quicker than a riser reactor. Because the solids move down quicker in a downer than the gas, the SOC flow in the reactor has to be larger. For the riser on the other hand the amount of SOC becomes less. A larger SOC flow has the advantage that the amount of heat that has to be transferred to the gas is stored in a larger amount of SOC, therefore the temperature gradient of the solids over the reactor decreases and consequently the temperature gradient of the gas does so as well. This is favourable for the DH and SHC reaction kinetics, since the temperature drop in the reactor is lower.

A second reason to choose a downer reactor is that a riser system has a higher plugging risk, due to the small channels of the monolith. This is also a very strong argument in favour of the downer reactor, because plugging ultimately results in a shut down of the process.

In the Hipphox design a lot of solid particles are needed because only 10% of the SOC reacts. The available oxygen per mole SOC is limited and therefore the residence time has to be short. Hence they have to move quickly in and out of the reactor.

R101 dimensions

In this paragraph the reactor will be designed in more detail. The results from the kinetic calculations (chapter 4.2.7) for dimensioning the reactor are listed in the table below.

Table 8.2 Input data for reactor dimension calculations

Reactor volume	71 m^3
Solid volume fraction	0.3
Gas volume	50 m^3
Residence time τ	3.65 s
Gas flow	13.6 m^3/s
SOC flow in reactor	10.0 kmole/s

With the calculated reactor volume different H/D ratio's are chosen, which are used to calculate the specific area. This is the gas flow area, since part of the reactor volume is occupied by the monolith. From the area and the gas flow the superficial gas velocity can be calculated. The absolute particle velocity is obtained by summing up the superficial gas velocity and the relative particle speed. The relative particle speed can be obtained by using the iteration procedure described in Appendix 8.2. The obtained relative particle speed is 0.68 m/s. The particle thus moves quicker down the reactor than the gas.

With the overall particle speed and the height of the reactor the residence time (τ_{SOC}) of the particle is obtained. The amount of SOC ensures a small enough temperature drop over the reactor in order to obtain a high conversion, see chapter 4.2.7. Since the residence time on the other hand is shorter than the residence time of the gas this value has to be altered in such way that the same amount needed for a sufficient reaction rate is present in the reactor. The factor with which the SOC flow has to be increased is called the tau ratio. This is the ratio of the residence times of the gas and the solids.

The results of the calculations are shown in table 8.3 for the various possible reactor dimensions.

Table 8.3 Possible reactor dimensions and parameters.

Diameter [m]	Height [m]	Effective area [m^2]	Superficial gas velocity [m/s]	Relative particle speed [m/s]	τ_{SOC} [s]	τ ratio [s]
6.72	2.00	25.00	0.54	0.68	1.63	2.24
4.75	4.00	12.50	1.09	0.68	2.26	1.61
3.88	6.00	8.33	1.63	0.68	2.59	1.41
3.36	8.00	6.25	2.18	0.68	2.80	1.30
3.01	10.00	5.00	2.72	0.68	2.94	1.24
2.74	12.00	4.17	3.27	0.68	3.04	1.20
2.54	14.00	3.57	3.81	0.68	3.12	1.17
2.24	18.00	2.78	4.90	0.68	3.23	1.13
2.03	22.00	2.27	5.99	0.68	3.30	1.11
1.86	26.00	1.92	7.08	0.68	3.35	1.09
1.74	30.00	1.67	8.16	0.68	3.39	1.08

Obviously the amount of SOC that has to be pumped around should be minimised, since this is energy-extensive. From table 8.3 it can be concluded that when the reactor height increases the τ ratio decreases and less energy has to be added to pump the solids around. A high and narrow reactor also has the advantage that it is easier to distribute the solids evenly over the cross-section. On the other hand when the reactor becomes higher it gets less stable, since it is a long and narrow tube. This type of configuration has another disadvantage, it has a very large surface to volume ratio and therefore a lot of heat will be lost. The optimal dimension was found to be a height of 10 meters and a diameter of 3.01 meter.

In Appendix 8.2 the pressure drop over the column is calculated. The resulting overall pressure drop is shown in the following figure as a function of the reactor height.

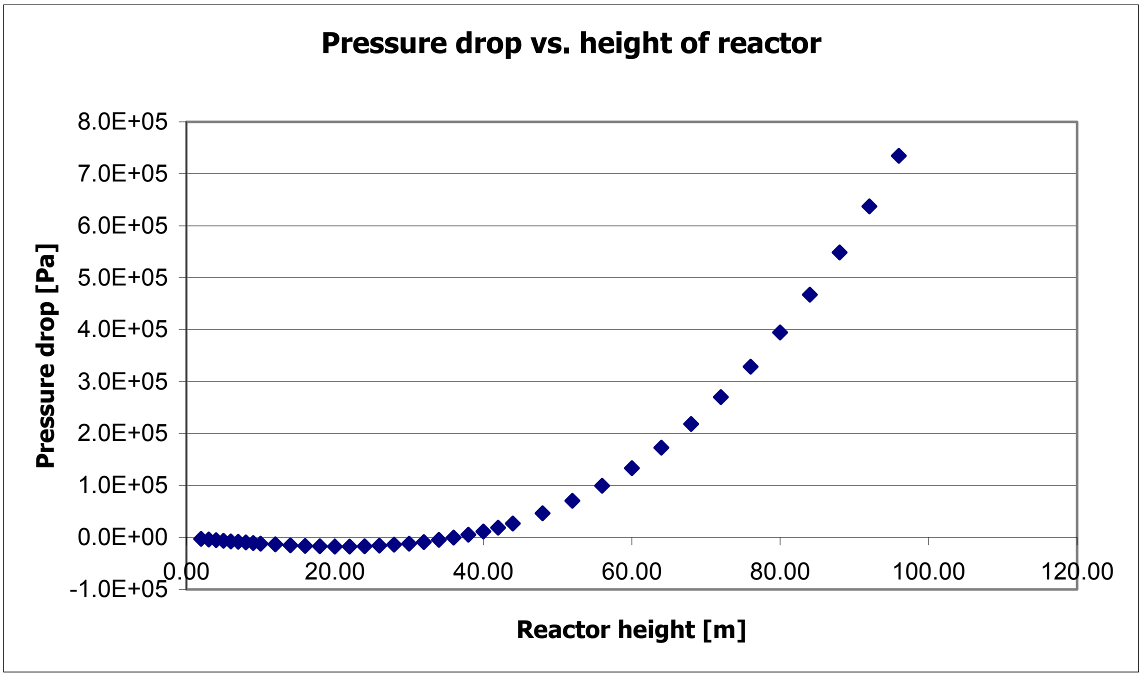


Figure 8.4 Pressure drop versus height of the reactor

In this figure can be seen that the static pressure drop for lower reactors is larger than the pressure drop caused by friction and for higher reactors it becomes much smaller.

Since the thermodynamic equilibrium for propylene production favours low pressure, the reactor pressure should be as low as economically possible. But due to pumping requirements in the downstream processing, the pressure cannot be too low. Also for safety reasons the pressure should be higher than atmospheric pressure. Therefore the pressure in the top of the reactor is chosen to be 2 bara and from the pressure drop a pressure in the bottom is obtained of about 1.9 bara.
In table 8.4 the reactor characteristics are shown:

Table 8.4: Summary of the reactor characteristics

Dimension		**Flow characteristic**		**Pressure**	
Volume [m^3]	71	Gas flow [m^3/s]	13.61	Pressure top [bara]	2
Height [m]	10	SOC flow [m^3/s]	0.33	Pressure bottom [bara]	1.9
Diameter [m]	3.01	Reynolds number	195.95		
Monolith volume fraction	0.3				

R102 design

In this paragraph a decision is made on the regeneration reactor type and it's dimensions.
The design criteria for the regeneration unit are a complete conversion of the SpentSOC, optimal heat transfer and fast enough solid transport.

The SOC that comes out of the reactor has to be regenerated and recycled to the top of the reactor with a minimum loss of heat. The solids can be moved upward mechanically or another possible option is to move the solids upward using a carrier gas. Moving hot solids upward mechanically has the advantage that probably no expensive equipment is used for transporting the solids. The problem with mechanical movement however is that the SOC will come in contact with other solids, e.g. transport band, and thus loose a lot of heat. A second disadvantage of mechanical movement is that a very large machine must be developed with a lot of moving parts. Engineering experience has shown that this has a lot of disadvantages like for example a lot of maintenance due to particle dust in the equipment. The carrier gas option does not have these two disadvantages, or at least to a lesser extent. Since the density and heat capacity of a gas are lower than that of a solid the heat loss will be much lower. Also there are no moving parts except for the compressor used to overcome a pressure drop.
In chapter 4 it is explained that the SOC can be regenerated with air. When the transport of the SOC is combined with regeneration this creates another advantage. The equipment for transport and regeneration is integrated and heat will only be lost to the exhaust air, which has a low density and heat capacity. From above arguments it is concluded that the most optimal configuration for the regeneration of the SOC is a riser reactor.

R102 dimensions

In this paragraph the riser will be designed more in detail. The input data for dimensioning the riser are listed in table 8.5.

Table 8.5 Input data for riser dimension calculations

Solid stream	10.0 kmole/s
Height of the riser	15 meter
τ ratio	1.24
Spent SOC flow	0.93 kmole/s

R101 has a height of 10 meter, but stands higher from the ground since the solids coming from the reactor are transported by gravity into the riser. Also when the solids come out of the riser gravity is used to transport them to the inlet of the reactor. A safe height of 15 meter therefore is chosen for the riser.

In the riser the solids will be moved up and simultaneously regenerated. First the minimal air required to regenerate the SpentSOC is calculated. The solid stream was estimated in chapter 4.2.7 as 10.0 kmole/s. With the chosen tau ratio of 1.24 this becomes 12.4 kmole/s. The density of the solids is 6690 kg/m^3 (see chapter 3.2.4); the solid stream is therefore approximately 0.33 m^3/s. Since an excess of SOC is used in the reactor, only the SpentSOC fraction of this solid stream needs to be regenerated. This amount of SpentSOC is estimated as 7.5 mole%, approximately 0.93 kmole/s. In chapter 4 is explained that to regenerate 10 moles of SpentSOC, 1 mole of oxygen is required. Thus to regenerate this solid stream a minimum of 0.44 kmole/s regeneration air is needed.

Another important parameter is the flow regime of the riser since dilute transport is only possible for certain combinations of the density of the gas, the particle size and the gas velocity. This is shown in the following figure.

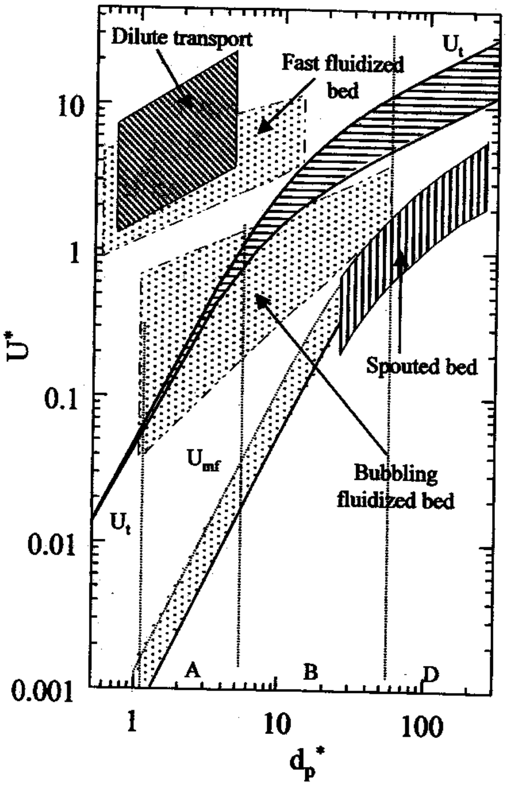


Figure 8.5 generalized map of fluidized regimes. ([59], page 319)

In this figure u* and d$_p$* are the dimensionless gas velocity and particle size defined by:

$$d_p^* = d_p \left[\frac{\rho_g (\rho_p - \rho_g) g}{\mu_g^2} \right]^{1/3} \tag{8.4}$$

$$U^* = U \left[\frac{\rho_g^2}{\mu_g g (\rho_p - \rho_g)} \right]^{1/3} \tag{8.5}$$

where d_p is the particle size and U is the gas velocity.

The particle size has been chosen to be at least larger than 20 μm in order to be able to separate it with a cyclone. In order to stay in the dilute transport regime the particle size was set to 60 μm, since this is a safe choice taking into account the variation of the density and viscosity of air with the temperature.

Taking these constraints into account, the regeneration is still possible with plain air, which is an advantage since this can simply be taken from the atmosphere without further costs.

An optimisation procedure was carried out to try to stay within the dilute transport regime, keeping an excess air stream of 1.1 times the stoichiometric required air stream, to ensure that all the in steady state stoichiometricly used SOC will be regenerated. In this way it is prevented that there is build-up of the amount of SpentSOC. The system will also be able to cope with small disturbances in the amount of SpentSOC.

The regeneration of the SOC is preferably carried out at high oxygen pressure. From an economic point of view it was initially tried to use plain air at an atmospheric pressure for the transportation and regeneration of SpentSOC. Mass transfer calculations will show that using these conditions it is possible for the regeneration to be completed.

The optimisation procedure that was carried out to come to the riser design parameters will be explained in the following. The design suffers from a few constraints. These are firstly the amount of SOC that has to be transported, secondly the amount of oxygen that is needed for the regeneration and finally the dilute transport regime wherein the dimensionless particle size and dimensionless gas velocity have to stay (fig 8.5) in order to be able to move the particles upward. Together with these constraints the riser design is determined by the temperature profile that is caused by the heat from regeneration and also by the pressure drop that was calculated. The pressure drop can be calculated in the same way as at the reactor (Appendix 8.2), this time only the static pressure drop has the same effect as the pressure drop due to friction. The pressure drop turned out to be 1 bar. The incoming gas, which does not have to be heated up before entering the riser, as will be explained below, will now be compressed to a pressure of 2 bara (hereby increasing the temperature). Due to the energy release and the almost immediate heat transfer to the gas (see below Heat and mass transfer), the gas will expand during the travel upward. The conditions in the top and bottom of the riser are shown in the following table (table 8.6). Throughout the riser the dilute transport regime (fig. 8.5) is maintained, despite of changes in the density of air caused by the temperature and pressure.

Table 8.6: Summary of the riser characteristics

	Bottom	**Top**
Temperature [K]	375	955
Pressure [bara]	2	1
SOC flow [m^3/s]	0.327	0.327
Gas flow [m^3/s]	7.59	19.42
Gas velocity [m/s]	12.45	30.96
Particle velocity [m/s]	11.58	30.53
Hold-up	0.0444	0.0168
d_p^*	3.86	1.8
u^*	10.2	1.99
Reynolds	973,518	481,520
Diameter [m]	0.9	0.9
Volume [m^3]		9.54

Increasing the pressure at the bottom would create a safer design in the sense that the flow regime would be more in the centre of the dilute transport. A result of this however would be that the particle speeds would increase too much. The particle speed at the top of the riser is in the chosen design already almost 31 m/s. Higher particle speeds are found to be unsafe and the particles would foul too much.

As became clear in chapter 4 the regeneration of the SOC delivers by far enough energy for the reactions in the reactor. With a heat loss of 6^0C of the SOC assumed in the gas-solid separation, it was found that the temperature of the incoming regeneration air did not have to be heated up. The remaining heat can be used to warm up the SOC, which on its turn partly heats the reactant stream entering the reactor. The dynamics of this will be treated in next section.

Heat integration

The following table (8.7) shows the heat balance over the riser

Table 8.7 Heat balance over the riser

	Enthalpy [kJ/s]	**Enthalpy [kJ/s]**
Heat released during regeneration	66180	
Heating up the SOC in the riser from 869 to 955 K		65945
Heating up the gas in the riser from 375 to 955 K		235
Total	66180	66180

Note that these values do not comply exactly with the values given in chapter 7.1.2, however this calculation was done in an earlier stage.

In the first stage of the reactor design the temperature of the SOC that was required for optimal heat integration was set to 923.6 K. However since the regeneration heat was of such an amount that the SOC could be heated up more, to 955.3 K, the idea arose that the SOC could be inserted into the reactor at this temperature as long as the heat transfer was fast enough. In doing this, the heat exchanger at the exit of the riser could be left out and the reactant stream going into the reactor did not have to be heated up to 873 but only to 652 K.

Heat transfer

In both the riser and the reactor the particles are moved by dilute transport. Characteristic of this type of transport is that unlike in a fluidized bed the particles do not or do not often encounter each other. Therefore the heat and mass transfer of the particles to the gas will be treated as convection to and from a single sphere. The calculation procedure can be found in appendix 8.3. This results in the values for the heat transfer for the riser and the reactor, shown in the following table (8.8).

Table 8.8: heat transfer properties for the riser and the reactor.

	Reactor	**Riser**
h_p [W/m^{2}K]	3027	1652
A [m^2]	$1.01*10^5$	$5.34*10^4$
Q [kW]	$3.94*10^6$	$2.75*10^6$

The values of the heat transfer have to be compared with the amount of heat that is being transferred per second in the riser and the reactor in order to make conclusions about the rate of the heat transfer. This is shown in table 8.9; here also the residence times of the solids are listed.

Table 8.9: Heat transfer comparison for the riser and the reactor.

	Reactor	**Riser**
Heat transferred [kW]	$4.64*10^4$	$7.50*10^5$
Residence time solids [s]	2.94	0.71
Heat transfer capacity [kW]	$3.94*10^6$	$2.75*10^6$

The heat transfer capacity in the reactor is by far large enough. In the riser the heat transfer is also sufficient, the heat transfer capacity is still a factor 3.7 larger than the amount of heat that is transferred.

The assumption that the heat transfer is large enough to heat the reactant stream of the reactor with the excess heat of the SOC that was made earlier will be proven valid now.

The amount of heat that is added extra when leading the SOC into the reactor at 955.3 K in stead at of 923.6 K is $1.94*10^4$ kW.
The time it takes to transfer this heat from the SOC to the gas will take about $1.94*10^4/2.75*10^6$ which is 0.007 seconds. Compared to the residence time of the gas in the reactor, which is 3.65 seconds, this is very short. The assumption therefore is justified.

Mass transfer

In this part it will be shown for the riser that the mass transfer between gas and the solids is sufficiently fast for the gas to reach the surface of the solids. It is common knowledge that the mass transfer in riser and downer reactors is good. Therefore the following calculation is done only to make sure this is also the case in this design. It will be done for the riser only and not for the reactor since the residence time of the riser is much shorter than of the reactor.

Riser

For the same reasons as with heat transfer the mass transfer of a single particle will be treated.

The rate of mass transfer between well-dispersed single spheres and the surrounding gas can be described by the following mass transfer equation as found in [59, page 288]:

$$\frac{dN_A}{dt} = k_{g,\text{single}} S_{ex,\text{single}} \left(C_A^i - C_A \right) \tag{8.6}$$

where dN_A/dt is the transfer rate of A from the particle surface to the gas stream or the other way around. $k_{g,\text{single}}$ is the mass transfer coefficient of the particle, $S_{ex,\text{single}}$ is the exterior surface of the particle, $C_A^i - C_A$ is the difference in concentration of A at the gas-particle interface and the gas stream.

$k_{g,\text{single}}$ can be found by calculating the dimensionless Sherwood number:

$$Sh_{\text{single}} = \frac{k_{g,\text{single}} d_{sph} y}{D} = 2 + 0.6 \left(\text{Re}_{sph} \right)^{0.5} \left(Sc \right)^{0.333} \tag{8.7}$$

where Re_{sph} is the particle Reynolds number defined as:

$$\text{Re}_p = \frac{\rho_g u d_{sph}}{\eta_g} \tag{8.8}$$

Sc is the Schmidt number defined as:

$$Sc = \frac{\eta_g}{\rho_g D} \tag{8.9}$$

In the above equations are defined; η_g the dynamic viscosity of the gas, ρ_g is the density of the gas, d_{sph} the diameter of the particle, u the relative velocity of the gas and the particle, y is the logarithmic mean mole fraction of the inert or non-diffusing component, and D is the gas phase diffusion coefficient.

The values of the parameters in the riser are defined as in the following table.

Table 8.10: Parameters for determining the mass transfer coefficient.

$S_{ex,single}$ [m]	1.13*10^{-5}	**d_{sph}** [μm]	60
C_A^i - C_A [mol/m^3]	0.006	**y**	0.9
η_g [Pa*s]	3.03*10^{-5}	**u**[m/s]	0.5
ρ_g [kg/m^3]	1.16	**D** [m^2/s]	8.00*10^{-5}

As the non-diffusing component nitrogen is used with a mole fraction of 0.8.

This results in using the specified formula's in an overall transfer rate (multiplying by the total number of particles present in the reactor) of $3.17*10^3$ mol/s
The required amount of oxygen mass transfer in the riser was found to be 93.2 mol/s.
The mass transfer is roughly a factor 34 better than needed. For the equipment data summary sheets of the reactors the reader is referred to chapter 8.3.

8.2.2 Columns selection and design

In this paragraph the separator columns following from the PFS are designed and optimised. As described in chapter 5, five columns are required. They will be described one by one here. The columns are first designed as stand-alone columns, which means they are not integrated with the rest of the process. This gives only a rough estimate for the operating conditions of the columns. Then the columns are optimised with respect to the process flow scheme.

Depropanizer C101, preliminary design
The design criteria for this column were mentioned in chapter 5: a high recovery of propane and low amount of C4 in the top stream. The feed for this column consists of the LPG feed stream mixed with the propane recycle stream.
There are no non-ideal mixtures present; no azeotropes are likely to be formed. For this column no overhead or bottom purity specifications are required. The end compositions will therefore represent optimization problems, and depend on process economics. As a first estimate 99.5 mole% recovery of the light key (propane) in the overhead is taken, as a rule of thumb, given in Douglas [24, section A2]. For the heavy key (butane) 99.5 mole% recovery in the bottoms is taken, also from Douglas [24]. It is also assumed that all components lighter than propane leave the column in the overhead stream and all components heavier than butane leave with the bottoms. The feed stream composition and the size of the mass flow are estimated from the preliminary mass balances of chapter 5.
The operating pressure is first designed by the economic desirability of using a condenser supplied with cooling water, rather than a refrigerated condenser. The overhead must then be condensed at preferably 310 to 330 K. A partial condenser is used, since light ends (mostly ethane) are present. The column pressure must therefore be sufficiently high to obtain an adequate supply of reflux. The bubble point pressure of the top stream is estimated with the following equation:

$$p_{bub} = \sum_i z_{i,top} p_i^{sat} \tag{8.10}$$

with:
p_{bub} = bubble point pressure [bar]
$z_{i,top}$ = mole fraction of component i in the top
p_i^{sat} = saturation pressure of component i [bar]

The saturation pressures of the components are estimated using the Wagner equation, which can be used over a wide temperature and pressure range, up to the critical point:

$$\ln p_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^{5}}{T_r} \tag{8.11}$$

with:
p_r^{sat} = reduced saturated vapour pressure = p^{sat}/p_c [bar]
p_c = critical pressure [bar]
T_r = reduced temperature = T/T_c [K]
T_c = critical temperature [K]
$\tau = 1\text{-}T_r$
A, B, C, D are empirical constants given for each substance, listed in [13].
For propylene and ethylene an extended Antoine-equation is used:

$$\log p^{sat} = A - \frac{B}{(T + C - 273.15)} + 0.43429x^{n} + Ex^{8} + Fx^{12} \tag{8.12}$$

with:

$$x = \frac{T - t_0 - 273.15}{T_c} \tag{8.13}$$

A, B, C, E and F are empirical constants; they are listed in reference [13].

This equation is valid for pressures between 1.863 en 19.87 bar and temperatures between 278.15 and 373.15 K.

By choosing a top temperature of 315 K and estimating the distillate composition $z_{i,top}$, the column operating pressure (p_{bub}) was calculated, as a first estimate. This lead to a operating pressure of 20 bara. At this column pressure the dew point temperature was calculated, as an estimate for the reboiler temperature.
For the dew point pressure, p_{dew}, the following equation holds:

$$p_{dew} = \frac{1}{\sum_{1}^{n} \frac{z_{i,bot}}{p_i^{sat}}} \tag{8.14}$$

With p_{dew} = 20 bara and the Wagner and extended Antoine equations given above, the dew point temperature was calculated.

The design of the column was continued with the use of AspenPlus, by using a DSTWU unit. The DSTWU is a shortcut distillation design using the Winn-Underwood-Gilliland method. The reflux ratio RR is chosen as a first estimate at RR = 1.2RR_{min}, with RR_{min} = the minimum reflux ratio (rule of thumb from [24]). By estimating a pressure drop of 0.5 bara, the required input for the DSTWU is complete. The DSTWU gives as output estimates for the minimum and actual reflux ratio (RR_{min} and RR respectively), a minimum and actual number of stages (N_{min} and N respectively), a feed stage (N_f), the number of actual stages above the feed, the distillate and bottom temperature and the distillate to feed fraction (D/F). This output can be used in the Radfrac unit of AspenPlus, which is used to simulate the final column. But before the Radfrac unit is used, the column is optimised and integrated with the rest of the process. This final input and output of the DSTWU and Radfrac units are described in this paragraph (see below in Columns optimization).

Glycol unit (C102 and C103)

Because the glycol unit is a standard technology, already commercially applied, the design of this unit didn't have a priority in the conceptual design of the Hipphox process. An estimate is made to determine the costs of removing the water from the gas stream.

De-ethanizer C104, preliminary design

The design criteria for this column were also mentioned in chapter 5: the light ends have to be completely removed, at least as far as possible, for the last column to operate well. Also the cooling duty has to be as low as possible, since cryogenic cooling is expensive. The feed for this column is estimated with the preliminary mass balances of chapter 5.

There are no non-ideal mixtures present; no azeotropes are likely to be formed. For this column also no overhead or bottom purity specifications are required. The same procedure as for C101 is used to estimate the column pressure. The light key is ethane and the heavy key is propylene. It is again assumed that all components lighter than ethane leave the column in the overhead stream and all components heavier than propylene leave with the bottoms.

The same procedure described for the depropanizer was followed for the de-ethanizer, again with a partial condenser, since hydrogen is present. This lead to a column operating pressure of 35 bara, with a chosen top temperature of 340 K. This means no cryogenic cooling is required to achieve the separation, but it requires a large operating pressure. The column is then optimised and integrated with the rest of the process, and the final input and output of the DSTWU and Radfrac units are described in this paragraph (see below in Columns optimization).

P/P-splitter C105, preliminary design

The most important overall specification is the product stream of 99.5 wt% propylene. Also, the propane recycle must be as small as possible, since the recycle costs must be minimized. The feed for this column is estimated with the preliminary mass balances of chapter 5, based on the product stream requirements.

There are no non-ideal mixtures present; no azeotropes are likely to be formed. For this column, the top stream must contain at least 250 kta product, and at least 99.5 wt% propylene. The light key is propylene and the heavy key is propane. Again the same procedure is followed, this time with a total condenser, since the product stream will contain mostly propylene. This lead to a column operating pressure of 24 bara, with a chosen top temperature of 330 K. The column is then optimised and integrated with the rest of the process, and the final input and output of the DSTWU and Radfrac units are described in this paragraph (see below in Columns optimization).

Columns optimization

Since the columns are not operated as one unit but as part of a complete process, the column designs were changed drastically to save costs, energy, etc. The final column design will be explained in this paragraph for each column.

C101

This column was preliminary designed at a pressure of 24 bara. Since the feed to this column consists of the LPG feed <101> and the propane recycle <151>, which have a pressure of 17 bara, and the overhead stream will be the feed stream for the reactor which operates at 2 bara, the column pressure is optimally slightly below 17 bara, to get a top stream which can be cooled with cooling water. A rough economic calculation showed this is less expensive than operating the column at lower pressure, with two turbines, one before and one after the column C101. The column was re-designed with a top pressure of 16,7 bara, due to the higher pressure of the feed it will then be able to enter the column, taking pressure drop into account. The pressure drop was first estimated, the DSTWU was run in AspenPlus with this estimate, and then the resulting number of trays was used to make a better estimate of the pressure drop. This procedure led to the following input for the DSTWU:

Table 8.11 Input of the DSTWU for column C101

RR	1,2RR_{min}
Light key	Propane
Heavy key	Butane
Condenser	Partial
Condenser pressure	16,7 bara
Pressure drop	0,2 bara

This resulted in the following output for the DSTWU:

Table 8.12 Output of the DSTWU for column C101

Minimum reflux ratio RR_{min} (mole)	0,82
Actual reflux ratio RR (mole)	0,99
Minimum number of stages N_{min}	12
Number of actual stages N	26
Feed stage N_f	14
Distillate temperature	320 K
Bottom temperature	359 K
Distillate to feed fraction	0.98

The pressure drop of the column was estimated with the formulas given in [21, page 571, 575] and [24, page 454, 456]. The calculation can be found in appendix 8.4.

The input for the Radfrac unit is based on the output from the DSTWU for column C101, with a pressure drop of 0.15 bara, resulting from the calculation in the appendix. The final output after complete optimalization of the flow scheme is given in table 8.13.

Table 8.13 Output of the Radfrac for column C101

Reflux ratio RR (mole)	0.99
Reflux rate	1294 kmol/hr
Distillate rate	1314 kmol/hr
Condenser temperature	321 K
Boilup rate	2494 kmol/hr
Bottoms rate	25 kmol/hr
Reboiler temperature	362 K

C104

This column was preliminary designed at a pressure of 35 bara. However operating the column at this pressure would require a very expensive compressor, and a rough economic evaluation showed that this would cost too much to be acceptable. Since the bottom stream is sent to a column operating at lower pressure, the pressure should be as low as economically feasible. The amount of propane and propylene loss should not be too high in the top stream. From economic calculations, taking into account the costs of the column, the condenser duty and the compressor costs, and the loss of propane and propylene in the top, the optimal operating pressure was found to be 24 bara.

The pressure drop was first estimated, the DSTWU was run in AspenPlus with this estimate, and then the resulting number of trays was used to make a better estimate of the pressure drop. This procedure led to the following input for the DSTWU:

Table 8.14 Input of the DSTWU for column C104

RR	1,2R_{min}
Light key	Ethane
Heavy key	Propylene
Condenser	Partial
Condenser pressure	24 bara
Pressure drop	0,24 bara

This resulted in the following output for the DSTWU:

Table 8.15 Output of the DSTWU for column C104

Minimum reflux ratio RR_{min} (mole)	35.6
Actual reflux ratio RR (mole)	42.8
Minimum number of stages N_{min}	16
Number of actual stages N	29
Feed stage N_f	16
Distillate temperature	216 K
Bottom temperature	334 K
Distillate to feed fraction	0.09

The calculation of the pressure drop can be found in appendix 8.4. The input for the Radfrac unit is based on the output from the DSTWU for column C104, with a pressure drop of 0.24 bara, resulting from the calculation in the appendix.

The results of the Radfrac unit, based on the output of the DSTWU, are given in table 8.16.

Table 8.16 Output of the Radfrac for column C104, Reflux Ratio = 42.8

Reflux ratio RR (mole)	42.8
Reflux rate	5382 kmol/hr
Distillate rate	126 kmol/hr
Condenser temperature	211 K
Boilup rate	7617 kmol/hr
Bottoms rate	1287 kmol/hr
Reboiler temperature	334 K
Heat duty condenser	-21582 kW
Heat duty reboiler	22607 kW

Since the heat duty of the condenser is very costly in case of cryogenic cooling, the reflux ratio was optimised to get an acceptable heat duty, and acceptable propane and propylene loss in the top. This led to a reflux ratio of 10 instead of 42.8. The other input was not further optimised, which means the same number of stages, the same feed stage, the same distillate to feed fraction etc. was used. This result of the optimised Radfrac unit is given in table 8.17.

Table 8.17 Output of the Radfrac for column C104, Reflux Ratio = 10

Reflux ratio RR (mole)	10
Reflux rate	1257 kmol/hr
Distillate rate	126 kmol/hr
Condenser temperature	211 K
Boilup rate	2075 kmol/hr
Bottoms rate	1287 kmol/hr
Reboiler temperature	334 K
Heat duty condenser	-5134 kW
Heat duty reboiler	6160 kW

This clearly shows the profit of the optimisation, the heat duty of the condenser is reduced to 5134 kW instead of 21582 kW. This means a saving of € 5.7 million per year is made in refrigerant costs. However more propylene and propane will leave with the top; a comparison is given below.

Table 8.18 Propylene and propane in <168> at varying reflux ratio

	RR = 42.8	**RR = 20**	**RR = 10**
	<168>	<168>	<168>
Propylene kmole/hr	1.54E-05	1.09E-04	0.064
Propane kmole/hr	6.18E-07	5.52E-06	0.005

This shows more product and raw material is lost, from sustainable point of view this is not desirable, but at this reflux ratio it is still acceptable. A sensitivity analysis performed in AspenPlus by varying the reflux ratio. The response of this variation was expressed as the flow of propylene in the overhead <168> of C104. This resulted in the following graph:

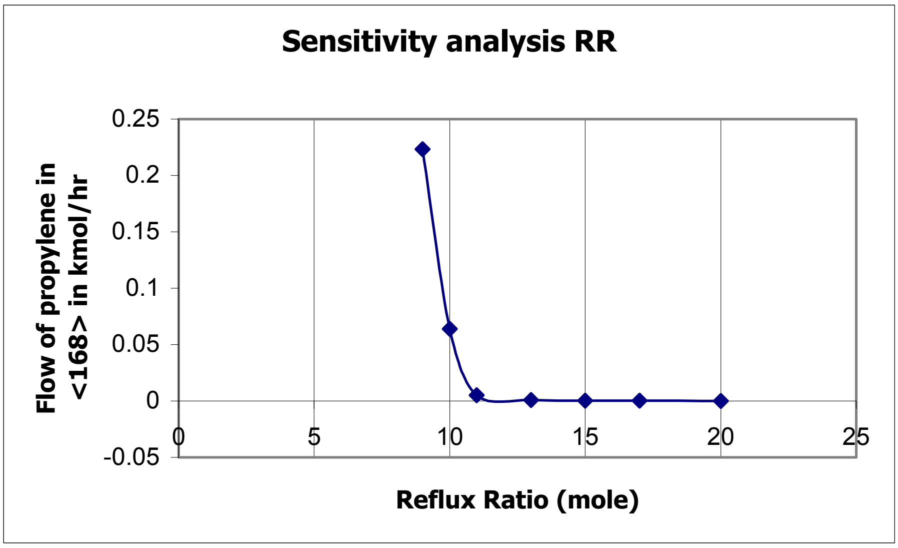


Figure 8.6 Result of sensitivity analysis for the reflux ratio of C104

This shows that below a reflux ratio of 10 the amount of propylene in the overhead stream, <168> increases very rapidly.

C105

This column was preliminary designed at a pressure of 24 bara. To save energy and to reduce the use of cooling water, a heat pump driven column has been designed. This is explained in chapter 5. The operating pressure can be reduced to 10 bara with this heat pump system. The calculation of the pressure drop can be found in appendix 8.4. In this heat pump system the column is designed as a Radfrac, the input and output of this column are given in the tables below.

Table 8.19 Input of the Radfrac for column C105

Number of actual stages N	119
Boilup ratio (mole)	18
Feed stage <119>	62
Feed stage <171>	1
Condenser	none

Table 8.20 Output of the Radfrac for column C105

Reflux ratio R (mole)	0.93
Reflux rate	10522
Distillate rate	11264 kmole/hr
Distillate temperature	292 K
Boilup rate	9798 kmole/hr
Bottoms rate	544 kmole/hr
Reboiler temperature	304 K
Heat duty condenser	0 kW
Heat duty reboiler	39702 kW

More information about the performance of this column can be found in chapter 5, the paragraph about the heat pump.

Column dimensions

The choice is made to use plate columns rather than packed columns, based on guidelines given in [21, page 587-588].

For the design of the columns it is assumed that the tray spacing is about 0.6 m (2 ft) [24, page 453]. Also some space is needed at the bottom and at the top of about 1.5 m. The column height can be calculated using the following formula:

$$H = 0.6\cdot(N_{trays} - 1) + 2 * 1.5 \qquad (8.15)$$

The column height should not be higher than 175 ft (=53.34 m) and the height-to-diameter ratio should be less than 20 to 30.

With these guidelines the column height and diameter are estimated.

The number of trays is determined in the preceding paragraphs of this chapter. With these values the height and the diameter for each distillation column can be calculated. As the number of the trays for the P-P splitter is too high for the height of the column is too high, this unit is split into two units. The division is done at the feed stage of the whole column designed in AspenPlus. In the following table the results are shown for the dimensions of the distillation columns.

Table 8.21 Dimensions of the distillation columns

Column	Name	N_{trays}	Height [m]	Diameter [m]
C101	Depropanizer	26	18.0	0.90
C104	De-ethanizer	29	19.8	0.99
C105 (1)	P-P splitter	62	39.6	1.98
C105 (2)	P-P splitter	57	36.6	1.98

For the equipment data summary sheets of the columns the reader is referred to chapter 8.3. For C101 the equipment data specification sheet is given as well in chapter 8.3.

8.2.3 Glycol unit selection and design

To design the glycol unit information from Natcogroup.com [64] was used. The glycol unit exists of a glycol contactor C102 and a glycol reconcentrator C103.

Glycol contactor C102

The 'wet' gas stream <184> is 2470 m^3/hr (=2.1 Mscfd). The design pressure is 12 bara, so no additional compressors are required. 12 bara equals 174 psig. Table 1 from [64] shows the glycol contactor capacities. From this table the glycol contactor is designed. With a gas capacity of 2.1 Mscfd and a design pressure of 174 psig, the vessel size has to be 16 inch (=0.41 m). A H/D ratio of 10 is chosen such that the height of the vessel becomes 4.1 m. The tray spacing is 18 inch [64]. When the column is 4.1 meter high, the number of trays is 8.

Glycol reconcentrator C103

For the glycol reconcentrator less information was available. However the glycol reconcentrator is a simple common distillation column and the boiling points of water and glycol differ a lot, so the separation is very simple. For the economic calculation (see chapter 11.2) a column of 15 meters and a diameter of 1 meter are chosen, with about 20 trays.

Amount of glycol

In the gas stream <184> entering the glycol unit 93.3 kg/hr of water is present. The ratio of glycol to water can be chosen and depends on the reconcentration capacity of the firebox and pump capacity. The ratio has to be at least 2 gallons of glycol per pound of water removed (this equals 0.02 m^3 glycol per kg water). In the economical calculation it is assumed that this amount of glycol can be neglected, as glycol is not very expensive.

8.2.4 Vessel selection and design

In the Hipphox process four vessels are required. The design is carried out following the procedure described in chapter 10.9 of Coulson and Richardson [21, page 459].

The settling velocity (u_t) can be estimated by the following equation:

$$u_t = 0.07\left[\frac{(\rho_L - \rho_V)}{\rho_V}\right]^{1/2} \tag{8.16}$$

A demister pad can used to improve the performance of the separating vessels, where high separating efficiencies are required.
When a demister pad is not applied, the value of u_t should be multiplied by a factor of 0.15 to provide a margin of safety and to allow for flow surges. The hold-up time should be at least 10 minutes.

Vessel for water separation (V102)

This vessel has as a primary design criterion that the water, produced in the reactor R101, is removed as much as possible, since no water is allowed in the upstream distillation column. The overhead of the vessel is sent to the glycol unit, which separates the remaining part of the water from the hydrocarbons. Since a phase split is less expensive than the glycol unit, it is desired to remove a large part of the water first. The effluent stream of R101 has a pressure of 1.9 bara. Column C104 operates at 24 bara. The pressure at which the phase split is performed is simulated in AspenPlus. The vessel was simulated with a simple flash vessel, with a zero heat duty. The property method chosen was PR-BM, the Peng-Robinson equation of state with Boston-Mathias modification, since this yielded better results compared to the SRKKD property method. A sensitivity analysis in which the pressure was varied is performed. The response of this variation was expressed as the flow of water in the overhead <113> of V102 and the flow of propylene and propane in the bottom <160> of V102. This resulted in the following graph:

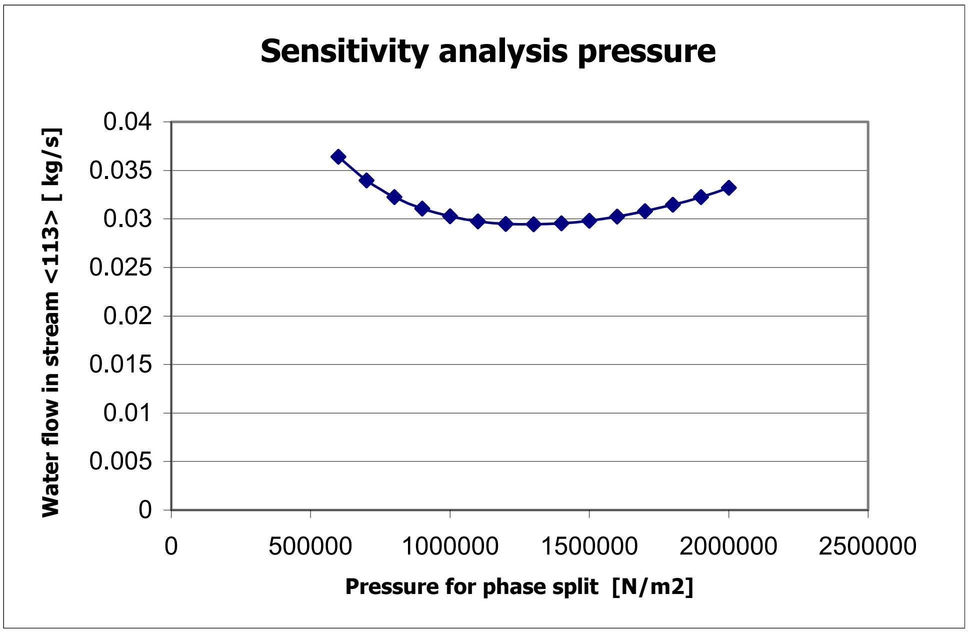


Figure 8.7 Result of sensitivity analysis for the pressure of water separation

It was found that the flow of propylene and propane did not depend very much on the pressure, but the water flow indeed changed with the pressure. From the figure it was chosen to operate the separation at 12 bara. Since the glycol unit is able to operate at a pressure near 12 bara, the configuration was found to be optimal in this way. This means two compressors are required, K101 is needed to compress the effluent of R101 to 12.2 bara and K102 compresses the overhead of C102 to 25.2 bara, taking some pressure drop into account for the coolers.

For the first separation of the water from the gas stream a vertical or a horizontal vessel can be designed. The design is somewhat different, but both types will have the same performance and a hold-up time of 10 minutes. Both types are calculated in the following.

Vertical vessel:
The diameter of the vessel must be large enough to slow down the gas down to a velocity at which the particles will settle out. The minimum diameter can be calculated with the following relation:

$$D_{\min} = \sqrt{\frac{4\phi_{vV}}{\pi u_s}} \tag{8.17}$$

With:
ϕ_{vV} = vapour volumetric flow rate [m^3/s]
u_s = u_t (demister pad) or 0.15*u_t (without demister pad) [m/s]

The actual diameter is chosen somewhat larger than the minimum diameter calculated.
With a 10 minutes hold up (τ), the liquid volume held in the vessel can be calculated:

$$V_L = \phi_{vL} \cdot \tau \tag{8.18}$$

With ϕ_{vL} = liquid volumetric flow rate [m^3/s]

The liquid height is then:

$$h_v = \frac{\text{volume held up}}{\text{vessel cross-sectional area}} = \frac{V_L}{\frac{1}{4}\cdot\pi\cdot D^2} \tag{8.19}$$

This height must be increased to allow space for positioning a level controller. The total height of the column can be calculated with the following formula:

$$H_{vessel} = h_v + 0.6 + 1 + 0.4 \tag{8.20}$$

Horizontal separator:
A horizontal separator can be designed with the following procedure. First the settling velocity can be calculated with formula 8.24. If no demister pad is used, the velocity should be multiplied by 0.15.
The liquid height is set at half the vessel diameter and the fraction f_v of the total cross-sectional area occupied by the vapour is also set at 0.5.

$$h_v = D/2 \text{ and } f_v = 0.5 \tag{8.21}$$

The vapour residence time required for the droplets to settle to liquid surface can be calculated with the following relation:

$$\tau_V = \frac{h_v}{u_t} = \frac{0.5\cdot D}{u_t} \tag{8.22}$$

The actual residence time is:

$$\tau_{actual} = \frac{L_v}{\text{vapour velocity}} = \frac{ratio_{L/D}\cdot D}{\dfrac{\phi_{vV}}{\frac{1}{4}\cdot\pi\cdot D^2\cdot f_v}} \tag{8.23}$$

The length over diameter ratio ($ratio_{L/D}$) is chosen with the valid operating pressure. As a design guide [21, page 461] a ratio of 3 is chosen at a pressure of 0 to 20 bara and a ratio of 4 at a pressure of 20-35 bara.

For satisfactory separation the actual residence time must equal the required residence time (τ_V).
This can be rewritten to get the following relation for the required diameter:

$$D = \sqrt{\frac{0.5\cdot\phi_{vV}}{u_t\cdot ratio_{L/D}\cdot\frac{1}{4}\cdot\pi\cdot f_V}} \tag{8.24}$$

The hold-up time is:

$$\text{hold-up time}=\frac{\text{liquid volume}}{\text{liquid flow rate}}=\frac{\frac{1}{4}\cdot\pi\cdot D^2\cdot(1-f_v)\cdot ratio_{L/D}\cdot D}{\phi_{vL}} \tag{8.25}$$

This hold-up time must be at least 10 minutes. If this is not the case, then the diameter should be increased such that the hold-up time is more than 10 minutes.

For vessel V102 it is chosen to use a demister, as it is preferable to remove as much water as possible. In table 8.22 the results of the calculation of a vertical and horizontal vessel are shown.

Table 8.22 Results for vessel V102

	Horizontal		**Vertical**
		Optimalization	
Settling velocity [m/s]	0.42		
Diameter [m]	0.83	1.3	1.44
Diameter rounded [m]			1.5
Ratio H/D	3	3	
Height or length [m]	2.50	3.9	4
Hold up time [min]	2.92	11.10	10
Volume vessel [m^3]		5.18	6.54

As the volume of the horizontal vessel is smaller than the vertical vessel, a horizontal vessel will be used.

Reflux accumulators (V101, V103 and V104)

The reflux accumulators will be designed as horizontal vessels following the same procedure described above. The results are shown in table 8.23.

Table 8.23 Results for the reflux accumulators V101, V103 and V104

	V101		**V103**		**V104**	
	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid
Flow rate [kg/h]	57598	56928	1144	37353	39701	442824
Density [kg/m3]	36.8	400	12.6	350	20.8	501.6
Pressure [bara]	16.2		23.8		10.0	
		Optimization		Optimization		Optimization
Settling velocity [m/s]	0.2		0.4		0.3	
Diameter [m]	2.4	3	0.4	2.5	2.1	5.3
Ratio L/D	3		4		3	
Length [m]	7.1	9	1.5	10	6.3	15.8
Hold-up time [min]	6.6	13.4	0.1	13.8	0.8	11.6
Volume vessel [m^3]		63.6		49.1		341.0

When water is present, Stainless Steel is chosen as the material of construction. For vessels V101, V103 and V104 Carbon Steel is chosen.

8.2.5 Gas-solid separation

Two separation systems are required to separate the SpentSOC from the product stream and to separate the regenerated SOC from the air stream. The properties of the streams are shown in the next table.

Table 8.24 Input data for gas-solid separation calculations

Stream	Flow [m^3/s]	Particle diameter [μm]	Loading [kg_{SOC}/m^3_{gas}]
Product stream with SpentSOC	13.6	60	127
Air stream with fresh SOC	23.2	60	97

The loading is calculated with the solids flow and gas flow in both reactors, and their residence times. For R101 this is:

$$Load = \frac{SOC\,flow \cdot \tau_{SOC}}{gasflow \cdot \tau_{total}} \cdot \rho_{SOC} = \frac{0.33 \cdot 2.94}{13.6 \cdot 3.65} \cdot 6690 = 127 \frac{kg_{SOC}}{m^3_{gas}} \qquad (8.26)$$

Design criteria for the separation are

Several options are possible for this separation. There are however some constraints. The efficiency of the separation has to be very high, as it is not preferable to lose any SOC.

The first option considered is a gravity settler. The efficiency is very low, about 50% [21, page 447]. Furthermore a large settling area is needed because the gas velocity is typically between 1.5 – 3 m/s. Another option is to use impingement separators that use baffles to achieve the separation. However the efficiency is not high enough.

Also a simple sieve or filter can be used. The problem is however that the gas flow is very high. To obtain a good separation, the filter area required becomes very large.

The options are therefore limited to cyclones or electrostatic precipitators. Cyclones are a good option and relatively cheap. Furthermore they are widely used. Electrostatic precipitators have one disadvantage. The space required is relatively large. Furthermore it is not known if the SOC can be charged. Therefore the choice is made to use cyclones. The design is done using the design procedure of Rhodes [60].

The most common type is the reverse flow type. A strong vortex is created inside the cyclone body. The solids are pushed downwards by the outer vortex and leave the cyclone at the bottom of the cyclone. This outlet is sealed to gas so the vortex reverses near the bottom and the gas leaves the cyclone via the top. The flow characteristics can be described with the following relations.

$$Eu = \frac{\Delta p}{(\rho_f v^2 / 2)} \qquad (8.29)$$

With:

Eu = the Euler number, resistance coefficient

ρ_f = gas density [kg/m^3]

v = characteristic velocity [m/s]

Δp = pressure change [Pa]

The characteristic velocity is a function of the gas flow rate (q) and the cyclone inside diameter (D).

$$v = \frac{4q}{\pi D^2} \qquad [\mathrm{m/s}] \tag{8.30}$$

The scale up of cyclones is based on a dimensionless group, the Stokes number. The Stokes number characterizes the separation performance of a family of geometrically similar cyclones. The Stokes number Stk_{50} is defined as

$$Stk_{50} = \frac{x_{50}^{2} \rho_p v}{18 \mu D} \tag{8.31}$$

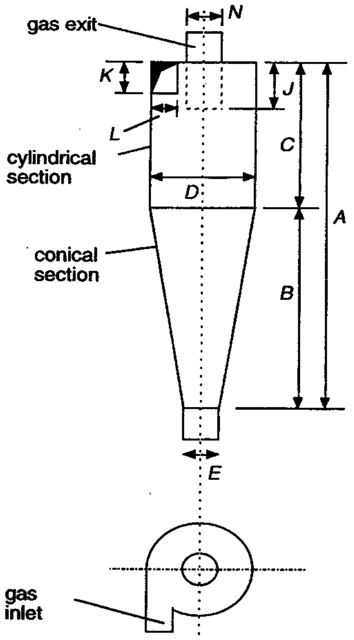
with:
x_{50} = cut size [m]
ρ_p = density of the particles [kg/m^3]
μ = gas viscosity [Pa·s]

The cyclone types can be divided into two groups: high efficiency design and high rate design. The choice is made for the 'high flow rate Stairmand cyclone' (HR), since a high flow rate has to be dealt with. This type will have a lower total efficiency, but is usually smaller and shorter. For this type Eu = 46 and $Stk_{50} = 6*10^{-3}$, see figure 8.8 below.

In principle all particles with a diameter larger than x_{50} will be collected. However in practice the cyclone does not achieve such a sharp cut-off. However, it is assumed that if the difference between the particle diameter and the cut size is high enough (more than 5 times) than the efficiency will be nearly 1. Several functions have been generalized based on measured data. For example the grade efficiency can be described by the following function:

$$\text{efficiency} = \frac{(x/x_{50})^2}{\left(1 + (x/x_{50})^2\right)} \tag{8.32}$$

This relation will be used to get an indication of the efficiency and to choose the number of cyclones.



HE – high efficiency Stairmand cyclone
$Stk_{50} = 1.4 \times 10^{-4}$
$Eu = 320$

HR – high flowrate Stairmand cyclone
$Stk_{50} = 6 \times 10^{-3}$
$Eu = 46$

Dimension relative to diameter D

Cyclone type	A	B	C	E	J	L	K	N
Stairmand, H.E.	4.0	2.5	1.5	0.375	0.5	0.2	0.5	0.5
Stairmand, H.R.	4.0	2.5	1.5	0.575	0.875	0.375	0.75	0.75

Figure 8.8 Cyclone types [60]

Cyclone S101

To design this separation section, first the characteristic velocity is calculated using formula 8.30. The pressure change is set on 1500 Pa. Then the cyclone inside diameter is calculated using formula 8.31. The cut size diameter can be calculated with formula 8.32. As the flow is relatively large and in order to obtain a high efficiency, two cyclones are placed in parallel. The results of the calculations are shown in the following table.

Table 8.25 Results for cyclone S101

	Gas flow rate [m^3/s]	Characteristic velocity v [m/s]	Cyclone diameter D [m]	Cut size x_{50} [m]	Efficiency
1q	13.6	8.47	1.43	7.39E-06	0.985
0.5*q	6.8	8.47	1.01	6.21E-06	0.989

Therefore two cyclones are needed with a diameter of 1.0 m. The other dimensions are given by figure 8.8 above.

Cyclone S102

This cyclone is designed in the same way as cyclone S101. The results are shown in the following table.

Table 8.26 Results for cyclone S102

	Gas flow rate [m^3/s]	Characteristic velocity v [m/s]	Cyclone diameter D [m]	Cut size x_{50} [m]	Efficiency
1q	19.36	9.46	1.35	9.86E-06	0.974
1/2*q	9.68	9.46	1.14	9.06E-06	0.978
1/4*q	4.84	9.46	0.81	7.62E-06	0.984
1/5*q	3.87	9.46	0.72	7.2E-06	0.986

Hence to separate the air stream from the SOC, five cyclones in parallel are required with a diameter of 0.72 m. The other dimensions are given by figure 8.8 above.

8.2.6 Hopper and SOC supply reactor R101 and R102

For controllability reasons two hoppers have been added to the system. These hoppers serve as temporary SOC containers; they ensure a steady flow of SOC into reactors 101 and 102. A drawback to this system is that while the SOC is present in the hopper for some time it will loose heat to the walls of the hopper and consequently to the surroundings. The design of the hoppers will not be done in detail in this report. A few design criteria however will be mentioned here. The first design criteria specifically for the hopper are the following: the hoppers should ensure a steady flow of SOC, so the residence time distribution of the SOC particles should be minimized, on the other hand however they should be as broad as possible in order to minimize the SOC/wall contact area.

Other criteria involve the system that regulates the SOC flow from the hopper into the reactor. The valve or other equipment that regulates the SOC flow into the reactor and the riser should be controllable. This could be done by a conventional valve, which closes the diameter of the opening. However another very important factor should be accounted for as well in both hopper designs. Cyclone S102 operates at a lower pressure than the pressure of the gas in R101 and it's feed stream <107>. In the bottom of the cyclone a seal is present that prevents regeneration air from coming into the hopper. However this seal is not designed for stopping gases coming the other way. The valve/other equipment therefore should be built in such a way that this is prevented at all time while it also should regulate the SOC flow into the reactor. In other parts of the report this will be called the seal in the bottom of the hopper. It is stressed here that this seal is of very great importance, since a mixture of exhaust air and the product stream is a very explosive mixture! The seal at the bottom of hopper H101 is of equal importance. Even though the pressure drop over the seal is less high the occurrence of a mixture of regeneration air and product stream is more explosive since the air has a higher concentration of oxygen.

The maximum valve opening of hopper H102 should be exactly the same as that of H101. In this way the tuning of the controllers controlling both valves becomes easier and also when the control system should fail this doesn't result in a build up of SOC in one of the two hoppers.

In chapter 7 a heat loss over the lines between the top of the riser (156) and the entrance of the SOC stream into the reactor (157) was assumed of 6 ^{0}C and over the exit of the reactor (108) and the entrance of the riser (155) of 3 ^{0}C was assumed. The reason for the higher temperature loss of the former was the leaving open of the option of purging the SOC stream before it enters the reactor with for example nitrogen. In a later stage of the design the purge was found unnecessary. Concluding a design criterion of the hopper is that the heat loss should comply with this temperature drop.

In order to obtain good mixing of the SOC with the gas of stream 107 the SOC must be poured into this stream before entering the reactor. Therefore stream 157 should, unlike drawn in the flow scheme, be connected to stream 107.

8.2.7 Heat exchangers selection and design

When all stream temperatures are known, a heat-exchange network can be designed, using the Pinch technology. From this technology it was known which streams can be coupled and which streams require extra heating or cooling.

The Coulson and Richardson design procedure [21] has been carried out in order to design the heat exchanger units. The general equation for heat transfer across a surface Q is:

$$Q = UA\Delta T_m \tag{8.33}$$

With:

U = the overall heat transfer coefficient (from table 12.1 [21])
A = heat-transfer area
ΔT_m = true mean temperature difference

As the shell and tube exchangers (see figure 8.9) are the most commonly used type of heat exchangers. The mean temperature difference is given by (for counter-current flow):

$$\Delta T_m = F_t * \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \frac{(T_1 - t_2)}{(T_2 - t_1)}} \tag{8.34}$$

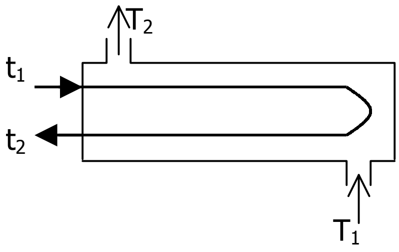


Figure 8.9 U-tube heat exchanger

The true mean temperature difference can be calculated by applying a correction factor. This correction factor is a function of the shell and tube fluid temperatures and the number of tube and shell passes. It is correlated as two dimensionless temperature ratios.

$$R = \frac{(T_1 - T_2)}{(t_2 - t_1)} \tag{8.35}$$

$$S = \frac{(t_2 - t_1)}{(T_1 - t_1)} \tag{8.36}$$

The correction factor (F_t) is estimated from the calculated dimensionless numbers R and S, figure 12.20 (page 657 of [21]) is used. This figure is for two shell passes and four or multiple tube passes.

Type of shell and tube heat exchangers (page 642 of [21])

- Fixed tube plate: This is the simplest and cheapest type, but difficult to clean and no provision for differential expansion of the shell and tubes. Use of this type is limited to temperature differences up to 80 degrees.
- U-tube: This type requires only one tube sheet and is therefore cheaper. This type is also difficult to clean. Internal floating head designs are suitable for high-temperature differentials and are easier to clean.
- For External floating head designs the shell side pressure is limited to about 20 bar and flammable and toxic materials should not be used on the shell side.

As mostly the temperature differentials are relatively large, the floating head type heat exchanger is the most suitable. If cleaning is needed, it is easy to do. Furthermore there is enough room for expansion. The price difference between floating head heat exchangers compared to other types is relatively small. The heat exchanger area, which is the most influential property on exchanger cost, can be calculated by the following formula:

$$A = \frac{Q}{U * \Delta T_m} \ [\mathrm{m}^2] \tag{8.37}$$

The overall heat transfer coefficient (U) is dependent of the stream properties. Besides exchanger area, both material type and operating pressure contribute to heat exchanger cost. The pressure of all streams is known. The heat exchanger cost can be estimated from figure 6.3a [21, page 253]. An overview of all heat exchangers is given in table 8.10.

Table 8.27 Heat exchanger overview

IN	OUT	PFS	IN	OUT	Area [m^2]	Material	Pressure [bar]
106	107	E102	158	159	1419	CS	2
106	107	E103	109	110	424	SS 410	2
117	118	E106	109	110	288	SS 410	24
C101 reboiler		E105	109	110	1184	SS 410	24
C104 reboiler		E107	109	110	1151	SS 410	24
C104 reboiler		E108	111	112	4619	SS 410	24
C104 reboiler		E111	115	116	927	CS	25
Heater		E118	C104 reboiler		183	SS	24
185	175	E109	111	112	20	SS 410	24
106	107	E104	115	116	2262	CS	25
Cooler		E110	111	112	668	SS 410	12
Cooler		E112	115	116	736	SS 410	25
Cooler		E116	158	159	50	SS 410	2
Cooler		E115	123	124	3088	SS 410	18
Cooler		E101	C101 Condenser		921	SS 410	17
Cooler		E113	C104 Condenser		?	?	?
Cooler		E117	154	170	?	?	?
122	123	E114	C105 reboiler		4394	CS	18

Heaters

One powerful 5349 kW heater is required to heat the C104 column reboiler. This heater uses low-pressure steam. The heater has been designed as a normal stainless steel heat exchanger. The exchanger area is 183 m^2.

Coolers

Temperature of cooling water needs to be chosen such that the temperature difference is large enough, at least 10. However, if the cooling water temperature difference becomes smaller, more water will be required, but the exchange area needed will be smaller. Most heat exchangers are designed with minimum temperature difference at least 10 degrees Celsius. This results in a minimal water usage.

For the equipment data summary sheets of the heat exchangers the reader is referred to chapter 8.3. For E101, E118 and E115 the equipment data specification sheet is given as well in chapter 8.3.

8.2.8 Pump selection and design and piping

Piping

In the pipelines friction losses occur because of miscellaneous losses due to equipment installed and roughness of the pipe. For liquid and gas streams this results in a pressure drop in the pipeline. To design the pumps and compressors in the process the friction losses has to be calculated. The friction losses depend on the design parameters.

To calculate the pressure drop due to friction, the friction losses in the pipes, miscellaneous losses in pipefittings, valves etc. and losses in process equipment had to be calculated. An estimate of the friction in the pipes is made with use of Reynolds number to calculate the friction factor equation 8.43. The absolute pipe roughness (ε) is 0.046 for a commercial steel pipe. With a chosen internal diameter in the pipe the relative roughness (ε/d) is calculated.

$$\Delta P_{f,pipe} = 8f\left(\frac{L}{d_i}\right)\frac{\rho u^2}{2} \qquad (8.38)$$

This is the pressure drop due to friction in the pipe.
The pressure drop due to miscellaneous losses and losses in equipment are calculated with number of velocity heads K. [21, p203]
To calculate the pressure drop due to miscellaneous losses equation 8.39 is used.

$$\Delta P_{f,misc} = \left(\frac{u}{2g}\right)\sum K_i \qquad (8.39)$$

The pressure calculations of the feed stream (from LPG storage to column C101) calculated below. For the other streams in Hipphox the estimates listed in table 8.28 are made for the friction due to equipment.

Table 8.28 Estimates for pressure drop due to fraction

Unit of equipment	**liquid**	**gas**
	ΔP_f [bar]	ΔP_f [bar]
Heat exchanger	1	0.2
Globe valve	0.5	0.1
Long pipeline <50 m	+/- 2	-

Pump design

The first pump in the Hipphox process is pump necessary to get the LPG from the storage vessel at the border of the site. For pump selection the total head has to be calculated. A pipeline of about 100 m is necessary from the storage vessel to the column C101. The feed stage of the column is 15, the tray spacing is 0.6 m, the height of the feed stage is 9 m. The elevation for the head calculation is set to 12 m.
The flow rate in the pipeline is 69.7 m^3/hr, 19.4 10^{-3} m^3/s. The pipe diameter is chosen at 12 cm. This results in a liquid velocity of 1.71 m/s. The head required for the pump is calculated by the following equation. [21, p. 198-212].

$$Head = \frac{\Delta P_f}{\rho g} - \frac{\Delta P}{\rho g} - \Delta z \qquad (8.40)$$

ΔP_f = pressure drop due to friction including miscellaneous and equipment losses [N/m^2]
ΔP = difference in system pressures [N/m^2] = 0 N/m^2
Δz = difference in elevations [m] = 12 m
ρ = liquid density [kg/m^3] = 507 kg/m^3
g = gravity acceleration [m/s^2] = 9.81 m/s^2

With a chosen internal diameter in the pipe the relative roughness (ε/d) is calculated. With a pipe diameter of 0.12 m this results in a friction factor f of 0.003. [21, p202] The pressure drop is calculated with 8.31. The pressure drop expressed in head is calculated by equation 8.41.

$$Head = \frac{\Delta P}{\rho g} \tag{8.41}$$

$\Delta P_{f,pipe}$ = 1.65 bar

Head loss pipe = 3.35 m. This is the pressure drop due to friction in the pipe. The pressure drop due to miscellaneous losses and losses in equipment are calculated with number of velocity heads K. In the stream a control valve is installed to control the incoming stream. Therefore the valve should be capable of giving smooth control over the full range of flow. Therefore is chosen for a globe valve. The values for the number of heads due to miscellaneous losses are listed in table 8.12.

Table 8.29 Friction coefficient

Fitting or valve	**K, number velocity heads**
Globe valve 1/2 open	8.5
6*elbow	6*0.8
Coupling	0.1
Entry	0.5
Exit	1
Total	14.9

To calculate the pressure drop due to miscellaneous losses equation 8.44 is used.

Velocity head=$u^2/(2*g)$=0.15 m
Head loss misc. = 2.23 m
$\Delta P_{f,misc}$ =1.09 bar
Total pressure drop
$\Delta P_{f,misc} + \Delta P_{f,pipe}$ =2.7 bar
Total head due to friction = 5.57 m
This results with use of equation 8.40 in total head of 17.57 m
The efficiency of the pump is estimated with use of Coulson & Richardson [21, p206] at 71%.

In the pump cavitations occurs when bubbles of vapour are formed in the pump casing. The Net Positive Suction Head (NPSH) is the pressure at the pump section above the vapour pressure of the liquid expressed as head of liquid. For a pump with a capacity below 100 m^3/h the NPSH should be at least 3 m.
The NPSH is calculated by the equation 8.42.

$$NPSH = \frac{P}{\rho g} + H - \frac{P_f}{\rho g} - \frac{P_v}{\rho g} \tag{8.42}$$

P = Pressure above the liquid the vessel = $17*10^5$ N/m^2
H = Height of liquid above the pump section = 8 m

P_f = Pressure loss in the suction piping [N/m^2]
P_v = Vapour pressure of the liquid at the pump suction = 17*10^5 N/m^2

The pressure loss in the suction piping is calculated as described above. This results in a pressure loss of 21185 N/m^2.
NPSH = 3.7 m. The NPSH is high enough to prevent cavitation in the pump casing. The required NPSH is specified by the pump manufacturer.

8.2.9 Compressors and turbines

In the Hipphox process four compressors and three turbines are needed. The design is done according to Coulson [21, chapter 3.13 and 10.12].
As the gas flows cannot be interrupted, continuous compression is required. Reciprocating, centrifugal and axial flow compressors are the principal types used in the chemical industries. From figure 10.60 centrifugal compressors are selected, as the flows of all stream for all compressors are larger than 1*10^3 m^3/hr and smaller than 1*10^5 m^3/hr.

The work done in a compressor can be calculated with the following expression:

$$-W = \int_1^2 P dV \tag{8.43}$$

For isentropic (reversible adiabatic) compressors: $PV^\gamma = \text{constant}$
with γ = ratio of specific heats, C_P/C_V

Centrifugal compressors are polytropic; then γ is equal to n, which is the polytropic exponent. The work required is given by the following expression:

$$-W = P_1 V_1 \frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] = Z\frac{RT_1}{M}\frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] \tag{8.44}$$

Where:

Z=compressibility factor
R=universal gas constant
T_1=inlet temperature
M=molar mass
W=work done

For C105 overhead compressor (K103) the work required was calculated. The flow to be compressed consists mainly of propylene.
Two compressibility functions X and Y are needed to calculate the work done; these functions supplement the compressibility factor Z. X , Y and Z can be estimated with figure 3.8, 3.9 and 3.10 [21].
X and Y are needed to calculate the polytropic exponent n and the polytropic temperature exponent m.

$$m = \frac{ZR}{C_p}\left(\frac{1}{E_p} + X\right) \text{ for compression} \tag{8.45}$$

$$m = \frac{ZR}{C_p}\left(E_p + X\right) \text{ for expansion} \tag{8.46}$$

E_p is the polytropic efficiency defined by:

$$\text{for compression } E_p = \frac{\text{polytropic work}}{\text{actual work required}}$$

$$\text{for expansion } E_p = \frac{\text{actual work required}}{\text{polytropic work}}$$

An estimate of E_p can be found in figure 3.6 of [21].
In the next table the results are shown for K103. P_r and T_r are the reduced pressure and the reduced temperature and can be calculated with the following equations:

$$P_r = \frac{P_1 + P_2}{P_c}; \quad T_r = \frac{T_1 + T_2}{T_c} \tag{8.47}$$

Table 8.30 C105 Compressor

C105 overhead compressor (K103)						
Flow rate [m3/s]	Flow rate [kg/s]	Pin - Pout [bara]	Tin-Tout [K]	W [J/g]	Work [kW]	Actual Work [kW]
6.45	1.34E+05	10 - 18	292-324	27.88	3878	5312
X	1.30		n	1.43		
Y	1.32		Pr	0.31		
Z	0.78		Tr	0.84		
m	0.27		Ep	0.73		

This compressor is also simulated in AspenPlus using an isentropic compressor. The work calculated with AspenPlus is 5301 kW. This corresponds very well with the work calculated with the procedure described above.
For the other compressors the same procedure can be followed. Also the turbines can be designed with this procedure.

8.3 Equipment data sheets

The equipment data sheets are presented in appendix 8.5. Several equipment units have been summarized:

- Reactors, Columns and vessel summary
- Heat exchanger summary
- Pumps and compressors summary

The following equipment is reviewed in detail in the equipment data specification sheets:

- Column C101
- Heat exchanger E101 (C101 overhead condenser)
- Heat exchanger E118 (C104 reboiler)
- Heat exchanger E115 (Heat pump trim cooler)
- Pump P109 (C101 LPG pump)
- Compressor K103 (C105 Overhead compressor)

9 Waste

The waste of the Hipphox process can be divided in two parts. First the process waste, i.e. the streams leaving the plant, is treated. Second the waste management of the other component in the process, such as the SOC and the utility streams are discussed.

9.1 Outgoing streams

From the input output diagram the main outgoing streams are defined. In table 9.1 the different direct waste streams are listed.

Table 9.1 Outgoing streams of the Hipphox process

Stream	Destination
Light Ends <185>	Fuel
C4+ <170>	Fuel
Water <176> <164>	Waste water treatment
Exhaust air <159>	Air (surrounding)

9.1.1 Light ends

The light ends stream contains valuable by products. The composition of the stream is listed in table 9.2.

Table 9.2 Composition of light ends stream <175>

Stream Nr. :		175	
Name :			
COMP	MW	kg/hr	kmole/hr
Propylene	42.08	2.70	0.06
Propane	44.10	0.21	0.00
Hydrogen	2.02	184.36	91.46
Methane	16.04	57.65	3.59
Ethane	30.07	613.18	20.39
Ethylene	28.05	37.63	1.34
CO	28.01	248.46	8.87
Total		1144.19	125.72
Enthalpy	kW	-815.86	
Phase		V	

As can be seen the main components are CO, hydrogen and ethane. In the design and for economic calculations the stream has only fuel value. The decision of further separation of this stream is an economic decision, which will be explained here. In the combustion of this stream CO_2 is produced. Therefore based on environmental aspects it is better to separate the stream in valuable by product streams.

There are two options for further separation. One options is to separate the hydrogen. This can be done by a hydrogen recovery unit. Different separation techniques can be used like absorption, distillation, membrane separation or with use of zeolites. The hydrogen has a value 0.65 $/kg. This results annually in about 1 million $ sales if all hydrogen would be recovered.

The other option is to separate the components heavier than ethylene, which results in a synthesis gas (syngas) stream and a hydrocarbon stream with fuel value. Since the storage of syngas is not feasible, the production of synthesis gas is only profitable if the syngas can be used in neighbouring processes. The fuel value of the light ends stream is 1.76 million $/a. Therefore in the design it is chosen not to separate the light ends stream. The fuel will be sold to neighbouring plants. To easily transport the light ends and for process control reasons the stream is expanded to 22 bara.

9.1.2 C_4^+

The C_4^+ stream is a liquid stream. The main component in this stream is butane. This stream is sold as fuel to neighbouring plants. The delivery specifications are determined by the demand of the consumer. In the design of Hipphox it is set to 17 bara and 15 ^oC. At these conditions the stream remains fluid.

9.1.3 Water

Two water streams are leaving the process. Stream <176> is leaving the flash vessel. This stream contains only traces (+/- 5 ppm) of hydrocarbons because of the large difference in boiling point of water and the other compounds. The waste water stream from the glycol unit <164> is also pure water again because of the difference in boiling point.

To calculate the costs for discharging the waste water into public waters the population equivalent (PE) is calculated [61]. The BOD_5 value is estimated at 0.100 g/l. The amount of waste water is calculated from the values in the PSS (Appendix 5.1) and is 14 m^3/hr. With one PE this equals 54 grams O_2 per person per day, this results in a PE of 626 people.

The cost for one PE is about € 60,- per year. The total costs for disposing the wastewater to public water is about € 37500,- per year. Although these costs are low, it is preferable to send the waste water to a waste water treatment plant, from sustainable point of view. If the amount of hydrocarbons should increase, then disposal to public water would be harmful to nature and to the company's image. Therefore the waste water produced in the Hipphox process is sent to waste water treatment, which is considered to be outside the battery limits. The discharge temperature is 30 ^oC.

9.1.4 Exhaust air

In the riser air is used to regenerate the SOC. The solids are separated from this stream with a cyclone. No solids are present in the exhaust air stream. This stream contains 1.7 wt% oxygen. This stream is discharged in the air with a temperature of 40^oC.

The nitrogen stream is not pure enough to be sold as nitrogen. Because it is a large stream it could be an option to purify the exhaust air stream. If the stream could be purified to 99.9 v% nitrogen this also becomes a valuable by product. It is not feasible to reduce the amount of air trough the riser, because the oxygen pressure will become too low and consequently also the reaction rate.

It is an economic question if it is useful to place a separation unit to purify the exhaust air stream. A purified nitrogen stream has a by-product value of about $ 22 million.

9.2 Other waste

9.2.1 Solid waste

Other waste streams in the Hipphox streams are the SOC stream and the monolith in the reactor. Both are renewed every three years. The spent SOC will not be reused nor regenerated. It is sent to waste disposal.

The platinum monolith will be send to platinum recovery. Platinum recovery is already done for monolith catalyst in car industry.

9.2.2 Waste from utilities

In the heat exchanger network mainly cooling water is used as coolant. This coolant can be sent to cooling towers, where a part is evaporated and a part is recycled, if no public waters are available. In this design it is assumed that the cooling water can be disposed to public waters, as these water streams are not contaminated. The temperature has to be the same as the surrounding water temperature.

For the cryogenic column C104 nitrogen is used as a coolant. This is disposed to the open air. The amount of nitrogen required is minimised by reducing the reflux ratio of this column, the amount of waste is hereby decreased.

10 Process safety

In order to design a safe plant for operating personnel and surroundings, the hazards and risks of the process have to be known. To be aware of all the critical safety aspects of this CPD project, the Hipphox process, two tools are used. These tools are the Hazard and Operability study (HAZOP) and the Fire and Explosion Index (F&EI).

In the Hipphox process carbon monoxide is produced, which is a toxic substance. The properties of the components, like the health factor and material factor, can be found in Appendix 10.1.

The airflow has to be hermetic separated from the hydrocarbon flow. That is also an important reason for using a solid oxygen carrier, instead of molecular oxygen.

The regeneration of the spent SOC is very exothermic; fortunately the amount of spent SOC is limited, as the regenerated SOC cannot react with the oxygen. The SOC particles are very small, they have a diameter of 60 μm. Therefore the spent SOC, which is a 'combustible solid', can cause a dust explosion. The riser unit must be designed very carefully.

Also care must be taken with the storage of LPG, as a failure of the storage vessel exposed to fire can cause a boiling liquid expanding vapour explosion (BLEVE).

The FEI index will be done for all important units; these are:

- Monolith reactor (R101)
- Riser regenerator (R102)
- Depropanizer (C101)
- De-ethanizer (C104)
- P/P-splitter with heat pump (C105)

The HAZOP study is only done for the most critical units; these are the reactor and riser. The other units are well-known separation columns.

10.1 Fire & Explosion Index (F&EI)

This method gives an evaluation of the potential risk from a process. A numerical "Fire and Explosion Index" (F&EI) is calculated, based on the nature of the process and the properties of the process materials. The outcome is a potential degree of hazard, which categorises the process. The larger the value of the F&EI, the more hazardous the process, see table 10.1.

Table 10.1 Assessment of hazard [21]

Fire and explosion index range	Degree of hazard
1-60	Light
61-96	Moderate
97-127	Intermediate
128-158	Heavy
>159	Severe

For the calculation of the F&EI, a number of important equipment will be considered. These are: the reactor system (R101), the regenerator (R102), the depropanizer (C101), the de-ethanizer (C104) and the P/P splitter with heat pump system (C105, K103, E109, E110, V104, valve). The procedure described in Chapter 9 of [21] and [63] is followed.

For each unit also the potential loss is calculated. Following the procedure described in the DOW F&EI index [63], first the loss control credit factor is calculated. This credit factor consists of three categories: process control, material isolation and fire protection. They are selected for the contribution they will actually make to reducing or controlling the unit hazards being evaluated.

Finally the Process Unit Risk Analysis (PURA) is made, which gives a summary of all of the important process unit risk analysis information, including the F&EI, loss control credit factor, the area of exposure, the damage factor and the actual maximum probable property damage.

10.1.1 Monolith Reactor (R101)

The Fire and Explosion Index calculation form for the reactor can be found in Appendix 10.2.

Material factor

For the reactor propylene, propane, hydrogen, methane, water, ethane, ethylene, butene, butane, CO, oxygen, nitrogen, SOC and spent SOC are present, therefore the material factor (MF) is 24, for ethylene.

General hazards

A. Exothermic chemical reactions: Not applicable
B. Endothermic processes: the penalty factor is 0.4, since all reactions are endothermic
C. Materials handling and transfer: hydrocarbons (LPG-type materials) are present, therefore the penalty factor is 0.5 (loading or unloading operation)
D. Enclosed or indoor process units: Not applicable
E. Access of emergency equipment: Adequate access would be provided
F. Drainage and spill control: The drainage will be appropriate, so that no penalty has to be applied.

Special process hazards

A. Toxic materials: CO is very toxic, the penalty factor is 0.2 times the health factor of CO (N_F), so the penalty factor is 0.2*3= 0.6
B. Sub-atmospheric pressure: Not applicable
C. Operation in or near flammable range: reactor could be in or near flammable rang, so a penalty of 0.3 is applied.
D. Dust explosion: combustible solids are present (SpentSOC), but there is no contact with air or oxygen, so no penalty is applied.
E. Relief pressure: the operating pressure is 2 bara, relief valve setting is 2.4 bara, 2.4 bara equals 240/6.895 = 35. From figure 2 [63] the penalty factor is 0.2.
F. Low temperature: operating temperature above 10°C, therefore not applicable
G. Quantity of flammable material: ethylene was selected as the material factor. The largest possible amount of ethylene in the reactor is the worst-case scenario when the whole gas volume of the reactor (51 m^3) is filled with ethylene. This amount is estimated at 50 kg. The heat of combustion of ethylene is 50.30 MJ/kg, which means

that 2515 MJ ($2.38*10^6$ btu) is released. The penalty factor for this is 0, as it is too small to register on figure 3 [63, page 27].

H. Corrosion and erosion: corrosion resistant material would be specified, but some corrosion is likely to occur, the penalty factor is 0.1.
I. Leakage – joints and packing: full equipment details are not available at the flow scheme stage, therefore the penalty factor is 0.1.
J. Use of fired heaters: Not applicable
K. Hot oil heat exchange system: Not applicable
L. Rotating equipment: Not applicable

This procedure leads to a General process hazards factor (F1) of 1.90, a Special process hazards factor (F2) of 2.30 and the degree of hazard is F1*F2*MF = 105, which means the degree of hazard for the reactor R101 is intermediate.

The process unit hazards factor (F3) is the product of F1 and F2. For the reactor F3 has a value of 4.37. This is within the normal range of 1 to 8.

Loss control credit factors

The loss control credit factor is the product of three categories of control features:
Process control credit factor (C1), material isolation credit factor (C2) and the fire protection credit factor (C3). For every credit factor the appropriate value is entered and these values can be found in appendix 10.7.

Process control credit factor (C1)

A. Emergency power: When an accident occurs it is not needed to use extra emergency power. It is for example not needed to maintain agitation to avoid a runaway reaction. Therefore no credit is applied.
B. Cooling: not needed
C. Explosion control: Normal overpressure relief systems are used. Also these systems protect the equipment from abnormal conditions, as there has to be dealt with hydrocarbons at high temperatures. A value of 0.98 is used.
D. Emergency shutdown: a credit factor of 0.99 is applied; the equipment will activate an alarm so that operators can intervene and maybe decide to shutdown the whole systems. All units in the whole Hipphox process are dependent, so if one unit has a problem this has consequences for all other units.
E. Computer control: on-line computers function are available as an aid to operators and will also be partly in direct control of the process. Therefore a value of 0.97 is applied.
F. Inert gas: no inert gas system needed
G. Operating Instructions / Procedures: a value of 0.92 is applied, as the operating instructions are complete and accurate.
H. Reactive chemical review: this program is a continuing part of the operations, so a factor of the 0.91 is used.
I. Other process hazard analysis: all hazard tools will be applied, so a factor of 0.91 is used.

Material isolation credit factor (C2)

A. Remote control valves: a unit is provided with remotely operation isolation valves so that storage tanks, process vessels and transfer lines can be quickly isolated. Therefore a value of 0.98 is applied.
B. Dump/blowdown: the gas stream will be piped to a flare system for emergency venting, so a value of 0.96 is applied.
C. Drainage: the drainage conditions have to be good, so a value of 0.91 is applied.
D. Interlock: an interlock system that prevents incorrect material flow is needed, so a credit factor of 0.98 is used.

Fire protection credit factor (C3)

A. Leak detection: as flammable hydrocarbons are present a gas detector is needed which both alarms and activates a protective system, so a value of 0.94 is applied.
B. Structural steel: fireproofing systems are needed; a credit factor of 0.97 is used.
C. Fire water supply: normal fire water supply is available, so a factor of 0.97 is applied.
D. Special systems: not needed
E. Sprinkler systems: normal sprinkler systems are available. There are no indoor manufacturing areas, so a factor of 0.97 is applied.
F. Water curtains: normal water curtains available, so a factor of 0.98 is applied.
G. Foam: not needed
H. Hand extinguishers / monitors: hand extinguishers will not be appropriate, so no credit factor is applied.
I. Cable protection: normal cable protection will be applied, so a factor of 0.98 is used.

The loss control credit factor is the product of the three credit factors and is 0.50.

This analysis is relatively general and applicable for the whole process. When applying this procedure for the other four units, it appeared that all values remain the same. Therefore for all the units a loss control credit factor of 0.50 is applied.

Process unit risk analysis (PURA)

The radius of exposure is function of the F&EI by multiplying the F&EI by 0.84. With this value the area of exposure can be calculated. The value of the area of exposure is obtained from the replacement value of the property, which can be calculated using the following formula.

$$\text{replacement value} = \text{original cost} \times 0.82 \times \text{escalation factor} \qquad (?.?)$$

The factor 0.82 is an allowance for items of cost not subject to loss or replacement. The escalation factor is the cost index for 2003 and has a value of 400.

The process unit hazards factor (F3) is used to determine the damage factor. From figure 8 of the Dow's FEI index the damage factor can be read. For the monolith reactor with a material factor of 24 the damage factor is 0.73.

The base maximum probable property damage (base MPPD) is determined to obtain a dollar value for the maximum probable property damage. It can be determined by multiplying the damage factor and the value of exposure.

The actual MPPD represents the property damage loss that could result from an incident of reasonable magnitude with adequate functioning of protective features. This can be calculated by multiplying the base MPPD with the loss control credit factor.

From the actual MPPD the maximum probable days outage (MPDO) can be calculated using figure 9 (basis 1986). The curve for the normal probability is used and the cost index of 2003 (400) and of 1986 (318.4) is used to escalate from 1986 to 2003. The curve can be described by the following relation:

$$MPDO = 10 \wedge (1.325132 + 0.592471(\log(actualMPPD)) \cdot \frac{400}{318.4}$$

This MPDO is needed to calculate the potential business interruption (BI) from a loss incident. This is calculated using the following formula:

$$BI = \frac{MPDO}{30} \cdot VPM \cdot 0.70$$

The VPM is the value of production for a month. Per month 22.5 ton of propylene is produced and this has a value of 22.5*375 = 8.4 M$ per month.

The process unit risk analysis summary is shown in the following table.

Table 10.2 Process unit risk analysis summary of the monolith reactor

Process Unit Risk Analysis			
Area/Country:	**Division:** -	**Location** -	**Date** 17/12/2003
Site -	**Manufacturing Unit** Reactor	**Process Unit** R101	
Materials in Process Unit Propylene, propane, hydrogen, methane, water, ethane, ethylene, butene, butane, CO, oxygen, nitrogen, SOC, SpentSOC			
State of Operation Design	**Basic Materials for Material Factor** Ethylene		
1. Fire & Explosion Index (F&EI)	105	[-]	
2. Radius of Exposure	27	[m]	
3. Area of Exposure	2265	[m^2]	
4. Value of Exposure	49.99	M$	
5. Damage Factor	0.73	[-]	
6. Base Maximum Probable Property Damage	36.49	M$	
7. Loss Control Credit Factor	0.50	[-]	
8. Actual Maximum Probable Property Damage	18.30	M$	
9. Maximum Probable Days Outage	149	days	
10. Business Interruption	29.26	M$	

10.1.2 Riser regenerator (R102)

The Fire and Explosion Index calculation form for the regenerator can be found in Appendix 10.3.

Material factor

For the regenerator only oxygen, nitrogen, SOC and SpentSOC are present, therefore the material factor MF is 16, for SpentSOC.

General process hazards

A. Exothermic chemical reactions: an oxidising reaction takes place, which is categorized as moderate exotherm. The penalty factor is 0.5.
B. Endothermic processes: Not applicable
C. Materials handling and transfer: hydrocarbons need to be completely removed before entering the regenerator; therefore the penalty factor is 0.5 (unloading operation).
D. Enclosed or indoor process units: Not applicable
E. Access of emergency equipment: Adequate access would be provided.
F. Drainage and spill control: Not applicable

Special process hazards

A. Toxic materials: no toxic materials are present.
B. Sub-atmospheric pressure: Not applicable
C. Operation in or near flammable range: Not applicable
D. Dust explosion: the spentSOC is a combustible solid, it is in contact with air and the particle size is 60 μm, the penalty factor is 2.0
E. Relief pressure: the operating pressure is 2 bara, relief valve setting 2.4 bara, 2.4 bara equals 240/6.895 = 35. From figure 2 [63] the penalty factor is 0.2.
F. Low temperature: operating temperature above 10°C, therefore not applicable
G. Quantity of flammable material: there are combustible solids present, the amount of SpentSOC in the regenerator is estimated at 63546 kg (V_{riser} = 9.5 m^3). The heat of combustion is 0.40 MJ/kg, so the amount is 25418 MJ(=$0.024*10^9$ btu) which is too small to read from figure 5, so the penalty factor is 0.
H. Corrosion and erosion: corrosion resistant material would be specified, but some corrosion is likely to occur, the penalty factor is 0.1.
I. Leakage – joints and packing: possibility of minor leaks, penalty factor is 0.1.
J. Use of fired heaters: Not applicable
K. Hot oil heat exchange system: Not applicable
L. Rotating equipment: Not applicable

This procedure leads to a General process hazards factor (F1) of 2.00, a Special process hazards factor (F2) of 3.40, and the degree of hazard is F1*F2*MF = 109, which means the degree of hazard for the reactor R102 is also intermediate.

The process unit hazards factor (F3) is the product of F1 and F2. For the riser F3 has a value of 6.8. This is within the normal range of 1 to 8.

Process unit risk analysis (PURA)

The same procedure is followed as for the monolith reactor.
In the following table the process unit risk analysis summary is given.

Table 10.3 Process unit risk analysis summary of the riser regenerator

Process Unit Risk Analysis			
Area/Country:	**Division:** -	**Location** -	**Date** 17/12/2003
Site -	**Manufacturing Unit** Regenerator	**Process Unit** R102	
Materials in Process Unit Oxygen, Nitrogen, SOC, SpentSOC			
State of Operation Design	**Basic Materials for Material Factor** SpentSOC		
1. Fire & Explosion Index (F&EI)		109	[-]
2. Radius of Exposure		28	[m]
3. Area of Exposure		2438	[m^2]
4. Value of Exposure		16.84	M$
5. Damage Factor		0.63	[-]
6. Base Maximum Probable Property Damage		10.61	M$
7. Loss Control Credit Factor		0.50	[-]
8. Actual Maximum Probable Property Damage		5.26	M$
9. Maximum Probable Days Outage		71	days
10. Business Interruption		13.98	M$

10.1.3 Depropanizer (C101)

The Fire and Explosion Index calculation form for the depropanizer can be found in Appendix 10.4.

Material factor

For the depropanizer propylene, propane, ethane, butane and 1-butene are present, therefore the material factor MF is 21, for propane, this is present in the largest amount.

General process hazards

A. Exothermic chemical reactions: Not applicable
B. Endothermic processes: Not applicable
C. Materials handling and transfer: hydrocarbons are present; therefore the penalty factor is 0.5.
D. Enclosed or indoor process units: Not applicable
E. Access of emergency equipment: Adequate access would be provided
F. Drainage and spill control: Adequate drainage would be provided

Special process hazards

A. Toxic materials: the penalty factor is 0.2 times the health factor of propane (N_F), so the penalty factor is 0.2*1= 0.2.
B. Sub-atmospheric pressure: Not applicable
C. Operation in or near flammable range: reactor could be in or near flammable rang (in case of a failure), so a penalty of 0.3 is applied.
D. Dust explosion: Not applicable

E. Relief pressure: the operating pressure is 17 bara, relief valve setting 20.4 bara, 20.4 bara equals 2040/6.895 = 295. From figure 2 [63] the penalty factor is 0.53.
F. Low temperature: operating temperature above 10°C, therefore not applicable
G. Quantity of flammable material: the amount of propane in the depropanizer is estimated at 10 kg (V_{C101} = 11.5 m^3) when the whole reactor is filled with propane in the worst-case scenario. The heat of combustion of propylene is 50.34 MJ/kg, which means 503.4 MJ (=$0.48*10^6$ btu) is released, which is too small to read from figure 5, so the penalty factor is 0.
H. Corrosion and erosion: corrosion resistant material would be specified, but some corrosion is likely to occur, the penalty factor is 0.1.
I. Leakage – joints and packing: possibility of minor leaks, penalty factor is 0.1.
J. Use of fired heaters: Not applicable
K. Hot oil heat exchange system: Not applicable
L. Rotating equipment: Not applicable

This procedure leads to a General process hazards factor (F1) of 1.50, a Special process hazards factor (F2) of 2.23, and the degree of hazard is F1*F2*MF = 70, which means the degree of hazard for the depropanizer is moderate.

The process unit hazards factor (F3) is the product of F1 and F2. For the depropanizer F3 has a value of 3.35. This is within the normal range of 1 to 8.

Process unit risk analysis (PURA)
The same procedure is followed as for the depropanizer.
In the following table the process unit risk analysis summary is given.

Table 10.4 Process unit risk analysis summary of the depropanizer

Process Unit Risk Analysis			
Area/Country:	**Division:** -	**Location** -	**Date** 17/12/2003
Site -	**Manufacturing Unit** Depropanizer	**Process Unit** C101	
Materials in Process Unit Propylene, propane, ethane, 1-butene, butane			
State of Operation Design		**Basic Materials for Material Factor** Propane	
1. Fire & Explosion Index (F&EI)		70	[-]
2. Radius of Exposure		18	[m]
3. Area of Exposure		1009	[m^2]
4. Value of Exposure		35.31	M$
5. Damage Factor		0.70	[-]
6. Base Maximum Probable Property Damage		24.72	M$
7. Loss Control Credit Factor		0.50	[-]
8. Actual Maximum Probable Property Damage		12.25	M$
9. Maximum Probable Days Outage		117	days
10. Business Interruption		23.07	M$

10.1.4 De-ethanizer (C104)

The Fire and Explosion Index calculation form for the de-ethanizer can be found in Appendix 10.5.

Material factor

For the de-ethanizer propylene, propane, hydrogen, methane, ethane, ethylene, 1-butene, butane and CO are present; therefore the material factor MF is 24, for ethylene.

General process hazards

A. Exothermic chemical reactions: Not applicable
B. Endothermic processes: Not applicable
C. Materials handling and transfer: hydrocarbons are present, and the top stream has to be cooled with a cryogenic coolant, therefore the penalty factor is 0.70.
D. Enclosed or indoor process units: Not applicable
E. Access of emergency equipment: Adequate access would be provided
F. Drainage and spill control: Adequate drainage would be provided

Special process hazards

A. Toxic materials: CO is toxic, the penalty factor is 0.2 times the health factor of CO (N_F), so the penalty factor is 0.2*3= 0.6.
B. Sub-atmospheric pressure: Not applicable
C. Operation in or near flammable range: reactor could be in or near flammable rang (in case of a failure), so a penalty of 0.3 is applied.
D. Dust explosion: Not applicable
E. Relief pressure: the operating pressure is 24 bara, relief valve setting 28.8 bara, 28.8 bara equals 2880/6.895 = 418. From figure 2 [63] the penalty factor is 0.63.
F. Low temperature: operating temperature above 10°C, therefore not applicable
G. Quantity of flammable material: the amount of CO in the de-ethanizer is estimated at 16 kg (V_{C104} = 15.2 m^3). The heat of combustion of CO is about 6.43 MJ/kg, which means that 103 MJ ($0.098*10^6$ btu) is released. This is too low to read from figure 5, so the penalty factor is 0.
H. Corrosion and erosion: corrosion resistant material would be specified, but some corrosion is likely to occur, the penalty factor is 0.1.
I. Leakage – joints and packing: full equipment details are not available at the flow sheet stage, therefore the penalty factor is 0.1.
J. Use of fired heaters: Not applicable
K. Hot oil heat exchange system: Not applicable
L. Rotating equipment: Not applicable

This procedure leads to a General process hazards factor (F1) of 1.70, a Special process hazards factor (F2) of 2.73, and the degree of hazard is F1*F2*MF = 111, which means the degree of hazard for the de-ethanizer C104 is intermediate.

The process unit hazards factor (F3) is the product of F1 and F2. For the de-ethanizer F3 has a value of 4.64. This is within the normal range of 1 to 8.

Process unit risk analysis (PURA)

The same procedure is followed as for the de-ethanizer.
In the following table the process unit risk analysis summary is given.

Table 10.5 Process unit risk analysis summary of the de-ethanizer

Process Unit Risk Analysis			
Area/Country:	**Division:** -	**Location** -	**Date** 17/12/2003
Site -	**Manufacturing Unit** De-ethanizer	**Process Unit** C104	
Materials in Process Unit Propylene, propane, hydrogen, methane, ethane, ethylene, butene, butane, CO			
State of Operation Design	**Basic Materials for Material Factor** Ethylene		
1. Fire & Explosion Index (F&EI)		111	[-]
2. Radius of Exposure		29	[m]
3. Area of Exposure		2555	[m^2]
4. Value of Exposure		3.61	M$
5. Damage Factor		0.80	[-]
6. Base Maximum Probable Property Damage		2.89	M$
7. Loss Control Credit Factor		0.50	[-]
8. Actual Maximum Probable Property Damage		1.43	M$
9. Maximum Probable Days Outage		33	days
10. Business Interruption		6.47	M$

10.1.5 P-P splitter and heat pump (C105)

The Fire and Explosion Index calculation form for the P-P splitter and heat pump can be found in Appendix 10.6.

Material factor

For the P-P splitter propylene, propane, ethane, 1-butene and butane are present; therefore the material factor MF is 21, for propylene.

General process hazards

G. Exothermic chemical reactions: Not applicable
H. Endothermic processes: Not applicable
I. Materials handling and transfer: hydrocarbons are present; therefore the penalty factor is 0.50.
J. Enclosed or indoor process units: Not applicable
K. Access of emergency equipment: Adequate access would be provided
L. Drainage and spill control: Adequate drainage would be provided

Special process hazards

M. Toxic materials: the penalty factor is 0.2 times the health factor of propylene (N_F), so the penalty factor is 0.2*1= 0.2.
N. Sub-atmospheric pressure: Not applicable
O. Operation in or near flammable range: reactor could be in or near flammable rang (in case of a failure), so a penalty of 0.3 is applied.
P. Dust explosion: Not applicable
Q. Relief pressure: the highest operating pressure (K103) is 18 bara, relief valve setting 21.6 bara, 21.6 bara equals 2160/6.895 = 313 psig. From figure 2 [63] the penalty factor is 0.55.
R. Low temperature: operating temperature above 10°C, therefore not applicable
S. Quantity of flammable material: the amount of propylene in the P-P splitter is estimated at approximately 200 kg (V_{C105} = 235 m^3). The heat of combustion of propylene is 48.91 MJ/kg, which means that 9782 MJ (=0.01*10^9 btu) is released. This is too low to read from figure 5, so the penalty factor is 0.
T. Corrosion and erosion: corrosion resistant material would be specified, but some corrosion is likely to occur, the penalty factor is 0.1.
U. Leakage – joints and packing: full equipment details are not available at the flow sheet stage, therefore the penalty factor is 0.1.
V. Use of fired heaters: Not applicable
W. Hot oil heat exchange system: Not applicable
X. Rotating equipment: Not applicable

This procedure leads to a General process hazards factor (F1) of 1.50, a Special process hazards factor (F2) of 2.25, and the degree of hazard is F1*F2*MF = 71, which means the degree of hazard for the P-P splitter C105 is moderate.

The process unit hazards factor (F3) is the product of F1 and F2. For the P-P splitter F3 has a value of 3.38. This is within the normal range of 1 to 8.

Process unit risk analysis (PURA)
The same procedure is followed as for the P-P splitter.
In the following table the process unit risk analysis summary is given.

Table 10.6 Process unit risk analysis summary of the P-P splitter

Process Unit Risk Analysis			
Area/Country:	**Division:** -	**Location** -	**Date** 17/12/2003
Site -	**Manufacturing Unit** P-Psplitter with heat pump	**Process Unit** C105	
Materials in Process Unit Propylene, propane, ethane, butene, butane			
State of Operation Design	**Basic Materials for Material Factor** Propylene		
1. Fire & Explosion Index (F&EI)		71	[-]
2. Radius of Exposure		18	[m]
3. Area of Exposure		1038	[m^2]
4. Value of Exposure		67.82	M$
5. Damage Factor		0.61	[-]
6. Base Maximum Probable Property Damage		41.37	M$
7. Loss Control Credit Factor		0.50	[-]
8. Actual Maximum Probable Property Damage		20.50	M$
9. Maximum Probable Days Outage		159	days
10. Business Interruption		31.30	M$

10.1.6 Overall conclusion from F&EI and PURA

The monolith reactor, the riser regenerator and the de-ethanizer have an intermediate degree of hazard. In the monolith reactor toxic materials are present, like CO, which has a high material factor. The riser regenerator has to deal with the spent SOC, which is combustible and can cause a dust explosion. The de-ethanizer also has to deal with toxic material, mainly with CO. The depropanizer and the P-P splitter have a moderate degree of hazard. Fortunately no units have a heavy or severe degree of hazard. In the process unit risk analysis summary, the business interruption can be read. For all units the business interruption has a value of 7 to 31 million dollars. These are high values, so care and good process control must be assessed to minimize the risk of a failure of a unit. To make a good process control system a HAZOP analysis is made, which is described in the next paragraph.

10.2 HAZOP

A Hazard and Operability study (HAZOP) has been done for the most critical units. These are the two reactors, the monolith reactor and the riser regenerator.

With the HAZOP tool a systematic, critical examination of the operability of the process is done. The process is studied vessel-by-vessel and line-by-line for the two reactor systems. Guide words are used to help generate thought about the way deviations from the intended operating conditions can cause hazardous situations.

In this paragraph the most important conclusions are given. In appendix 10.8 the whole HAZOP can be found. The conclusions are used to design a good control system.

Monolith reactor (R101)

The monolith tubes are very small. Care must be taken to prevent blockage of the monolith reactor by accumulation of the SOC. The SOC particles are very small and they must be designed so that they do not agglomerate. Blockage of the reactor will lead to a shutdown of the plant, as no propane is converted to propylene.

The gas feed stream must have a constant composition, as the temperature and composition of the gas feed stream has a high effect on the conversion. Thanks to the fact that the reactions are endothermic there is no possibility for a runaway. For example if more propane is fed into the reactor, in first instance the reactions run faster and more propane will be converted. However as the reactions go faster, the temperature decreases, which causes eventually a decrease in the equilibrium conversion.

The reactor is designed as a so-called downer-reactor. The gas feed stream enters the reactor at the top and flows down. To this gas feed stream a solids stream is added. The inlet of the reactor is designed in such a way that there is no possibility that the gas flows upward due to a lower pressure in the cyclone causing a solids ‘fountain’. Below the cyclone a hopper is “designed” so that the solids are forced to go down and can be mixed with the gas feed stream. The mixing of the exhaust gas, which contains traces of oxygen, and the reactant/product stream must be prevented at all time.

This hopper must also be designed so that there is a constant flow of SOC into the reactor. Change in the SOC flow has consequences for the temperature in the reactor, as the SOC is also used as a heat carrier.

Riser regenerator (R102)

If the riser regenerator fails, then the spent SOC is not regenerated, which has consequences for the temperature of the SOC that flow in the reactor (R101). As there is an excess of SOC in the hopper (H102) the reaction will continue to work for some time. When the SOC in the hopper is used up the feed stream of the reactor will be heated up with utilities. The conversion will be lower since no hydrogen is combusted.

The air feed stream must be controlled, so that the flow is high enough to lift the SOC particles. The airflow cannot be too high, because then the SOC is lifted too fast.

The control system provides all necessary actions mentioned up until now, see chapter 6. Another problem may occur when not enough oxygen is present in the regeneration air stream. This problem does not create a hazardous situation and is therefore explained further in chapter 6, paragraph *Riser (102)*

By far the most hazardous situation that can occur is similar to that in the reactor, namely the possible contact of the product/reactant stream with the regeneration air. This however is much more hazardous in hopper H101 then in H102 because the air hasn’t reacted jet with the SpentSOC. This stream therefore is still rich with oxygen, which gives when it comes in contact with the product stream gives a highly explosive mixture. The seals at the bottom of the hopper as well as the seal at the bottom of the cyclone (in both cases) have to be designed in such a way that this is prevented at all time.

11 Economy

In this chapter an economic evaluation of the Hipphox process is made. The cash flow will be calculated which will show the certainty about the installation earning back its investment. Local effects like taxes, subsidising and grants are not included at this stage of design. Successively the following economic information will given about the capital investment, operating costs, gross income and cash flow. Finally an economic evaluation will be given using some economic criteria like the rate of return. All exact values can be found in Appendix 11.1.

11.1 Capital investment costs

For the equipment costs values of Matches [55] and Coulson and Richardson [21] are used. Matches is an engineering company which has a well working website which calculates the costs of various equipment. In Appendix 11.1 all the calculations are carried out.

Most equipment costs are calculated for 1998, using Coulson&Richardson. The costs are calculated for 2003 using Chemical Engineering Plant cost index (Marshall and Stevens index) from Chemical Engineering journal (www.che.com). The cost indexes for 1998 – 2003 are presented in the following table.

Table 11.1 CEP Cost indexes

Year	M&S cost index
1998	389.5
2003	400

The equipment costs consist of the cost for the reactors, columns, heat exchangers, compressors, expanders, cyclones and vessels. Costs for pumps are neglected.

With the Lang method, the fixed capital costs can be calculated. The Lang method gives a quick estimate of the capital costs based on the total purchased equipment costs. The investment costs are the sum of the fixed capital costs and the working capital. The working capital costs is a percentage of the fixed capital costs, namely 10%. In the following table the values can be found.

Table 11.2 Total investment costs

Total Investment Costs (euro million)	**36.4**
Fixed Capital Costs @ 2003 (euro million)	32.8
Working Capital (euro million)	3.6

11.2 Operating costs

The costs of producing a product are divided into two groups: variable costs (raw materials among other things) and fixed costs.

The raw materials can be directly calculated; the same goes for the utilities. The costs for the glycol are neglected, as this was not designed and glycol is not very expensive.

The fixed costs consist of maintenance and laboratory costs etcetera that are estimated by taking a percentage of the fixed capital costs. The costs of operating labour are based on the costs for one operator, namely 90000 euro per year. To have three shifts a day, five

shifts are needed. Each shift consists of three operators. The other fixed costs are determined using table 6.6 from Coulson&Richardson [21].
The total production costs are 77.18 million euro per year. The production costs for 1 ton of propylene are therefore 309 euro/ton or 383 $/ton.

11.3 Income and net cash flow

Apart from the product, also a light ends stream and a C_4^+ stream is produced. These streams have at least a fuel value. Therefore they are a part of the income. The fuel value of the streams is calculated using the mole streams of each component and their heat of combustion from the handbook. The total income is shown in the table 11.3.

The net cash flow is the difference between the income and the production costs. In this stadium of design no local effects like taxes, subsiding and grants are included. So the capital charges are not included in the net cash flow.
The net cash flow is 6.85 million euro per year, see table 11.3.

Table 11.3 Gross income and net cash flow

Gross Income				
Stream	Production rate	Price		Income
	[t/a]	[$/ton]	[euro/ton]	[M euro/a]
Propylene <128>	250,000.0	375	302.6	75.66
	[W]	[$/GJ] [54]	[euro/GJ]	
Light ends <175>	18,000,000	4	3.2	1.67
C4 <170>	19,190,000	4	3.2	1.78
Total				**79.11**
Production costs (excl. depreciation)				**72.26**
Net Cash Flow				**6.85**
1 $ = 0.807 euro				

The net future worth (NFW) is the cumulative cash flow.
To calculate the time value of money an interest rate of 8% (r=0.08) is assumed. The net present worth (NPW) can then be calculated using the following formula:

$$NPW = \frac{NFW \text{ in year n}}{(1+r)^n} \tag{11.1}$$

The plant lifetime is set on 20 years, with two years to build the plant and one year of salvage. For salvage the value of the working capital is taken.
The rate of return (ROR) is the ratio of annual profit to investment. The ROR can be calculated using the following formula:

$$ROR = \frac{\text{cumulative net cash flow at end of project}}{\text{life of project x original investment}} \text{x100 per cent} \tag{11.2}$$

The rate of return for this project is 18.4%.
Pay out time: This is the time required after the start of the project to pay off the initial investment from income. The pay-out time is 7.4 years.

The discounted cash-flow rate of return (DCFRR) is a measure of the maximum rate that the project could pay and still break even by the end of the project life.
It can be calculated by trial-and-error of the following relation:

$$\sum_{n=1}^{n=t} \frac{NFW}{(1+r^{'})^{n}} = 0 \tag{11.3}$$

This calculation is also done in appendix 11.1. The DCFRR for this project is 16.6%, which is high enough as the actual rate will be lower, so that this project will make profit. This is shown by choosing an interest rate of 10%.

In figure 11.1 the project cash-flow diagram is shown.

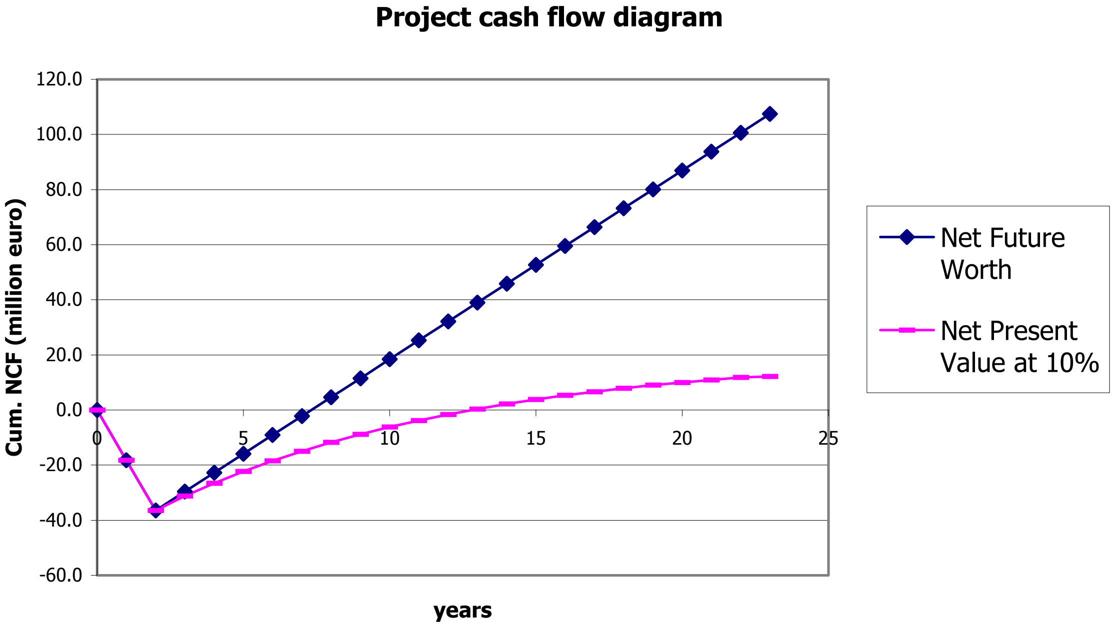


Figure 1.1 Project cash flow diagram

In this figure the time value of money is clearly shown. Money earned in the early years of the project is more valuable than that earned in later years.

Costs of monolith reactor [65]
After a relatively long search on the internet and sending emails to companies producing monoliths, it was decided to ask for an estimate at the department of Reactor & Catalysis engineering. In the thesis of Theo Vergunst the costs for a cordierite monolith were estimated at 7000 \$/m^3 (1999). As the research and the development of the monolith have improved very fast during the last four years, the costs were estimated at 10% of the number mentioned in the thesis. Also it is expected that the costs for the monolithic reactor will be reasonable, as they are not produced at a commercial scale. Furthermore it was estimated that the coating of the monolith with the Pt catalyst would have the highest costs.
The costs for the monolith reactor of 71 m^3 are therefore 49700 \$. As the Pt catalyst has a lifetime of three years, the costs per year for monolith reactor are 49700/3 = 13400 \$/a.

Pt catalyst

It was estimated that you need 1 kg of Pt in 1 m^3 of monolithic reactor. The costs of the Al_2O_3 support were neglected. The costs for pure Pt are estimated at 16880 $ per kg [46]. The volume of the monolithic reactor will be 71 m^3 and will be coated with 71 kg Pt. The costs for the Pt catalyst will therefore be: 71*16880 = 1.18 million $. The Pt catalyst has a lifetime of about 3 years.

Price of SOC

The price of SOC is estimated at 4 $ per kg and has also a lifetime of three years. The SOC mass stream is 2180 kg/s. The cycle time of the SOC is estimated at 60 seconds. Therefore the amount of SOC that is present is 130738 kg. This amount has to be replaced every three year. The costs per year are therefore 130738*4/3 = 174318 $.

11.4 Cost review

Investment

The main costs of the equipment are the costs for the heat exchangers and compressors and turbines. The costs for the reactor are negligible compared to that of the heat exchangers. The investment costs can therefore be reduced by looking critically at the number of heat exchangers.

From the heat exchanger network design (chapter 5.4) the maximum number of heat exchangers is designed. The number of coolers and heaters is because of this design minimized. In practice however, more coolers and heaters will be needed, because the heat exchange network will not work in practise. For example, a stream at one side of the plant cannot easily be coupled to a stream at the other side of the plant.

Production costs

The main production costs are the costs for the LPG feed stream. Also the costs for the utilities contribute a lot to the total production costs.

In the following table an overview of the costs is given together with percentages and value per ton of propylene.

Table 11.4 Overview of the costs of the Hipphox process

Item	**$/ton propylene**	**Euro/ton propylene**	**Percentage [%]**
Feedstock (LPG)	212.7	171.6	58
Utilities	54.3	43.8	15
Catalyst and chemicals	3.3	2.7	1
Fixed expenses	112.2	90.5	31
By products (credits)	-17.1	-13.8	-5
Total	365.4	294.9	100

From this table it can be seen that the feedstock counts for more than 50% of the total production costs.

11.5 Sensitivities

A sensitivity analysis is done with respect to investment, propane price, utilities costs and propylene price. A variance of +/- 10 % is used. In the following table the results are shown.

Table 11.4 Results of the sensitivity analysis

			Fixed capital costs [M euro]	**Production costs [euro/t]**	**Net cash flow [M euro/a]**	**Pay back time [years]**
Without change			32.8	309	6.85	7.4
	M euro					
Investment +10%	40.0		36.0	312	6.46	8.3
Investment -10%	32.8		29.5	305	7.25	6.5
	euro/t	$/ton				
LPG price +10%	169	209		329	1.70	no
LPG price -10%	138	171		288	12.00	5
	M euro/a					
Utilities +10%	12.06			314	5.53	8.6
Utilities -10%	9.86			303	8.17	6.4
	euro/t	$/ton				
Propylene price +10%	333	413			14.52	4.5
Propylene price -10%	272	338			-0.62	no

A change in the total investment costs does effect the net cash flow, but not very much. The cash flow is much more sensitive to a change in the LPG price. If the LPG price is 10% higher, than the cash flow becomes too small. No profit will be made and therefore there is no pay back time. The same accounts for a change in the propylene price. When the propylene price decreases with 10% the cash flow even become negative. However, the price of propylene will depend on the price of propane. For the Hipphox process it is important that the difference between the propylene and propane price is high enough. A change in the costs for the utilities does not have a large influence on the cash flow.

12 Hipphox process versus Oleflex process

As the Oleflex process is chosen as a reference a comparison will be made in this chapter. Details of the Oleflex process can be found in Appendix 1.1.

12.1 Process comparison

The main difference between the two processes is of course the use of the SOC. In the Hipphox process the DH reaction is combined with the SHC reaction, in one reactor unit.
Therefore the reaction section of the Hipphox process is different than that of the Oleflex process. Because of the use of the SOC, the hydrogen formed in the DH reaction is removed. Due to the removal of hydrogen the equilibrium is shifted towards propylene. This leads to a higher conversion of propane; 57% compared to 29% for the Oleflex process. The recycle stream of propane is therefore smaller.
The Hipphox process uses a Pt catalyst that does not require regeneration. The CCR unit of the Oleflex process is therefore not needed. However the Hipphox process introduces a new solid: the solid oxygen carrier. This SOC needs to be regenerated, which is also a new piece of equipment. However the SOC is used as a heat carrier, to transfer heat from the regeneration section to the reactor section. In the regeneration section a large amount of heat is produced, which can be supplied to the reaction section. By using the SOC as a heat carrier the Hipphox process does not require interstage heaters, whereas Oleflex requires 3 interstage heaters.
The regeneration unit is integrated in the Hipphox design, whereas in the Oleflex process an independent regeneration section is applied. This is a large advantage of the Oleflex process, since it offers better controllability of the plant. In the Oleflex process the production of propylene can continue if the CCR unit should be off-stream. In the Hipphox process, the complete reaction section must be shut down if the SOC stream is interrupted in case of problems with the regeneration unit.
The downstream processing is almost the same as the Oleflex process. A difference is that in the Hipphox process no unit is needed to separate the hydrogen from the product stream. Another difference is the presence of water in the Hipphox process; this increases costs for equipment due to corrosion.

Summarizing the above arguments the main advantages and disadvantages of the Hipphox process are given below.

Advantages Hipphox:

- Less propane needed
- Less costs for utilities
- No Pt catalyst regeneration required
- SOC for heat integration

Disadvantages:

- No high credit for hydrogen
- Large solid stream to be handled
- No independent regeneration section
- Water present in system increases equipment costs

12.2 Economical comparison

In order to compare the costs of the Hipphox process with the costs for the Oleflex process, table 12.1 is made. In this table the price per ton product for items such as feedstock are given. In literature [8] these numbers are found for the Oleflex process. However, these values are from 1990. In 1990 the prices for propane and propylene were a lot different. Nevertheless, from the percentages some comparisons can be made. The costs for the feedstock contribute for more than 50% to the total production costs. This is also the case for the Oleflex process. In the Hipphox process the costs for the utilities are less, the same applies for the catalyst and chemicals costs. The fixed costs are almost the same. But the Oleflex process produces a lot of hydrogen, which is a valuable by-product. For the Oleflex process the credits are therefore a lot higher. However, from this table it can be concluded that the Hipphox process is advantageous compared to the Oleflex process.

Table 12.1 Economical comparison between the Hipphox and Oleflex process

	Hipphox			Oleflex	
Item	$/ton propylene	Euro/ton	Percentage	$/ton propylene	Percentage
Feedstock (LPG)	212.7	171.6	58	158	71
Utilities	54.3	43.8	15	50	22
Catalyst and chemicals	3.3	2.7	1	12	5
Fixed expenses	112.2	90.5	31	76	34
By products (credits)	-17.1	-13.8	-5	-72	-32
Total	365.4	294.9	100	224	100
Without credits	382.5	308.7		296	

In the following table the flow rates of the Hipphox and Oleflex process are given. In order to achieve the same production rate the Oleflex process requires a higher flow rate of propane.

Table 12.2 Comparison between flow rates of the Hipphox and Oleflex process

Component	Hipphox Flow rate [kta]	Oleflex Flow rate [kta]
Propane	280	295
Propylene	250	250
H2	1.47	20.3

On the internet [75] an indication of the investment costs for a new dehydrogenation plant using the Oleflex technology built in Tarragona (BASF, completed in 2002) was found. This plant will produce 350 kta and the investment costs are about 200 million dollar. Although this new plant produces more propylene, the investment costs are much higher than the investment costs for the Hipphox process. Investment costs for the Hipphox process are only 36.4 million euro (45.1 million $). The Oleflex technology requires much more complex and larger units than the Hipphox process. For example, the reaction section of the Hipphox process consists of one reactor of 71 m^3, which is not very large. Also the regeneration section of the Oleflex will be much larger than the regeneration section of the SOC.

13 Creativity and group process tools

In this chapter the creativity during the process design is described. Several tools for creativity were used. The group process was reviewed and finally the Piquar (Plant design Improvement by QUAlity Review) method is described and the results from this are discussed.

13.1 Creativity during the first weeks

To implement creativity in a structured way in the design process there are a few creativity tools, which the team has agreed on to use in the conceptual process design.

First of all the idea pocket book is used for writing down spontaneous ideas at all times. All team members carry this booklet with them (almost) all the time. In all group meetings, going over these ideas is a fixed item on the agenda. The team found it very useful to discuss these ideas, because in some cases it even led to new creative ideas. The team will therefore continue using the idea pocket book.

Cross fertilisation is used as well. This means that tasks are rotated within a team to get idea transfer between various disciplines. This proved to be very efficient, because a fresh view leads to new insights, and in some cases also errors, for example in Excel files, were taken out.

Other tools were specifically used during creativity meetings. These tools are:

- Brainstorming
- Brainwriting
- Thinking hat tool
- Expression, for example drawing: to increase insight and create new ideas it can help to draw the problem.
- Associating, for example associating a reactor with an animal will give new ideas on possible configurations of the reactor.

These tools are used in a so-called divergent-convergent approach. Idea generating is divergent, followed by evaluation of all the ideas and picking out the best ones (converging). It can help to prevent ideas from being thrown away immediately and to narrow down the solutions when converging, in a short time.

In the first week, the team presented their findings at the kick-off meeting on Thursday. On Friday the 10th of October the team had a group meeting, in which the four process options, as discussed in the kick-off meeting, were drawn on a blackboard, and the team discussed possible opportunities these four options could have. The four options meant here are: separation of the regeneration and reaction in time and/or in space. The ideas were noted in minutes of meeting of the group meeting. During this meeting no specific tool was used, since it was just an exchange of views on these options. It was not intended to evaluate the options already.

In the second week, the team had a creativity meeting everyday, except for Thursday when the team visited the principals in Amsterdam. Two of those meetings are discussed in more detail here.

On Tuesday, the 14th of October, the team decided to have a brainstorm session on process options. It was agreed that the brainstorming rules would be: no judgement or evaluation of ideas was permitted, since during an ideas generation activity almost any proposed idea could be criticized. All ideas, even ridiculous ones, are considered useful, because they might trigger other solutions. This encourages a person to come up with more ideas without being fearful of criticism and evaluation. To practice these rules first, the team had a brainstorm session by using a flip-over to generate a name for the new process. All known boundary conditions were first summed up. By associating the process with different animals, finally Hipphox came out: Heat Integrated Propylene Production with Hydrogen OXidation.

The flip-over method was used further to discuss process options. Next to known boundaries that the team has to satisfy, such as reactions, regeneration and safety issues, also process configurations were generated, such as immobilisation of the catalyst or SOC, use of a membrane etc. During the brainstorming it became clear that it was necessary to go into more detail of the reactions. To get a better insight of what really happened during the reactions, drawings were made of how everybody thought the reaction on the Pt-catalyst developed.

In the last flip-over sheet possible negative and positive aspects of putting the SOC and Pt-catalyst in the same reactor were summed up. All of this was very useful to increase the insight of the various options. The outcome of this session was four process options, these options are explained in detail in chapter 2.3.

On Wednesday the 15th of October, these four options were evaluated. First, a brain writing session was held. Brain writing differs from brainstorming in that the generation of ideas is recorded individually on a piece of paper. Individuals may feel inhibited in brainstorming sessions; brain writing reduces inhibitions because ideas are recorded anonymously and all participants have an equal opportunity to contribute ideas. The goal of the meeting was to note all positive and negative issues regarding these four options, to know which one was considered the best option. The sheets of papers rotated between the team members, to get the most issues possible, a divergent approach. Then, all these issues were converged into 24 criteria, and in a discussion the four options were evaluated on these criteria. This resulted in table 2.1 of chapter 2.3. In that chapter the evaluation is explained in more detail. The final result of this creativity meeting was a best option, namely option 3.

In the third week, two creativity meetings were planned, on Monday and Thursday. One of those meetings is discussed here.

On Wednesday the 22nd of October an evening creativity meeting was held. The reason why this meeting was held in the evening, was that in this way each team could relax for a few hours and get his or her mind off CPD for a while during dinner at home. This so-called incubation time can lead to refreshing views. The goal for the meeting was to find creative process schemes for option 3. The team used the hat method this evening. The hat tool involves six thinking hats. Each team member puts on the same hat when using this method. First the green hat was "put on", this hat represents creative ideas and possibilities. This hat was used to generate as much as possible ideas, in a divergent way. Ideas like implementing monoliths, a fluidized bed, membrane etc. were opted. From these ideas a new option was generated, namely the continuous regeneration of the SOC and the batch regeneration of the Pt-catalyst. Basically this option was not included in option 3, but is between option 2 and 3; see also chapter 2.3. Then, each team member drew one possible process scheme, to get an idea of what it represented. After the drawing, the red hat was "put on". This hat represents feelings and intuition. It turned out that all team members had the same feelings about the possible schemes, all believed most in the fluidized bed option. To see if it was possible to rule out one scheme already the black hat was "put on". This hat signifies negative perceptions, arguments why something is bound to fail. For all options a few disadvantages could be mentioned, but nothing was found to be decisive at this point. At last, the yellow hat was used, which represents optimism, and all ideas were found to be acceptable.

13.2 Creativity after preliminary BOD

After handing in the pre-BOD report, a new creativity session was planned on November 6th. In this session the main question was: How can the Oleflex process be improved? The aim of this session was to create more ideas on the improvement of the dehydrogenation, as maybe there were better alternatives that did not use SOC. So first the green hat was put on and all ideas were written down on the blackboard. Ideas like fuel cells, water gas shift, hydrogen immobilisation or storage in a zeolite, hydrogen separation by membranes and propylene immobilisation by direct polymerization were opted. After this the red hat was put on and it was believed that the fuel cell will be hard to apply to the dehydrogenation of propane. Furthermore this technique is based on small scale and probably not developed enough. All the group members had a good feeling about improving the equilibrium by removing the hydrogen. For removing the hydrogen there are various options, of which one option is using the SOC. But the option using a membrane to separate the hydrogen looks also very promising. Hydrogen can also be stored in a zeolite. The option of storing the propylene was reviewed as well, but this is not possible, as the hydrogen will also be stored in the zeolite. From the session with the red hat, four possibilities were left over:

- Storage of hydrogen
- Separation of hydrogen using a membrane
- Using a SOC to convert the hydrogen to water
- Polymerization of propylene

These options were divided among the team members to investigate if the option was possible.

Another question in this creativity sessions was: do we want to produce energy or do we want to produce hydrogen, which can be sold. As we could not directly give an answer to this question it was decided to calculate how much hydrogen can be produced and what this would yield.

Finally we came back to our four options and option 3 and 4 were drawn, as continuous regeneration is very desirable. From this evaluation the main question still was, do we have to regenerate the Pt catalysts and SOC separately or can we do it simultaneously. If the solid streams have to be separated, then option 2 is no longer feasible. So another action point was to look into more detail in the regeneration sections.

After the BOD meeting the four options had to be reviewed again, as some ideas, especially on the exothermal/endothermal aspects of the reactions were changed. After the BOD meeting some assumptions were made which determined some important aspects of the whole process.

To prepare this session, two members of the group made a list of criteria on which the options had to be assessed. So on November 17th the four options were drawn again and all the criteria were assessed. After this the criteria were classified according to the Piquar criteria. From this assessment session again option 3 is the most promising one followed by option 4. The results are described in chapter 2.

In week 8 it was time to think about what kind of reactor is suitable for the Hipphox process. Therefore a creativity session was planned on November 27th. For the process good gas-solid mixing is needed. The fixed bed reactor was not possible anymore, as the regeneration has to be done continuously. So also the solids have to be transported. From this it was concluded that there are several reactor options with the gas flow upward, downward or radial and the solids flow upward or downward.
These options were drawn on paper. Then the existing reactors were studied and coupled to four options. The results are shown in figure 12.1

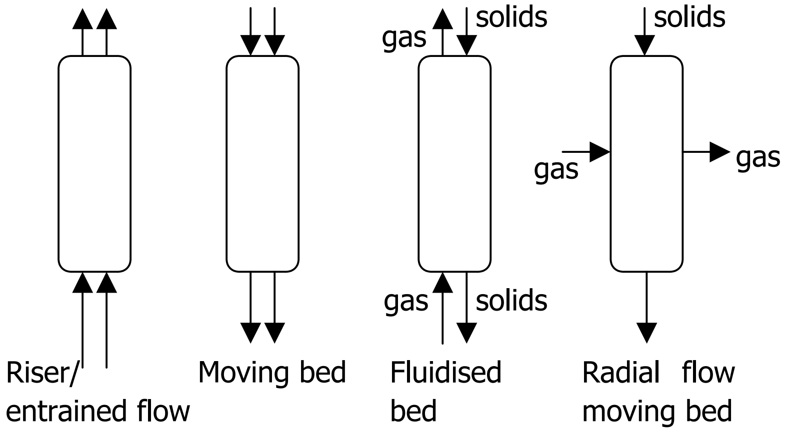


Figure 13.1 four process options

Another option is the FCC reactor. In this reactor the solids stream and the gas stream come upward. The solids will fall down again and leave the reactor at the bottom.
For every reactor the aspects were studied. From this it was clear that a riser was not possible, as the solids load will only be a few percent. This is too low to obtain a high conversion. A fluidized bed has one big disadvantage. The residence time in a fluidized bed is very large. The moving bed and the radial flow moving bed reactor look very suitable. As the solids stream have to be separated an idea came for a combination of the moving bed and the riser reactor counter current. In this combination the two solids must differ in size. For example the Pt catalyst is very small and will go with the gas stream. The SOC is heavy enough to go down and can leave the reactor at the bottom.

This session was very useful as the whole group got a clearer view on the reactor possibilities.

During the following weeks Dr. Dimian proposed the idea of not regenerating the Pt catalyst. If this was possible, than our design could be simplified, which is a big advantage. This idea was verified by literature and by professor Moulijn and the decision was made not to regenerate the Pt catalyst. However, this decision has a big influence, because a new option was now possible. As the Pt catalyst will not be regenerated, it is not necessary to take the Pt catalyst out of the reactor and put it back. So the immobilization of the Pt catalyst had to be studied. This was done during the group meeting of December 4th. Several possibilities for immobilization were proposed, like the monolith reactor and the trickle-flow-reactor. Also the following question was raised: Why not immobilize the SOC stream, as the SOC amount will have to be very large? It will however be easier to transport the smallest solid stream. However, when the SOC will be immobilized option 3 is not possible anymore, because the regeneration cannot be done continuously. It was then decided to look into more detail in the monolith option and the trickle-flow-reactor. At the end of the day, the decision was made to choose for a monolith reactor, as this is a very promising reactor type and a lot of information is available. Furthermore the solids load can be relatively high, so this will not be limiting for the kinetics of the reaction.

13.3 Group process review

A group profile analysis was made at the start of the project. This showed some weaknesses and strengths of the team, which could be taken into account during the 12 weeks of designing. Agreements were made on working hours and meetings. The group tried to lunch together each day, and agreed not to talk about the CPD-project during this lunch, to have some time to take their mind off the project during the day. Even though all these agreements were made, still some friction between team members is inevitable. Therefore these issues were discussed in the group meetings, which were held frequently (at least once in a week). In this way the team worked with an open mind, since there was room for discussion and fresh views.

The group made a planning for the full twelve weeks. This planning was adjusted during the project, since it is always difficult to predict the time planning of such a large project. In the week before the BOD meeting some problems were encountered with the thermodynamic and kinetic data availability. This delayed the progress of the designing, which meant somewhere this time had to be catched up. The team had to work harder in the next weeks and some time was spent in weekends and evenings. This had a negative effect on the team spirit, but the team discussed this during the group meetings. These discussions were always very open so that the team spirit improved.

All team members learned a lot these twelve weeks about teamwork and believe that they have made a thorough and a well-sophisticated design together.

13.4 PIQUAR Analysis

Piquar stands for "Plant design Improvement by QUAlity Review". The Piquar tool is a method to keep the design team focused on the goals that have been set in the beginning of the project. The goals were set by means of criteria chosen at the kick-off meeting. Once the criteria and the weighing factors were known the group evaluated each week to what extent the accomplishments of that week complied with these criteria and a number from 0 to 1 had been assigned to it. Each individual gave a number to each of the criteria. This number was multiplied by the weighing factor and this was added up resulting in the individual Piquar number. Since the wishes of the project coach and principals are also very important they have had a big contribution in the choice of the criteria and their weighing factors.

The criteria are shown in the following table. For a detailed description of the procedure that led to the choice of the criteria, their weighing factors and the Piquar number can be found in Appendix 13.1.

Table 13.1 Piquar criteria and weighing factors

Criterion	WF
Product quality and quantity	0.368
Economically feasible	0.175
Energy efficient	0.092
Intrinsically safe	0.087
Efficient use of raw materials	0.081
Waste management	0.044
Process must be robust	0.042
Team spirit with an open mind	0.040
Comply with (future) environmental legislation	0.035
Safety for operators in plant and surrounding	0.034

The individual Piquar numbers were added up and averaged over the group. This resulted in the Piquar number for that particular week. The Piquar number is a measure for the quality of that week, or the amount on which the group has complied with the criteria. In assigning the values to the criteria the group members kept in mind the maximum amount of work they would ideally put into this subject. A Piquar number of 1 means that nothing can be thought of else to do on the subject. In figure 13.2 an example of a Piquar graph of week 7 is shown.

Figure 13.2 Piquar graph of week 7.

Usually the assignment of the values to the Piquar criteria was done on a Friday and on Monday the results were discussed in the group meeting. This was not only very helpful for maintaining a focus on the project goals, but also the differences between values assigned by the group members gave rise to discussions about the project and the group process.

The criterion "group process with an open mind" was a frequent subject of discussion and a helpful way for people to show how they felt about the group process.
The Piquar numbers of all weeks is shown in figure 13.3.

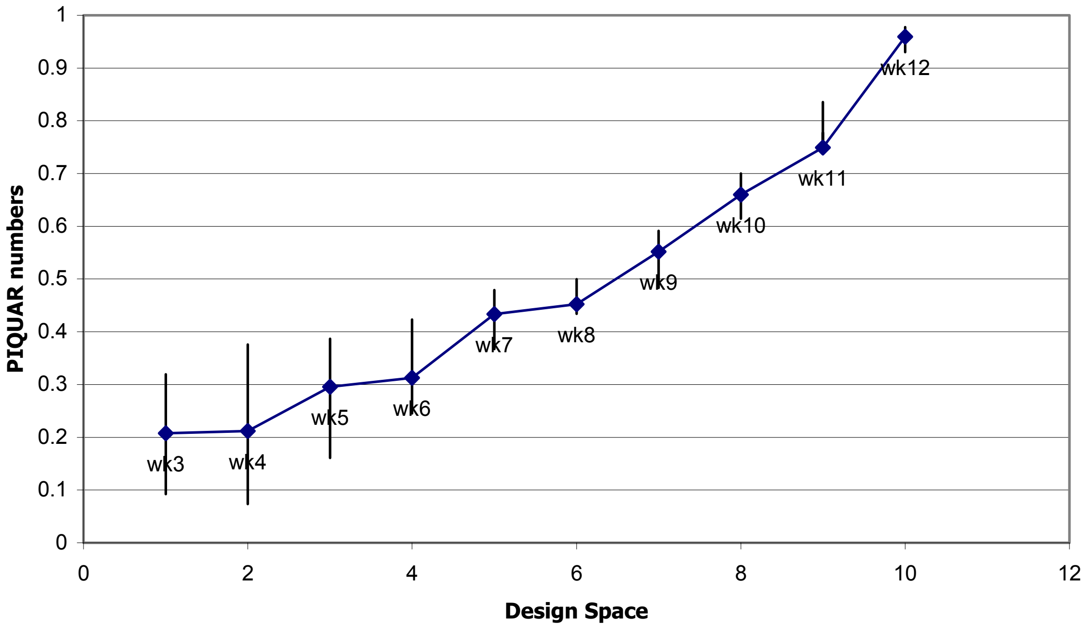


Figure 13.3 Piquar numbers of all weeks.

In this figure a clear rise can be observed in the Piquar numbers of the weeks, which is a clear indication of the good planning of our project. The work was more or less evenly spread over the project time span. In weeks 4, 5 and 6 a lower increase in the Piquar number is observed. The reason for this was the slow progress of the thermodynamics part. A lot of time and energy has been put in that and therefore less attention could be put into other subjects. In week 8 a minor crisis can also be observed, the progress was not high enough, as can bee seen in figure 13.3. At the end of that week finally the decision was made to use a self-regenerating Pt-catalyst, so we could move on.
A second remark about figure 13.3 can be made, namely that the deviation of the individual Piquar numbers decreases throughout the project. This means that the group increasingly agreed on how the project was going.
Concluding it can be said that the Piquar tool was experienced to be a very useful tool to keep a focus on the project goals. It makes you think repeatedly whether the subject you are working on at that moment is really important or if it is trivial.

14 Conclusions and recommendations

In this chapter the main conclusions drawn about the Hipphox process are given. Also some recommendations for further work are treated.

14.1 Conclusions

The problem statement of the Conceptual Design project is defined as:

How can propylene be produced by using the new solid oxygen carrier in the dehydrogenation of propane coupled with selective hydrogen combustion?

A design is made for the simultaneous DH and SHC. This was found to be the most promising way of producing propylene in the dehydrogenation of propane by using the SOC. It results in a propane conversion of 57%, with a selectivity of 99%. In the reference process (Oleflex) the conversion is only 29% and the selectivity is 90%. The high selectivity in the Hipphox process is achieved by a new reactor design with a short contact time. Furthermore the Pt catalyst is self-regenerating in this process.
The heat produced in the regeneration of the SOC is integrated in the design. The SOC acts as a heat carrier, to transfer the heat that is produced to the reactor. The heat that is required by the DH and SHC reaction can be delivered completely by the SOC. This makes interstage heaters, which are required in the Oleflex process, redundant.

The product quality is met; the product should be 99.5 wt% propylene. The amount of ethane is nevertheless too large if polymer grade propylene is desired. The product quantity is also met, since the plant should produce 250 kta. This is shown in table 14.1.

Table 14.1 Propylene product stream quantity and quality

	kta	**wt%**
Propylene	248.9	99.6
Propane	0.9	0.3
Ethane	0.2	0.1
Ethylene	0.0	trace
Methane	0.0	trace
CO	0.0	trace
Total	250.0	100

The economic evaluation of the Hipphox process shows that the cash flow is positive. The production costs are mainly determined by the costs for propane. The difference in price of propylene and propane has to be high enough to make profit. The investment costs are 36.4 M€, the payback time is 7.4 years and the discount cash flow rate of return (DCFRR) is 16.6%. This is only an estimate of the actual costs, but these results show that the process has a great potential.
The Fire & Explosion Index showed that all units have a moderate or intermediate degree of hazard. The conclusions from the Hazard and Operability study (HAZOP) are implemented in the process control and the risks are minimized.
The process lifetime is 20 years. In the next 20 years the environmental legislation will be met. In the Hipphox process no real toxic substances are used. Furthermore no interstage

heaters (Oleflex process) are required in the Hipphox process, so this reduces the carbondioxide emission.
For the production of propylene 280 kta of propane is needed. This is lower than the amount needed in the Oleflex process (295 kta).

These arguments show that the application of SOC in the DH of propane is feasible.

14.2 Recommendations

A problem encountered in the design was the non-availability of data about the thermodynamics and kinetics of the SOC. A major recommendation is therefore to do a number of experiments with the SOC that determine:

- Heat effect of SHC reaction and entropy change.

  A change in the enthalpy change or entropy change of the SHC reaction and the SOC regeneration reaction has a heavy impact on process design. The equilibrium constant is dependent on the enthalpy and entropy. Therefore a change will lead to a different reactor conversion. This effect will finally result in differences in the separation section and the recycle size. Furthermore the amount of required SOC in the reactor is also dependent on the required heat, since the SOC is used as a heat carrier. If for example, the SHC reaction appears to be less endothermic, the SOC stream towards can be decreased. This has a major impact on the SOC regenerator (R102) design. In the design literature on the thermodynamics of CeO_2 is used, however the influence of doping with Tungsten on the thermodynamics is not known.
- Kinetics of the SHC separately and mixed with DH

  No current research on SHC reaction kinetics is available. Kinetic experiments should be done in order to estimate hydrogen concentration effects and reaction constants. A change in reaction kinetics will have a significant impact on the SOC stream size to the reactor. The experiments performed by Rothenberg et al. [9] are done with an excess of hydrogen. In the Hipphox process there is no excess of hydrogen, as this is combusted as soon as it is formed. Just of all an excess of SOC is used in the Hipphox process.

It is estimated that only 10% of the available oxygen on the surface of the SOC can react with the hydrogen. As the SOC amount in the Hipphox is high enough, the effect of the assumption is not very high. However increasing the percentage oxygen that can be freed out of the SOC lattice can decrease the amount of SOC. It would be good to look for ways to increase the percentage.

The SOC combusts also hydrocarbons, as the SOC has a selectivity of 97% for the combustion of hydrogen. It was assumed that the hydrocarbons were converted to CO and not to CO_2 based on thermodynamics. This assumption should be checked, as it is likely that some CO_2 will be formed.

In order to integrate the two reactions (DH and SHC) an idea is to make one catalyst that catalyzes the DH and SHC reaction (two-way catalyst). The problem with the Pt catalyst is that it cannot resist high oxygen concentrations. Therefore the SOC regeneration has to be done separately or with low oxygen concentration, but that makes the regeneration very slow. So the 'two-way' catalyst has to resist high oxygen concentrations.

In this design it is assumed that the Pt catalyst is self-regenerating. However this assumption is based on discussions with professor Moulijn en dr. Dimian, but no literature was found that confirms this assumption. In combination with the two-way catalyst the self-regeneration should be further investigated.

The by-products (light ends and C_4^+) will probably have more value than fuel value. The light ends can for example be processed further to yield hydrogen or syngas. In the design a small economic evaluation was done, but this could be done in more dept.
Furthermore the exhaust air contains little amount of oxygen and a high concentration of nitrogen. Maybe the exhaust could be further processed to yield pure nitrogen.

The product specifications for polymer grade propylene are not exactly met, as too much ethane is present. This amount should be reduced to sell the propylene for the production of polypropylene.

The investment costs can be reduced by looking critically at the number and the size of the heat exchangers. Furthermore the heat exchange network is designed to minimize the number of coolers and heaters. In practice the costs for the heat exchange network will be higher, since it will not be possible to completely integrate all flows. This should be critically reviewed.

The removal of water is not fully designed. Alternatives for the glycol unit for example should be reviewed in more depth.

A difference in this design compared to the Oleflex process is the non-production of hydrogen. Although the Oleflex has a lower conversion, it produces a lot of hydrogen, which is a valuable product. The conversion of the dehydrogenation can maybe be increased by removing the hydrogen in another way. For example the hydrogen can be removed by a membrane.

The riser has been designed at a lowest possible pressure due to the rapidly increasing costs of the air compressor with increasing pressure. A consequence of this is that the particle and gas speed is high, 30 m/s, and the dimensionless particle size and gas speed are just within the dilute transport regime. Increasing the pressure would result in lower particle and gas speeds and the dilute transport regime would be more sure obtained. Another drawback of the current pressure of the riser design is that the pressure at the top is 1 bara. Therefore the pressure drop over cyclone S102 and heat exchanger E102/E116 is not accounted for. A recommendation is therefore to review the low pressure chosen and to look if the design should be done at a higher pressure.

The control system does not react on itself to a lower concentration of oxygen in the regeneration air. For now this is designed as being done manually. A recommendation therefore is to look for a better solution of this.
Since not very much knowledge was obtained of the heat pump of the P/P-splitter it was not known whether splitter SP101 was controllable or not. In the control system design the assumption was made that it has a constant split fraction. No further design was done and it is not known yet if the heat pump functions in this way in practice. This should be reviewed.

The design of the hopper and the seal at the bottom, including the mechanism that puts the SOC into the target stream has not been done yet. Also there has not been looked at ways to distribute the particles evenly over the gas stream.

A last recommendation is to re-analyze the maximum catalyst load in a monolith reactor. A lot of different monoliths are available and the catalyst load differs and can be increased by using a better monolith. This will have an impact on reactor size and residence time.

List of symbols

C_p>	Average heat capacity
°C	Degree Celsius
A	heat transfer area
$\hat{a}_i$	activity of component I
A_i, B_i,..	Parameters per component
bar	0.9869232 atmosphere [standard]
bara	absolute pressure
BI	business interruption
BLEVE	Boiling liquid expanding vapour explosion
BOD	Basis of Design
BOD	biological oxygen demand
CA	concentration of A
cat	catalyst
CCR	Continuous Catalyst regeneration
CEP	Chemical enginering plant (cost index)
CISOLID	Conventional Inert Solid
CPD	Conceptual process design
cpsi	cells per square inch
D	gas phase diffusion coefficient
D/F	Distillate to feed fraction
DCFRR	Discounted
DCT	DelftChemTech
DH	Dehydrogenation
dN_A/dt	transfer rate of A
Δp	pressure change
dp	particle size
dp*	dimensionless particle size
d_{sph}	particle diameter
ΔT_{ad}	adiabatic temperature change
ΔT_m	true mean temperature difference
Δz	difference in elevations
ε	absolute pipe roughness
ε/d	relative roughness
E_a	Activation Energy
ε_j	extent of reaction j in mole/hr.
Ep	polytropic efficiency
Eu	Euler number
F&EI	Fire & Explosion Index
f_propane	flow of propane
F1	general process hazards factor
F2	special process hazards factor
F3	process unit hazards factor
FC	Flow controller
F_i	molar flowrate of component i
F_t	total molar flowrate
ft	feet
F_t	correction factor
ϕ_v	volumetric flow rate
f_v	fraction of total cross-sectional area

G	Gibbs free Energy
γ	ratio of specific heat
g	gravitational coefficient
GJ	giga Joule
H	Enthalpy
h	hour
η	dynamic viscosity
h	height
HAZOP	Hazard
HEN	heat exchange network
Hipphox	Heat Integrated Propylene Production with Hydrogen OXidation.
hr	hour
h_v	liquid height
K	Kelvin
K	Equilibrium constant
k	rate constant
$k_{g,single}$	mass transfer coefficient of particle
kg/yr	Kilograms/year
kJ	kilo Joule
kta	kilo tonnes per annum
kW	kilo watt
kWh	kilo wat
l	liquid
lb/yr	pound/year
LC	Liquid level controller
LPG	Liquefied Petroleum Gas
LSS	Liquid separation section
LY	Length of this project in light years
m	meter
μ	gas viscosity
M	molar mass
m^3	cubic meters
MF	material factor
MJ	Mega Joules
μm	micometer
MMscd	Million standard cubic feet per day
mol%	Mole percent
MPDO	Maximum probable days outage
MPPD	Maximum probable property damage
MW	Mega Watt
n	year
N	number of stages
n_0	overall quantity,
NBP	normal boiling point
Nf	feed stage
NFW	Net Future Worth
n_{i0}	quantity of component i at the beginning,
nm	nanometer
N_{min}	minimum number of stages
NPSH	Net positive suction head
NPW	Net present Worth
oz	ounce troy (1 ounce troy = 0.0311035 kilogram)

p	Pressure
p/p-splitter	Propane/Propylene-splitter
p_{bub}	bubble point pressure
PC	Pressure controller
P_c	critical pressure
p_{dew}	dew point pressure
PE	population equivalent
PFR	Plug flow reactor
PFS	Process Flow Sheet
p_i	partial pressure of component I
PIQUAR	Plant design improvement by quality review
ppm	parts per million
PRBM	Peng Robinson Boston Mathias - thermodynamic properties model
p_r^{sat}	reduced saturation pressure
p^{sat}	saturation pressure
PSE	Process systems engineering
PSS	Process stream summary
PURA	Process unit risk analysis
q	gas flow rate
Q	heat transfer
QF	quality factor
R	Universal gas constant
ρ	density
r'	DCFFR Discount cashflow rate of return
R_cal	Gas constant [cal/mol K]
Reg.	Regeneration
Re_{sph}	dimensionless particle Reynolds number
R_H	rate of hydrogen formation
r_i	rate of a reaction
ROR	rate of return
RPF	Recent performance factor
RR	reflux ratio
RR_{min}	minimum reflux ratio
s	solid
S	Entropy
Sc	Schmidt number
Sep.	Separation
$S_{ex,single}$	exterial surface of particle
SHC	Selective Hydrogen Combustion
SHC	Selective Hydrogen Combustion
Sh_{single}	dimensionless Sherwood number
SOC	solid oxygen carrier
SOC	solid oxygen carrier
SRK	Soave Redlich Kwong - thermodynamic properties model
SRKKD	Soave Redlich Kwong Kabadi Danner - thermodynamic properties model
Stk	dimensionless Stokes number
T	Temperature
t	ton
τ	tau, residence time
τ	1-Tr
t/h	tonnes per hour
TC	Temperature controller

Tc	critical temperature
TEG	Triethylene glycol
TNW	Technische Natuurwetenschappen
Tr	reduced temperature
U	overall heat transfer coefficient
u	relative velocity
u*	dimensionless gas velocity
UQF	un-quality factor
u_t	settling velocity
v	vapour
V	Volume
v	characteristic velocity
V/L/S	Vapour Liquid Solid
VLE	Vapour Liquid Equilibria
vol%	volume %
VPM	value of production for a month
VSS	Vapour separation section
W	Work
WF	Weighing factor
wt%	Weight percent
x_{50}	cut size
x_i	solid fraction of component i
y	logarithmic mean mol fraction of inert or non-diffusing component
y_i	fraction of component i
z	mole fraction
Z	compressibility factor
$\Delta_f G^0$	Gibbs free Energy of formation at standard conditions
$\Delta_f H^0$	Enthalpy of formation at standard conditions
$\Delta_f S^0$	Entropy of formation at standard conditions
$v_{i,j}$	stoichiometric coefficient of component i in reaction j
v_j	overall stoichiometric coefficient.
$C_{p,i}^{ig}$	heat capacity of component i as an ideal gas
$\Delta_r G^0$	Gibbs free Energy of reaction at standard conditions
$\Delta_r H^0$	Enthalpy of reaction at standard conditions
$\Delta_r S^0$	Entropy of reaction at standard conditions
γ_i	Activity coefficient
k_{app}	apparent rate constant
k_{site}	rate constant per active site
N_{site}	Number of sites

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Appendices Table of Content