

Simulation of a Hydrogen Peroxide Oxidation Tower

Master's thesis in Innovative and Sustainable Chemical Engineering

SARA LARSSON

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2022
www.chalmers.se

MASTER'S THESIS 2022

Simulation of a Hydrogen Peroxide Oxidation Tower

SARA LARSSON



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2022

Simulation of a Hydrogen Peroxide Oxidation Tower
SARA LARSSON

© SARA LARSSON, 2022.

Supervisors: Johan Lif and Ulf Andersson, Nouryon
Examiner: Derek Creaser, Chemical Reaction Engineering

Master's Thesis 2022
Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: The setup of a hydrogen peroxide oxidation tower in HYSYS.

Abstract

Hydrogen peroxide is a strong oxidizing agent used in a great variety of applications. Its main usage is as a bleaching agent where the pulp and paper industry dominates. One of the world's producer of hydrogen peroxide is Nouryon, who produce about 4% of the market volume. The primary way of producing hydrogen peroxide today is by the cyclic hydrogenation and autoxidation of anthraquinones (usually referred to as the AO process). The most commonly used raw materials for this process are hydrogen produced by steam reforming and air. With the current technical development, it is expected that electrolyzers producing green hydrogen is going to be used to a greater extent in the future. If this were to be implemented in a hydrogen peroxide plant it would enable the use of the by-produced oxygen as a cheap raw material in the oxidation tower. Using this pure oxygen would in turn make it possible to use a higher concentration of air in the gas feed which could be utilized in a smaller oxidation tower and with smaller ancillary equipment. This is therefore interesting since it may lead to lower investment and operating costs.

This work has been done for Nouryon with the purpose to set up a simulation tool to be used for simulation of a hydrogen peroxide oxidation tower. The aim was also to use this simulation tool to investigate how different tower designs and operating conditions may affect the size and operating conditions of the tower. The project has successfully resulted in a simulation tool set up in the process simulation software HYSYS v12.1. The simulation tool consists of a kinetic model for the oxidation reaction and a flowsheet setup representing the oxidation tower. The model was designed and successfully validated by the use of reference data from multiple oxidation towers.

The simulation tool has been used to simulate the operation of a hydrogen peroxide oxidation tower with higher inlet oxygen concentrations, lower oxygen excess and higher operating pressure. It has also been used to simulate an oxidation tower with recirculation of the off-gas. From these simulations it have been concluded that it is possible to operate the oxidation tower with a higher inlet oxygen concentration with the drawback of getting a higher outlet oxygen concentration. The results have suggested that this higher outlet concentration may be decreased by the operation with lower oxygen excess or recirculation of a part of the exhaust gas. As expected, the simulations have implied that the use of a higher oxygen concentration indeed should make it possible to reduce the oxidation tower size and still maintain the same productivity of hydrogen peroxide. Simulating the tower with a higher pressure has implied that it may also be possible to use an increased pressure to reduce the required tower volume. It has also been proposed that a higher pressure may be used to increase the productivity of a tower of a certain set size.

Keywords: *hydrogen peroxide, oxidation tower, AO process, simulation , HYSYS*

Acknowledgements

Most of all I would like to thank my supervisors Johan Lif and Ulf Andersson from Nouryon who have supported me throughout the project. They have gladly shared their knowledge about the hydrogen peroxide production process and been interested in the work I have done. A special thanks to Johan who have put a lot of extra effort and time supporting me with discussions, finalization of the report and preparation of the presentation. Lastly, I would like to thank Derek Creaser for being the examiner of my project.

Sara Larsson, Gothenburg, May 2022

Nomenclature

Below is the acronyms and parameter nomenclature that is used in the report listed.

Acronyms

AO	Autoxidation
AQ	Anthraquinone
HAQ	Hydroanthraquinone
HP	Hydrogen peroxide
WS	Working solution

Parameters

ΔH_f	Heat of formation
ΔH_r	Heat of reaction
A	Pre-exponential factor
a_i	Interface area
C	Concentration
d	Diameter
E	Activation energy
H	Henry's constant
h	Height
H°	Degree of hydrogenation
J_L	Mass transfer rate through a liquid film
k_L	Mass transfer coefficient in a liquid film
k_{ox}	Kinetic constant for the oxidation reaction
$\dot{m}$	Mass flow rate
$\dot{n}$	Molar flow rate
P	Pressure
p_{Ai}	Interface partial pressure of component A
Q	Volumetric flow rate
r	Rate of reaction
R	The gas constant
T	Temperature
V	Volume
x	Fraction

Contents

1	Introduction	1
1.1	Aim	1
1.2	Limitations	2
1.3	Specification of issues under investigation	2
2	Theory	3
2.1	Hydrogen peroxide and its usage	3
2.2	Production processes	4
2.2.1	Wet chemical process	4
2.2.2	Electrochemical process	4
2.2.3	2-Propanol process	4
2.2.4	Anthraquinone autoxidation (AO) process	5
2.3	Kinetics of the anthraquinone oxidation	10
2.4	Aspen HYSYS	11
3	Methodology	13
3.1	Literature search	13
3.2	Design of the simulation tool	13
3.2.1	Assumptions and model	13
3.2.2	Component list set up and property validation	14
3.2.3	Property package selection	15
3.2.4	Calibration tower set up	15
3.2.5	Kinetic fitting	17
3.2.6	Reference towers set-up	17
3.3	Optimization	18
3.3.1	Higher oxygen concentration in feed gas	19
3.3.2	Lower oxygen excess in feed gas	19
3.3.3	Higher operating pressure	19
3.3.4	Recirculation of exhaust gas	20
4	Results and discussion	22
4.1	Literature search	22
4.1.1	Patent search	22
4.2	Property validation	24
4.3	Property package selection	26
4.4	Kinetic fitting	29
4.5	Higher oxygen concentration	33
4.6	Lower oxygen excess	37
4.7	Higher operating pressure	39
4.8	Lower oxygen excess and higher pressure	42
4.9	Recirculation	45
5	Conclusions	46
A	Tower setup details	48

B Calculation of theoretical heat of reaction	49
--	-----------

1 Introduction

Nouryon is a global company operating in over 80 countries, delivering specialty chemicals used in a great variety of markets [1]. Markets where their products are used, amongst others, are agriculture, cleaning, paints, personal care, packaging material, food, pulp and paper and transportation. One of their products is the *Eka HP* which includes hydrogen peroxide solutions in various concentrations (mainly 35%, 50%, 59% and 70%) and at different grades (aseptic, chemical, food and technical) [2]. Nouryon has hydrogen peroxide production plants located in Sweden, Norway and the USA.

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent used in numerous applications [3]. The main usage of hydrogen peroxide is as a bleaching agent, mainly in the pulp and paper industry but also for bleaching of various textile fibres, teeth whitening and in hair colours [2]. Another large area of usage is in chemical manufacturing of for example organic peroxides, percarbonates and propylene oxide. It is also used as a disinfectant with applications in aseptic packaging materials, wound cleaning and household cleaning products. Beside these applications, Nouryon delivers products with hydrogen peroxide for fish-delousing and water treatment systems.

Historically there have been multiple ways of producing hydrogen peroxide [4]. Nowadays it is the so called autoxidation (AO) process that dominates in industry. This process is cyclic and hydrogen peroxide is received after hydrogenation and oxidation of dissolved anthraquinones using hydrogen and oxygen as raw material. The oxygen is most commonly supplied as air and the hydrogen is produced by steam reforming.

This work is done for Nouryon and will focus on the oxidization step of the hydrogen peroxide production process. With the current technical development, electrolyzers producing green hydrogen are expected to be improved and used to a greater extent. This enables the use of green hydrogen in the hydrogenation step and the possibility to utilize the by-produced oxygen as a cheap raw material in the oxidation step. The possibility to utilize pure oxygen in the oxidation tower would make it possible to use a higher concentrated gas than air, or even pure oxygen, as oxidizer. If higher concentrated oxygen may be used, the tower and ancillary equipment (compressor and off-gas treatment system) should be able to be smaller which would lead to lower investment- and possibly lower operating costs.

1.1 Aim

The aim of the work is to use simulation software to investigate if it may be possible to design the oxidation tower in a hydrogen peroxide plant in a more efficient way. The design parameters will be the oxygen concentration, operating pressure and flow design. The work is expected to result in a relative measure of size of the expected oxidation tower depending on different operating conditions.

1.2 Limitations

The work will only focus on the oxidation tower itself and it is the only equipment that will be designed and simulated. There will not be any consideration of the up- or downstream process design or to the possible oxygen sources. It will be assumed that oxygen-nitrogen mixtures are available at any concentration.

1.3 Specification of issues under investigation

The work should answer the following questions:

- What relevant parameters (e.g. expression for rate of reaction and solubility of oxygen in the working solution) gives a realistic simulation setup of the oxidation tower in the simulation software?
- Is it possible to design a safe-to-operate oxidation tower using a more concentrated oxygen source than air?

2 Theory

The theory chapter presents the results of the literature search. Here, basic information about what hydrogen peroxide is and what it is used for can be found as well as methods of producing it. There is also a section reviewing research found on the kinetics regarding the oxidation step in the anthraquinone (AO) process. The last section displays some theory related to the used simulation software, Aspen HYSYS.

2.1 Hydrogen peroxide and its usage

Hydrogen peroxide is a molecule consisting of two hydrogen and two oxygen atoms with the chemical formula H_2O_2 . At room temperature it is a clear and colourless liquid which is miscible in water at any concentration [3][4]. It is weakly acidic and a non-combustible compound, however it may decompose when in contact with various impurities, such as metals, organic material or other oxidizers or reducing agents [5]. Also light, heat or high pH may initialize and accelerate the decomposition. The decomposition result in water, oxygen and heat. The heat of decomposition for pure hydrogen peroxide can, together with the produced oxygen, result in the start of fire.

The two main usage areas of hydrogen peroxide is as a bleaching agent and in the chemical manufacturing industry [6]. It is also used as a disinfectant and in wastewater treatment. The broad area of usage is mainly due to the hydrogen peroxide being a strong oxidizer which, furthermore, is considered environmental friendly due to its decomposition products being just water and oxygen. As a bleaching agent, it is used mainly in the pulp and paper industry but also for bleaching textiles, teeth whitening and in hair colours. In the 2021, it was reported that the annual world production of hydrogen peroxide was around 6,3 billion tonnes where Nouryon produced approximately 4% of this [7].

In the bleaching process of pulp and paper, hydrogen peroxide oxidizes light absorbing structures, e.g. conjugated bonds (chromophores), which gives the pulp its colour. These double bonds are oxidized in alkali solutions generating the hydrogen peroxide anion (hydroperoxyl anion, HOO^-) [8]. The same principle is used in textile bleaching, where the colouring chemicals also are destroyed (namely the conjugated structures in those impurities) by the application of hydrogen peroxide under alkaline conditions [9].

As a disinfectant it is used in aseptic packaging materials and wound cleaning as well as in dishwash detergents and household cleaners [2]. In the chemical manufacturing industry it is amongst others, used to produce percarbonates, different organic peroxides and propylene oxide [5].

In wastewater treatment, hydrogen peroxide may be used stand alone or together with for example UV or ozone [10]. It reacts with different organic and inorganic pollutants producing less harmful chemicals. Combining its use with UV and/or ozone increases the oxidative power by generating the hydroxyl radicals ($\text{OH}^\cdot$) and makes it possible to oxidize more chemically stable pollutants.

2.2 Production processes

Hydrogen peroxide has, since its discovery in 1818, been industrially produced using three different processes; the wet chemical, the electrochemical and the organic autoxidation (AO) process [4][6]. In addition, there are multiple alternative processes known but not used industrially, for example direct synthesis from gaseous hydrogen and oxygen, production from carbon monoxide, oxygen and water and production by cathodic reduction of oxygen. Today, the organic AO process is dominating and almost all hydrogen peroxide is produced using this process. The most common AO process is the anthraquinone process, but also the 2-propanol process has been used to some extent.

2.2.1 Wet chemical process

Hydrogen peroxide was discovered by Thenard as a product when treating barium peroxide with nitric acid [4]. This process came to be the first commercial production process for hydrogen peroxide with the adaption to use hydrochloric acid instead of nitric acid. The process was introduced around 1880 and was in use until the mid 1900s. The hydrogen peroxide solution obtained from this process was low concentrated (around 3%) and rather unstable due to impurities. The profitability was an issue and depended a lot on the sales market for the barium sulfate produced simultaneously. By the year 1900, approximately 2 000 tonnes of hydrogen peroxide was produced using this process.

2.2.2 Electrochemical process

A great improvement for the hydrogen peroxide production process was made in 1853, when Meidinger discovered that hydrogen peroxide was formed in the electrolysis of aqueous sulfuric acid [4][10]. The first plant producing hydrogen peroxide with this process was introduced in 1908. In the following years, the process was developed and two alternate processes were proposed. The Pietzsch-Adolph process (developed in 1920) electrolyzed ammonium sulfate solutions to form potassium peroxodisulfate and the Münchner process (developed in 1924) used the electrolysis of ammonium sulfate to form ammonium peroxodisulfate instead. In both processes, the formed peroxodisulfate was hydrolysed to form hydrogen peroxide. The developed methods lead to a great increase in the worldwide hydrogen peroxide production capacity which by 1950 was approximately 30 000 tonnes per year.

2.2.3 2-Propanol process

One organic AO process is the oxidation of 2-propanol to hydrogen peroxide and acetone [4][6]. The reaction was discovered by Harris in 1945 but the industrial process was first proposed by Rust. The reaction is conducted in the liquid phase and it is self-catalyzed by the formed hydrogen peroxide. The product stream is separated by evaporation and distillation. Shell Oil Company operated a plant with this technology in Louisiana 1957-1980 and as of today, there are two plants operating in the former Soviet Union since 1968 and 1972. Today these plants produce approximately 8 000 tonnes per year [7].

2.2.4 Anthraquinone autoxidation (AO) process

The development of the anthraquinone AO process was a giant improvement for the hydrogen peroxide production industry. With this process, larger-scaled plants could be built and after its introduction in the 1950s the yearly worldwide production capacity of hydrogen peroxide quickly increased and is today 6,3 billion tonnes [6][7]. Today, the anthraquinone AO process is by far the most common way to produce hydrogen peroxide commercially.

The initial discovery, leading to the development of the AO process, was made in 1901 by Manchot [4][10]. He discovered that hydrogen peroxide could be produced by reacting hydroquinones or hydrazobenzenes with oxygen. However, it took until 1932 before the first AO process was proposed by Walton and Filson, this one hydrating and oxidizing hydrazobenzene in a cyclic manner. Shortly thereafter, Pfeiderer (BASF) developed a commercial plant using AO of hydrazobenzene under alkaline conditions. This process used sodium amalgam to reduce the azobenzene and gave sodium peroxide as a product. This process was only operated commercially by Kymmene AB at a plant in Finland.

Further development of the AO process was made by Pfeiderer and Riedel (BAFS) during 1935-1945 [4][10]. They discovered that using alkylated anthraquinones instead of azobenzene, eliminated the need of using sodium amalgam and the alkaline conditions (which were the two major drawbacks when using azobenzene). The new process was operated and developed in a pilot plant with a monthly output of 30 tonnes until the end of World War II when it was shut down. The Reidel-Pfeiderer AO process was commissioned for the first time in 1953 by Dupont and has come to be the basis for almost all present hydrogen peroxide production plants.

The Reidel-Pfeiderer process is a cyclic process where the quinones are hydrogenated and oxidized to produce hydrogen peroxide [4][10][6]. After the oxidizing step, the hydrogen peroxide is extracted to an aqueous phase and further purified. The working solution, that is the mixture of quinones and organic solvent, leaving the extraction step are purified and sent back to the hydrogenation step again. Figure 1 illustrates the general process outline. There have been multiple developments and alternative designs of the individual process steps over the years, consequently, the different plants worldwide are looking somewhat different. Following in this section, the different parts of the process will be presented in some detail.

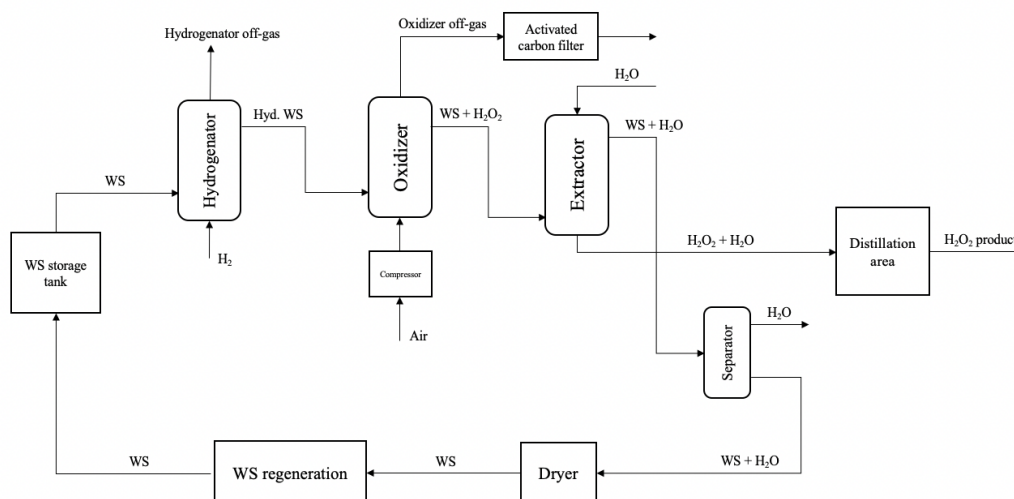


Figure 1: A general and basic scheme of a hydrogen peroxide plant. WS is referring to working solution.

Quinone and solvent

Different anthraquinones and solvents can be used. The quinones are solids at room temperature and must be dissolved in a solvent, this solution is often referred to as the working solution [4]. Typical differences of the anthraquinones are how they are substituted and different quinones need different solvents. The quinone and hydrated quinone (hydroquinone) have different solubility properties, hence it is common to use a mixture of different solvents. The quinone dissolve well in a nonpolar and aromatic solvent, whereas the hydroquinones dissolve in polar solvents, usually alcohols and esters. When choosing anthraquinone, it is important to consider which degradation reactions that are possible for the chosen quinone and how easy it is to convert it back to active quinone again. The quinone must also have good resistance to consecutive oxidation. Regarding the choice of solvent, except having a good solubility of the quinone, the solvent must have good stability in the process steps (i.e. in the hydrogenator and oxidizer), low solubility in water, properties to ensure good separation in the extractor (i.e. lower density than water) plus low volatility and toxicity.

The most commonly used anthraquinone is the 2-ethylanthraquinone, illustrated in Figure 2a [4]. The hydrogenation and oxidation reactions this quinone undergoes in the hydrogen peroxide process are illustrated in Figure 2b.

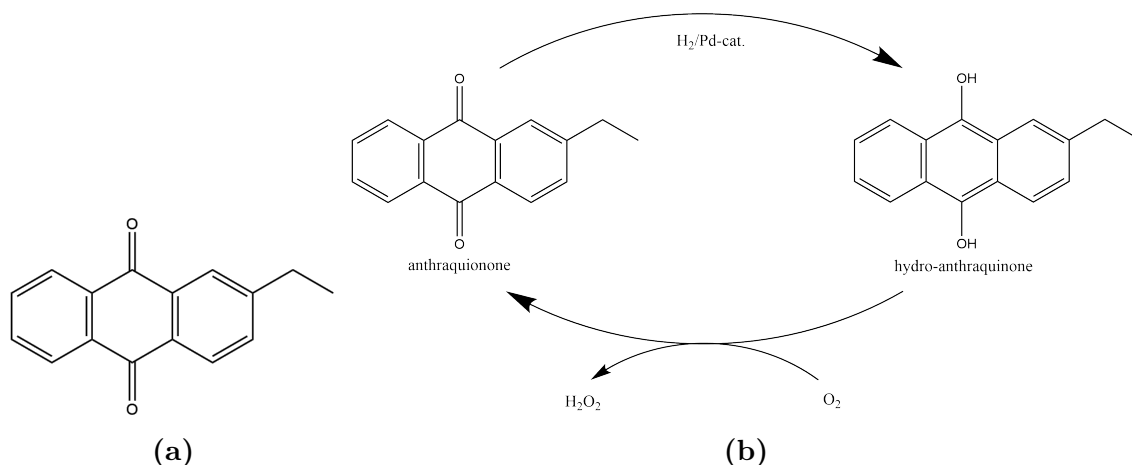


Figure 2: (a) Illustration of the most commonly used quinone, the 2-ethylanthraquinone and (b) the cyclic hydrogenation and oxidation reaction scheme of it.

An important side reaction for the 2-ethylanthraquinone is the hydrogenation of the ring that does not hold the ethyl group [4]. This happens spontaneously in the hydrogenation step as described in Figure 3. The resulting molecule is 2-alkyltetrahydroanthraquinone (usually referred to as tetra).

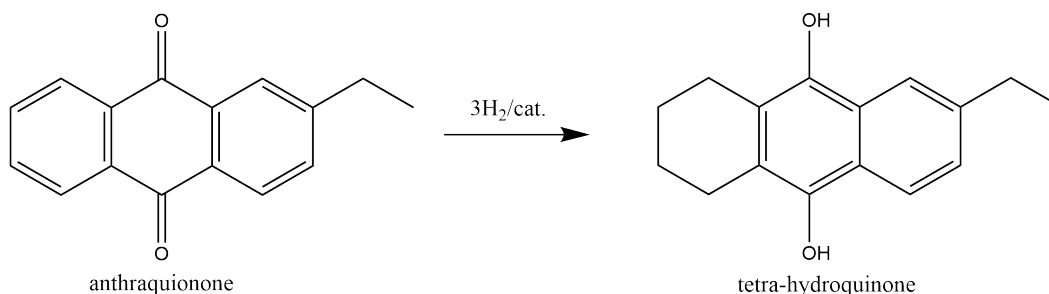


Figure 3: The spontaneous side reaction of 2-ethylanthraquinone resulting in the formation of 2-alkyltetrahydroanthraquinone.

The tetra molecule is also oxidized in the oxidizer but with more difficulty than the anthrahydroquinone [4]. The hydrogenation of tetra is however more easily done compared to the anthraquinone. The chemical hydrogenation and oxidation process of tetra are shown in Figure 4.

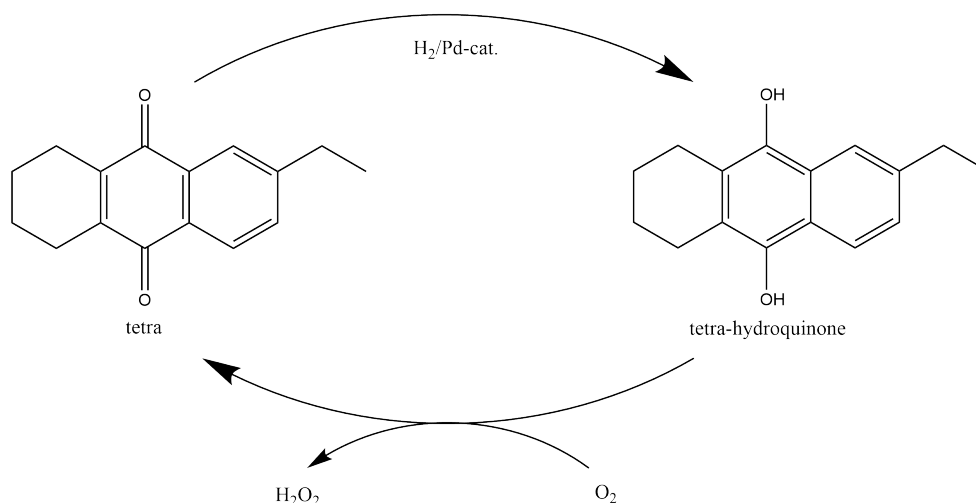


Figure 4: The oxidation and hydrogenation of tetra.

Tetra formation may be suppressed using, for example, special solvents, mild hydrogenation conditions and selective catalyst [4]. It is also possible to dehydrogenate the tetra in presence of aluminium oxide to regenerate the anthraquinone. A design parameter for the AO process is to operate it with suppression of tetra formation (anthra system) or not (all-tetra system). In the latter case, an equilibrium between the anthra- and tetraquinone will eventually be obtained resulting in a quinone-mixture of around 30% anthraquinone and 70% tetraquinone [11]. Nevertheless, there are multiple other side-reactions, in addition to the tetra formation, both in the hydrogenator and the oxidizer which affects and may deactivate the quinone [4]. Some of these may be reversed and accounted for in regeneration steps.

Hydrogenation

The hydrogenation is done with a palladium catalyst [4]. Earlier, a Raney nickel catalyst (BASF hydrogenation) was sometimes used but due to the need of alkaline operation conditions, its toxicity and pyrophoric properties it is no longer in use industrially.

A palladium catalyst overcomes the drawbacks of Raney nickel [4][10]. It is used in different forms, e.g. Degussa used palladium black enabling easy exchange and regeneration of catalyst when needed. Another example is Laprote chemicals who made a breakthrough employing supported palladium particles as catalyst. However, both Degussa and Laporte methods need a filter after the hydrogenator to prevent catalyst from entering the oxidizer or it becomes a risk for decomposition of hydrogen peroxide. To eliminate the need of a filtration step, FMC developed a fixed-bed hydrogenation step. Nouryon uses their own patented fixed-bed palladium-catalyst which also makes it possible to operate without a filtration step [2].

Oxidation

After the hydrogenator and possible filters, the working solution is sent to an oxidizer. The oxidizer is usually designed as a bubble column, where the hydroquinones are oxidized with the use of air, usually flowing co-currently to the working solution [6]. The air is usually slightly pressurized and the operating temperature is at

30-60°C. As for the hydrogenator, also the oxidizer has multiple designs proposed and used by various companies [4][10]. Common for all designs are, that after the oxidation, the off-gas and hydrogen peroxide rich working solution are separated whereupon the off-gas is sent to purification in activated carbon adsorbers and the working solution to an extraction step.

Degussa proposes a multi-staged oxidation process in which the air and working solution overall flows counter-currently but with segments of co-current flow [4]. Solvay, on the other hand, operates a plant (originally by Laporte) with a single, packed, column for oxidation [4][10]. The air and working solution flows co-currently up through the tower. There are also examples of completely counter-current oxidation steps, for example by Allied Chemical and Laporte [4]. This to shorten the working solution residence time in the oxidizer. Allied Chemical also propose using perforated trays with small holes to improve the space-time yield. The design of Nouryon's oxidation tower is similar to Allied Chemicals design, including perforated trays with small holes and in a co-current set up.

When designing the oxidation tower, there are some economical aspects to take into account [4]. First off, it is desired to have an efficient utilization of air, consuming as much as possible of the oxygen to reduce the off-gas volumetric flow. This to minimize the size of the needed compressor and gas purification system. Secondly, a near atmospheric pressure of the air is favourable to reduce the compressor energy consumption. Lastly, the oxidizer size should be minimized to reduce the investment cost.

Furthermore, there are some safety issues that have to be taken into account when designing the oxidation tower. For example, the tower temperature must not exceed the flash point of the solvents in the vapour mixture to avoid explosions [4]. The flash temperature of the solvents are typically 62°C [12]. In addition to this, the concentration of oxygen in the off-gas must not exceed 10% (preferably being around 6%) to avoid risk of fire in the downstream carbon filter. It is also important to control the amount of impurities in the feed stream since the presence of hydrogenator catalyst may cause explosions as a result of hydrogen peroxide decomposition [4].

Extraction

After the oxidizer, the produced hydrogen peroxide is extracted using water [4]. The extraction process is a very important economical factor, since unextracted hydrogen peroxide will be reduced to water in the hydrogenator consuming hydrogen. Therefore, multiple extractor designs have been proposed and used. For example, the first BASF plant used a sieve-tray extraction column whereas others have proposed using packed columns and pulsed packed columns. The efficiency of the extraction does not only depend on the extraction column design, but also on the composition of the working solution. The extraction efficiency is important since it determines the crude concentration of hydrogen peroxide from the plant.

Working solution purification and regeneration

After the extraction step, the working solution must be purified and possibly regenerated before being recycled to the hydrogenator [4]. The first purification step is to remove excess water and adjusting the dissolved water content in the working solu-

tion. This is done by separation and drying. Then, the working solution must also be purified from degraded anthraquinones and solvents. This is done by different treatments, e.g. by contacting the working solution with alumina, and sometimes a portion of the working solution is exchanged to new solution.

Crude hydrogen peroxide treatment

The crude hydrogen peroxide from the extractor must be purified from dissolved organics and droplets of working solution [4]. The former is usually removed by oxidation of the organics using heat, followed by extraction with a proper solvent. After the purification steps, the hydrogen peroxide concentration is adjusted by distillation.

2.3 Kinetics of the anthraquinone oxidation

The oxidation tower is a two-phase reactor where the chemical reaction takes place in the liquid phase. The oxygen is supplied in the gaseous phase and has to be dissolved/absorbed into the liquid phase for the reaction to occur. Thus, in the oxidation tower, simultaneous absorption and reaction takes place. There have been found a few publications on the oxidation of hydrated working solutions. One early and well cited work is the one made by Santacesaria et al. [13]. They conducted multiple experiments of a working solution with a mixture of 30% anthraquinone and 70% tetra to investigate the solubility of oxygen in the working solution and the kinetics of the oxidation reaction. From this study it was concluded that the oxidation reaction is of second order with respect to the tetra and oxygen liquid bulk concentration. Hence, the reaction rate, r , may be modelled as in Equation 1 where k_{ox} is a kinetic constant, $[\text{THEAQH}_2]$ is the tetra concentration and $[\text{O}_2]$ is the oxygen concentration.

$$r = k_{ox}[\text{THEAQH}_2][\text{O}_2] \quad (1)$$

The same study concluded that the oxidation reaction is moderately slow and mainly occurs in the liquid bulk [13]. This by calculating the Hatta number (i.e. the rate of reaction compared to the rate of mass transfer of oxygen into the liquid) to be in the range 0,2-0,4 which corresponds to an enhancement factor of around 1 (i.e. the rate of gas absorption in comparison to the maximum absorption rate without reaction). This result indicates that the mass transfer rate of oxygen into the liquid bulk can be important and may affect the overall rate of oxidation. Using the two-film theory and assuming that the mass transport resistance of oxygen in the gas film is negligible, it is the mass transport through the liquid film that is affecting the oxidation rate. The mass transfer rate in the liquid film can be derived from Fick's law, Equation (2) presents the mass transfer rate of specie A in the liquid film (J_L), where k_L is the mass transfer coefficient for the liquid film, a_i is the interfacial area, p_{ai} is the partial pressure of A at the gas-liquid interface, H is the Henry's constant and C_A is the concentration of A in the bulk liquid [14]. In the equation, Henry's law ($p_{Ai} = HC_{Ai}$) has been used to eliminate the need of the interface liquid concentration of specie A , C_{Ai} .

$$J_L = k_L a_i \left(\frac{p_{ai}}{H} - C_A \right) \quad (2)$$

The study made by Santacesaria et al. resulted in the liquid film mass transfer coefficient and Henry's constant at 20°C and 50°C presented in Table 3 [13]. They also reported a value of the kinetic constant, however only at 50°C. The kinetic constant value are presented together with the mass transfer coefficient and Henry's constant i Table 3, all data in the table are averaged results from multiple experiments. However, the mass transport of oxygen, and thus the oxygen concentration in the liquid, is handled by the modeling program HYSYS. Therefore, the mass transportation of oxygen will not be discussed further in this work.

Table 3: Experimental values of H , k_L and k_{ox} for the AO process [13].

Parameter	20°C	50°C
H [atm cm ³ /mol]	112 100	109 000
k_L [cm/s]	$5,5 \cdot 10^{-3}$	$6,6 \cdot 10^{-3}$
k_{ox} [cm ³ /(mol s)]	-	3830 ± 300

Santacesaria et al. published a paper some years later, providing an expression for the rate constant on the Arrhenius equation form, giving its temperature dependence [11]. The expression is derived from the runs made in the first work and is presented in Equation (3), where R is the gas constant (J/mol K) and T is temperature (K). The activation energy has the unit J/mol.

$$k_{ox} = (1,14 \pm 0,08) \cdot 10^{10} \exp\left(\frac{-(59695 \pm 4351)}{R T}\right) \left[\frac{dm^3}{mol s}\right] \quad (3)$$

Another kinetic study, in which a microstructured system was used, has been reported by Tan et al. [15]. Due to the small size of the dispersed gas bubbles in the system, they assumed that it is the intrinsic reaction rate that is rate-controlling, neglecting possible mass transfer limitations. They assume, based on the results from Santacesaria et al., that the reaction is of second order as in Equations (1) and use their experimental results to derive the kinetic constant presented in Equation (4). This kinetic constant is calculated from experiments using pure oxygen as oxidant.

$$k_{ox} = 2,8773 \cdot 10^{10} \exp\left(\frac{-56760}{R T}\right) \left[\frac{dm^3}{mol s}\right] \quad (4)$$

Additionally, there have been studies that provides the activation energy for the oxidation of the tetra molecule. One investigation using DFT calculations, report the rate-determining step's activation energy as 13,5 kcal/mol (56,5 kJ/mol) [16]. Another source refers to an experimentally received value of 62,7 kJ/mol [6].

2.4 Aspen HYSYS

Aspen HYSYS is a process simulation software provided by AspenTech. It may be used to simulate a wide range of chemical process operations. The version available from Chalmers was HYSYS v12.1 and this one was used for all the simulations.

All HYSYS-simulations builds upon the selection of the components physical and chemical data and on the so called property package. A property package represents

a certain property calculation method, which is a method for calculating the properties of the components at a certain temperature, pressure and flow composition [17]. The property package selection is based on which components that are to be used in the simulations. This since different packages are developed for different types of systems and applications. There are mainly two different types of property packages, Equations of state (EOS) models and activity models. EOS property packages are developed for systems containing non-polar or only slightly polar components, e.g. these are applicable to most hydrocarbon systems. Activity models on the other hand are developed to be able to handle highly non-ideal systems, e.g. systems containing polar components. Most of the property packages uses binary coefficients to anticipate the interactions between components. HYSYS provides a large database with these parameters for the different models. Some models allow for estimation of the coefficients if no data are available in the databank.

Examples of property packages that may be applicable to the simulation of the hydrogen peroxide oxidation column are UNIQUAC, Wilson, NRTL, Chien-Null, PRSV and CPA. PRSV and CPA are EOS models whereas the others are activity models. PRSV is able to handle moderately non-ideal systems with water-alcohol and hydrocarbon-alcohol systems as examples [17]. CPA can also handle polar chemicals, e.g. alcohols and esters. The activity models are all suited for highly non-ideal chemical systems. NRTL is an extension of the Wilson model that, for example, does not have the limitation of only one liquid phase as Wilson. Chien-Null is a model that has the possibility to use multiple methods for calculation of the binary coefficients depending on the individual chemicals. The basic setting is that it uses the NRTL model for vapor-liquid and liquid-liquid binaries but Henry constants for vapor-vapor binaries. UNIQUAC is a more detailed and sophisticated model compared to the other activity models. It is good at representing both vapour-liquid equilibrium and liquid-liquid equilibrium and can be used for a wide range of mixtures containing for example, water, alcohols, amines, esters and ketones.

To calculate chemical equilibrium, i.e. the mass transport of chemicals in a multiphase and multicomponent system, activity coefficient models uses activity coefficients to account for deviations from Raoult's law [?]. The activity coefficients for a mixture are related to the excess Gibbs energy and e.g. UNIQUAC uses two adjustable parameters per binary pair of components to calculate this energy. The adjustable parameters can be obtained from experimental data from binary systems or from estimations using e.g. UNIFAC.

3 Methodology

The project can be divided in to three main parts. The first part is a literature search, providing the theory section and a patent search. The second part is the building of the simulation tool including choice of which components that should be included and which property package that should be used. It also includes the design of the simulation of the oxidation tower, modifications of the kinetic expression and finally validation of the model versus known data. The third part is using the simulation tool to investigate different operating and tower designs. In this section, the methodology for these three parts are described.

3.1 Literature search

The literature search was done using databases accessed through the Chalmers Library website. The databases mainly used were SciFinder, Science Direct and Knovel. Also the website of Nouryon was used to some extent. To broaden the search, citations of, as well as references in, interesting publications were searched. The search for patents was only done with the use of SciFinder. All literature sources were critically reviewed regarding their relevance for the studied topic.

Examples of words/expressions used in the literature search are *hydrogen peroxide*, *hydrogen peroxide production process*, *autoxidation process*, *AO process*, *anthraquinone*. SciFinder provides a tool where you can explore publications related to different substances, this was used for the anthraquinone (2-ethylanthraquinone) and hydroanthraquinone. This feature was also used when searching for patents, then choosing hydrogen peroxide as substance and adding search strings composed of words such as *anthraqui**, *anthrahydroqui**, *quino**, **quinone*, *oxygen*, *oxidat**, *oxida**, *oxidi**, *concentrat** and *partial pressure*. The star (*) is used to specify that there can be different ends or beginnings to the word. There were also patent searches made with 2-ethylanthraquinone as substance instead of hydrogen peroxide, then *hydrogen peroxide* was added as a search word.

3.2 Design of the simulation tool

This part of the project was where the oxidation tower was modelled and built in the simulation software. All the simulations were done using the process simulation software Aspen HYSYS v12.1. General assumptions made and how the oxidation tower was set up in HYSYS are accounted for here, as well as the procedure for validation of chemical properties and property package selection.

3.2.1 Assumptions and model

In HYSYS, the oxidation tower was modelled as multiple separator units in series, where one separator should represent one stage/tray in the tower. The separator unit performs flash-calculations for two- or three-phase systems and may account for chemical reactions simultaneously. There is also a possibility to account for pressure drops and heating/cooling within the unit. One important assumption

that was made due to this selection, is that the tower stages can be regarded as ideal. The reason for using the multiple separator units in series was that HYSYS did not seem to be able to mimic the oxidation tower design as built in the real process with any of the other unit operations available.

3.2.2 Component list set up and property validation

Some simplifications were made regarding the choice of components since HYSYS did not include all ordinary molecules included in the hydrogen peroxide plant. The anthraquinone (further referred to as AQ) used instead of the 2-ethylantraquinone was the non-substituted quinone illustrated in Figure 5. This simplification was done since this was the only anthraquinone for which chemical and physical data was available for in the HYSYS databank. There were also simplifications made concerning the composition of the working solution, where only one component was chosen to act as solvent, namely 1,2,3,4-tetramethylbenzene (further referred to as the solvent). In most of the simulations also a realistic amount of water and unhydrogenated quinone was included in the working solution. These simplifications were justified due to the fact that the simulations were intended to work as a relative measure of different operations and not to generate an exact outcome.

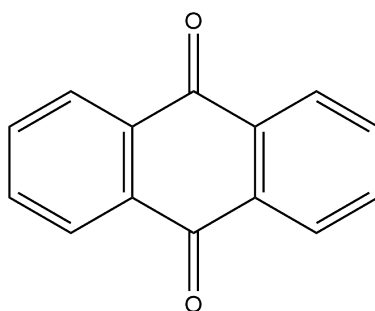


Figure 5: The molecular structure of the anthraquinone that was used in the simulations.

All chosen components but the hydroanthraquinone (further referred to as HAQ) are available in the HYSYS component databank. Their physical and chemical properties were validated by comparing some of the listed properties with the NIST databank properties. The NIST databank contains both experimental and predicted properties of a large number of chemicals and was for the project accessed through the Aspen Plus software. The properties that were used in the validation were the, by HYSYS called, base and critical properties which are normal boiling point, ideal liquid density, critical temperature, critical pressure, critical volume and acentricity. It was assumed that the other chemical and physical properties are reasonable if these base and critical properties can be validated.

HAQ was user-defined as a hypothetical component, defining its molecular structure using the UNIFAC structure. The structure was defined as $(ACH)_8(AC)_4(ACOH)_2$ where AC stands for aromatic carbon and the number indicates the number of a certain group included. As for the chemical and physical properties of HAQ, there

seems to be little known and for this work no experimental data was found. It was therefore assumed that AQ and HAQ have similar properties, due to the small differences in molecular structure. The properties of HAQ were initially estimated by HYSYS and thereafter tuned in relation to those of AQ. To get the expected relative properties between HAQ and AQ, the estimation tool in NIST was used to estimate the properties of both AQ and HAQ as user-defined components. The assumption that AQ and HAQ have similar properties may not be fully true since it is known that there are differences in solubility of them. However, for the simulation of the oxidation tower this is assumed to be negligible.

3.2.3 Property package selection

The property package selection was based on a guide [18] and information provided in the HYSYS Help [17]. The property packages that were relevant for the simulation case were chosen and further investigated. The investigation was done in four steps; comparison of important properties, testing on a single oxidation tower, testing on the calibration tower and validating on reference oxidation towers. The comparison of important properties was done by comparing important properties like vapor pressure, density and heat capacity. Vapor pressure is important for the vapor-liquid equilibrium, density for flow calculations and heat capacity is important for the heat transport. Hence, the property package validation was limited to these three properties. The experimental data was collected from NIST. Note that HAQ was not included in the study or property package selection due to the lack of experimental data.

The property packages' performance was thereafter compared by simulating one stage (the first one) of an oxidation tower as well as a whole tower. For this the calibration tower was used. The simulations with only one stage were run both with and without water included in the working solution. This to investigate how much the results were affected by its presence to know if it was important to include it in the simulations or not. Finally the chosen packages were validated using the reference towers.

3.2.4 Calibration tower set up

The calibration tower is a tower for which more performance data is available. The operating conditions, such as feed flow rates, compositions, temperatures and pressure, are presented in Table 4. The tower was simplified by assuming isobaric operation and that only the hydrated quinone (i.e. only HAQ and no AQ) was present in the working solution feed. The gas feed was assumed to consist only of oxygen and nitrogen and the specified inlet temperatures were assumed to be for the operating pressure. Simulations of the first stage of the tower were set up both with and without water included in the working solution feed. Based on the knowledge gained from the first stage simulations, the whole tower was set up only with water included.

Table 4: Operating conditions for the calibration tower.

Parameter	Value
$Q_{\text{feed, WS}}$ [m^3/h]	■
$C_{\text{HAQ, WS feed}}$ [g/dm^3 WS]	■
$C_{\text{H}_2\text{O, WS feed}}$ [g/dm^3 WS]	■
$Q_{\text{feed, gas}}$ [Nm^3/h]	■
$C_{\text{O}_2, \text{gas}}$ [%]	■
$T_{\text{in, WS}}$ [$^{\circ}\text{C}$]	■
$T_{\text{in, gas}}$ [$^{\circ}\text{C}$]	■
P [kPa]	■

The dimensions of the tower are shown in Table 5. The tower has six stages with varying height but with constant diameter of ■ m. The temperature and degree of hydrogenation (H°) expected for each stage in the calibration tower is also listed in Table 5. The degree of hydrogenation is used as a reference when fitting the kinetic data. Other expected operating parameters for the whole tower are the concentration of hydrogen peroxide in the off-gas that should be ■ g/dm^3 and the volume ratio in a condensate of the off-gas that should be ■ for water:solvent [12]. It is also expected to have a temperature increase of ■ $^{\circ}\text{C}$ per degree of hydrogenation.

Table 5: The calibration tower' dimensions and expected performance.

Stage	Height [m]	T [$^{\circ}\text{C}$]	H° [kg HP/ m^3 WS]
1	■	■	■
2	■	■	■
3	■	■	■
4	■	■	■
5	■	■	■
6	■	■	■

In HYSYS, the tower was built as six ideal two-phase separator units in series, one unit representing one stage. The temperature was adopted by adding cooling in each step and the oxidation reaction was accounted for in all the stages. The separators were designed as vertical cylinders filled fully by liquid. The inlet nozzles were placed in the middle (height-wise) for both the gas and liquid feed with the, by HYSYS, default settings for nozzle size. Since the separator unit can be regarded as a continuous stirred tank reactor, the position of the inlets are unimportant. Pure gas was set to leave at the top and pure liquid at the bottom. The reaction was defined as a kinetic reaction and specified to only occur in the liquid phase. There were no possibilities to define the mass transport of oxygen into the liquid in HYSYS, instead HYSYS assumed that vapor-liquid equilibrium was reached in each separator unit. Figure 6 illustrates the whole tower setup built in HYSYS. Appendix A provides more details about the HYSYS setup.

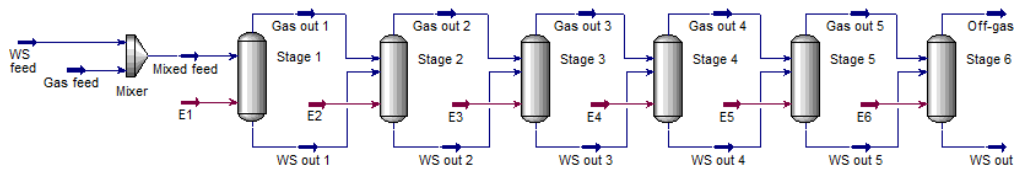


Figure 6: The calibration tower setup in HYSYS.

3.2.5 Kinetic fitting

The calibration tower was used to fit the kinetic expression and heat of reaction. The two kinetic expressions found in the literature (Equation (3) and (4)) were applied and the generated output was compared to the expected performance of the tower (in terms of degree of hydrogenation found in Table 5). The most suited kinetic expression was then modified by changing the magnitude of the pre-exponential factor and the activation energy and manual iteration was used to reach an acceptable results in comparison to the expected performance.

The heat of reaction was fitted to generate a temperature increase of $\blacksquare$ °C/H°. This was done by modifying the heat of formation of HAQ. The theoretical heat of formation that should result in $\blacksquare$ °C/H° was calculated and used as a starting point. This calculation may be found in Appendix B. When the heat of formation and kinetics were fit to produce the expected performance of the calibration tower, the model was applied to a number of reference towers. This to enable even further validation of the model.

3.2.6 Reference towers set-up

There are six reference towers with different operating parameters and dimensions that were used for validation and simulation of the model. The operating parameters, both inputs and expected results, for them are presented in Table 6. The degree of hydrogenation is here for the whole tower and as for the calibration tower the inlet temperatures were assumed to be for the compressed liquid and gas. All reference towers except Tower 6 are operated with air as oxygen source (i.e. the gas feed composition is assumed to be 21% O₂ and 79% N₂). Tower 6 is operated with an inlet oxygen concentration of $\blacksquare$ %.

Table 6: Operating parameters for the reference towers.

Parameter	Tower 1	Tower 2	Tower 3	Tower 4	Tower 5	Tower 6
$Q_{\text{feed, WS}}$ [m^3/h]						
$C_{\text{quinone, WS feed}}$ [g/dm^3]						
$C_{\text{H}_2\text{O, WS feed}}$ [g/dm^3 WS]						
$Q_{\text{feed, gas}}$ [Nm^3/h]						
$T_{\text{in, WS}}$ [$^{\circ}\text{C}$]						
$T_{\text{in, gas}}$ [$^{\circ}\text{C}$]						
$T_{\text{out, stage 1}}$ [$^{\circ}\text{C}$]						
$T_{\text{out, top}}$ [$^{\circ}\text{C}$]						
P_{in} [barg]						
ΔP_{tower} [barg]						
H° [g HP/ dm^3 WS]						
$C_{\text{O}_2, \text{out gas}}$ [%]						

The dimensions of the reference towers, both diameter and stage heights, are presented in Table 7. The reference towers were set up in the same manner as the calibration tower (see Appendix A), with the differences that cooling was only used in the first stage and that a pressure drop was included. The total pressure drop listed in Table 6 was distributed between the separators so that the pressure drop per height meter was kept constant throughout the tower. The amount of HAQ was calculated from the degree of hydrogenation assuming that full conversion of HAQ should generate the expected degree of hydrogenation. Then AQ was added so that the total quinone concentration listed in Table 6 was satisfied.

Table 7: The reference towers' diameters and stage heights.

Parameter	Tower 1	Tower 2	Tower 3	Tower 4	Tower 5	Tower 6
d [m]						
h_1 [m]						
h_2 [m]						
h_3 [m]						
h_4 [m]						
h_5 [m]						
h_6 [m]						
h_7 [m]						
h_8 [m]						
h_9 [m]						

3.3 Optimization

The optimization part was where different design and operating alternatives for the oxidation tower were simulated and investigated. In this section, the methodology and assumptions for the different design and operation alternations are accounted for. All optimization simulations used the reference Tower 2 as base design.

3.3.1 Higher oxygen concentration in feed gas

The first design alternation investigated was how different oxygen concentrations in the feed gas affected the operation of the tower. The concentration was varied from 25% to 100% with steps of 5%. The simulations were designed so that the amount of oxygen in the gas feed was kept the same as when the tower was operated with air, thus the oxygen concentration was adjusted by lowering the amount of nitrogen in the feed. The working solution feed flow, the inlet and stage one temperature as well as the operating pressure were also kept the same as when the tower was operated with air.

The tower diameter was scaled so that the fluid residence time was kept constant in the tower even when the flow of gas was changed. This was done iteratively, using the residence time in each step for when the tower was simulated with air and the new total volume flow (liquid plus gas) into each stage to calculate a new tower diameter. Also, the pressure drop over the tower was scaled using the density difference in the feed. Note that the pressure drop was scaled before the diameter was.

The outcome of the tower when operated with higher inlet oxygen concentration was compared to the outcome when reference Tower 2 was operated with air. If the conversion of HAQ was much higher over the tower, compared to when it was operated with air, the height of the tower was shortened by removing one  m high stage at the time. However, the outlet molar flow of HAQ was not allowed to get higher than for the tower operated with air. If so, the higher tower and higher conversion was maintained.

3.3.2 Lower oxygen excess in feed gas

The original reference Tower 2 was operated with a excess of oxygen, almost 25% more moles of oxygen than HAQ in the feed. It was therefore investigated how lowering this excess affected the results. In these simulations, the working solution feed mass flow was kept the same as for when the tower was operated with air. The oxygen concentration in the gas feed was kept at a set value (60% oxygen) and the oxygen excess was lowered by decreasing the total mass flow of gas sent into the tower. The pressure drop and tower diameter were scaled to the new flow composition throughout the tower in the same manner as it was done when changing the inlet oxygen concentration.

3.3.3 Higher operating pressure

Since about 90% of the volume flow through the tower is made up by the gas, it was of interest to investigate how a higher pressure would affect the performance of the tower. This since a higher pressure will compress the gas phase and increase the absorption of oxygen in the liquid phase. With a compressed gas phase the total volume flow through the tower will be lower resulting in that the size of the tower could be decreased.

Also for these simulations the reference Tower 2 was used as base and reference. The

pressure was increased by steps of 100 kPa, from the original pressure of 413,3 kPa to 713,3 kPa. These simulations were designed with the same working solution feed mass flow as for the base case and with a set value of gas feed oxygen concentration (35% oxygen). Also in these simulations were the diameter and pressure drop adapted to the new flow composition in the same way as it was done for different inlet oxygen concentrations.

It was also of interest to investigate how much the productivity of a certain tower could be increased if the pressure was increased, i.e. instead of assuming a smaller tower, a set tower size was used and the decreased volume flow was compensated for by increasing the total flow into the tower. For this reference Tower 2 was still used but with its original dimensions and air as oxygen source. The pressure was increased in two steps up to 613,3 kPa. The working solution and gas feed increase was made so that the relation between the amount of working solution and gas was kept constant, i.e. the oxygen inlet excess and compositions of the liquid and gaseous feed were held constant. Since the feed composition was maintained the same as for the original pressure, there was no need for changing the tower pressure drop.

3.3.4 Recirculation of exhaust gas

Another interesting design alternation was to design an oxidation tower with partly recirculation of the off-gas. This was most relevant for a higher inlet oxygen concentration and was believed to result in a more efficient utilization of the oxygen sent into the tower and a lower off-gas oxygen concentration. The reference Tower 2 operated with a inlet oxygen concentration of 80% was used as reference for these simulations.

To facilitate the simulation of a recirculating stream, the recycle tool available in HYSYS was used. The simulations was designed so that the majority of the off-gas was recirculated to the inlet of the tower. The recirculated stream was mixed with a fresh feed so that the original amount of oxygen was still sent into the tower, i.e. the same oxygen excess in relation to the HAQ feed was desired. As fresh feed was a gas with a 80% oxygen concentration used. The recirculated gas and fresh gas feed were mixed and then cooled and pressurized to the original inlet conditions before it was fed into the tower. The HYSYS setup can be seen i Figure 7. The working solution feed flow rate was kept the same as for the base case.

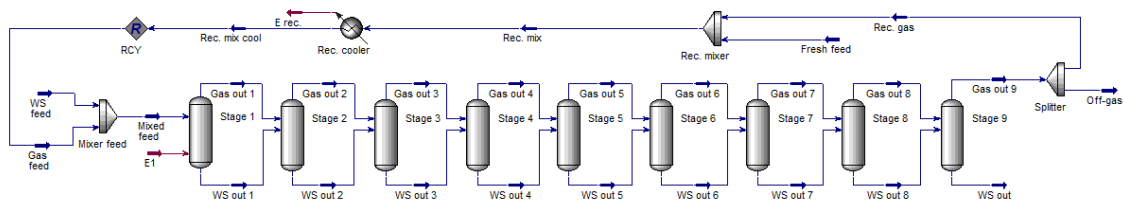


Figure 7: The HYSYS tower setup for a tower with recirculation.

The pressure drop and tower diameter were scaled in the same way as done in the

previous simulations. However, in these simulations more iterations both for the diameter and pressure drop were needed to get the system to steady state. This since a change in the tower initially (before steady state was obtained) affected the inlet conditions.

4 Results and discussion

The results gathered throughout the project are presented in this section. The presentation of the results are combined with the discussion of them.

4.1 Literature search

The literature search was done mainly using the databases SciFinder, Science Direct and Knovel. It resulted in a number of publications that gave the foundation of the information in this work. The most interesting articles are the ones included in the reference list. The outcome of the patent search is presented separately.

4.1.1 Patent search

The patent search was done using SciFinder and a number of different searches were made during the study. The searches made are presented in Table 8 in chronological order, where the first row represent the first search done and last row the last search done. The number of search strings were limited by the search engine to a maximum of 3. The "*" in the beginning or end of a search word implies that there can be different starts or ends of the word in the results, parentheses means that the words inside it should all be included in the results. The searches where the number of patents have been marked with ^α are patents that were gone through to check for relevance.

Table 8: Different searches made within the patent search.

Substance	Search within results	Substance role	Number of patents
Hydrogen peroxide	anthraqui*; oxidat*; oxygen and (concentrat* or (partial pressure))	None selected	64
Hydrogen peroxide	anthraqui*; oxidat*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	29 ^α
Hydrogen peroxide	(anthraqui* or anthrahydroqui*); oxidat*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	29
Hydrogen peroxide	(*anthraqui* or *anthrahydroqui*); oxidat*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	29
Hydrogen peroxide	(*anthraqui* or *anthrahydroqui*); oxida* or oxidi*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	29
Hydrogen peroxide	quino*; oxida* or oxidi*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	172
Hydrogen peroxide	*quinone; oxida* or oxidi*; oxygen and (concentrat* or (partial pressure))	11 selected ^β	0
Hydrogen peroxide	quinone; oxida* or oxidi*; oxygen and (concentrat* or (partial pressure))	None selected	38 ^α
Hydrogen peroxide	quinone; oxidation; oxygen and (concentrat* or (partial pressure))	None selected	27 ^α
Hydrogen peroxide	anthraqui*; oxidation; oxygen and (concentration or (partial pressure))	None selected	28 ^α
2-ethylanthraquinone	(hydrogen peroxide)	None selected	258
2-ethylanthraquinone	(hydrogen peroxide)	5 selected ^γ	157
2-ethylanthraquinone	(hydrogen peroxide); oxygen and (concentrat* or (partial pressure))	None selected	4 ^α
2-ethylanthraquinone	(hydrogen peroxide); oxidation	5 selected ^γ	74
2-ethylanthraquinone	(hydrogen peroxide); oxidation; oxygen	5 selected ^γ	29 ^α

^α These patents have been examined for relevance.

^β See Figure 8.

^γ See Figure 9.

The substance roles used in the different searches are presented in Figure 8 and Figure 9. Figure 8 shows the substance roles selected when 11 selections were made whereas Figure 9 shows the same but with 5 selections made. The substance refers to either hydrogen peroxide or 2-ethylanthraquinone.

The screenshot shows a 'Substance Role' dialog box with a close button (X) in the top right corner. It has two tabs: 'By Count' (selected) and 'Alphanumeric'. Below the tabs, it says '11 Selected'. There are three columns of checkboxes, each with a label and a count in parentheses. The checked items are: Preparation (14), Industrial Manufacture (11), Reactant or Reagent (11), Process (8), Reagent (6), Reactant (5), Synthetic Preparation (4), Catalyst Use (2), Formation, Non-preparative (2), and Formation, Unclassified (1). The unchecked items are: Uses (32), Biological Study (16), Other Use, Unclassified (14), Biological Study, Unclassified (6), Technical or Engineered Material Use (5), Therapeutic Use (5), Biological Use, Unclassified (3), Modifier or Additive Use (2), Agricultural Use (1), Cosmetic Use (1), Diagnostic Use (1), and Pharmacological Activity (1). At the bottom are 'Apply' and 'Cancel' buttons.

Substance Role	Count	Selected
Uses	32	☐
Biological Study	16	☐
Other Use, Unclassified	14	☐
Preparation	14	☒
Industrial Manufacture	11	☒
Reactant or Reagent	11	☒
Analyte	8	☐
Analytical Study	8	☐
Physical, Engineering, or Chemical Process	8	☒
Process	8	☒
Biological Study, Unclassified	6	☐
Reagent	6	☒
Reactant	5	☒
Technical or Engineered Material Use	5	☐
Therapeutic Use	5	☐
Synthetic Preparation	4	☒
Biological Use, Unclassified	3	☐
Catalyst Use	2	☒
Formation, Non-preparative	2	☒
Modifier or Additive Use	2	☐
Agricultural Use	1	☐
Cosmetic Use	1	☐
Diagnostic Use	1	☐
Formation, Unclassified	1	☒
Pharmacological Activity	1	☐

Figure 8: The substance roles available for filtration when searching for patents connected to hydrogen peroxide. The ones who are ticked were the 11 used for filtration in the search.

The screenshot shows a 'Substance Role' dialog box with a close button (X) in the top right corner. It has two tabs: 'By Count' (selected) and 'Alphanumeric'. Below the tabs, it says '5 Selected'. There are three columns of checkboxes, each with a label and a count in parentheses. The checked items are: Reactant or Reagent (64), Reactant (59), Process (19), Reagent (5), and Physical, Engineering, or Chemical Process (19). The unchecked items are: Uses (28), Preparation (23), Other Use, Unclassified (18), Properties (4), Synthetic Preparation (4), Industrial Manufacture (3), Catalyst Use (2), Formation, Non-preparative (2), Formation, Unclassified (2), Technical or Engineered Material Use (2), and Removal or Disposal (1). At the bottom are 'Apply' and 'Cancel' buttons.

Substance Role	Count	Selected
Reactant or Reagent	64	☒
Reactant	59	☒
Uses	28	☐
Preparation	23	☐
Physical, Engineering, or Chemical Process	19	☒
Process	19	☒
Other Use, Unclassified	18	☐
Reagent	5	☒
Properties	4	☐
Synthetic Preparation	4	☐
Industrial Manufacture	3	☐
Catalyst Use	2	☐
Formation, Non-preparative	2	☐
Formation, Unclassified	2	☐
Technical or Engineered Material Use	2	☐
Removal or Disposal	1	☐

Figure 9: The substance roles available for filtration when searching for patents connected to 2-ethylanthraquinone. The ones who are ticked were the 5 used for filtration in the search.

Generally, the results from the patent searches were not referring to specifically the oxidation step. Instead were they referring to the whole anthraquinone AO process with different working solution compositions, hydrogenation reactors and only some variations of the oxidation tower. However, one interesting patent regarding this project, was a patent for a countercurrent oxidation tower. The patented oxidation tower is operated with air, or other oxygen containing gas, entering in the bottom of the tower and with working solution entering in the top [19]. The patent contains specific operating conditions concerning flow rates and temperatures, as well as some design parameters for trays to be in the tower. The patented tower uses cooling and is specified to be used for the anthraquinone AO process. This patent was not limiting the work for the current project.

Other patents that would have been interesting for this project is those where another oxygen source than air is specified. More specifically those where a feed gas with higher concentration of oxygen than 21% is used. In this study, there were patents found where the oxygen source was not specified or specified as for example "oxygen-containing gas". However, these patents either also included some special kind of hydrogenation process, a special composition of the working solution or a completely different design of the oxidation process. One example of a patent such as this is the patent of a microchannel oxidation reaction where air or other oxygen-enriched gas are specified as oxygen source [20]. There is also another patent specifying a oxygen concentration of 10-100% for the oxidation gas [21]. However, this invention disperses the gas in the hydrogenated working solution before it is sent through a "delay pipe" after which the gas and liquid are separated again. Both these examples are not considered relevant or limiting for the current project.

A last example of a patent that was of some interesting for this project, is that for an oxidation reactor where the off-gas is recirculated [22]. The recirculated gas is mixed with an oxygen-enriched gas (having an oxygen concentration of 40-100%) however, only to obtain a recirculated mixed gas with not more than 21% oxygen content. Furthermore, this oxidizer is specified to be used to produce hydrogen peroxide by a so called hydrazine method which makes the patent non-limiting for this project.

4.2 Property validation

The simulation results depends on which input that is given to HYSYS and one important input is the physical and chemical data for the components included in the simulations. Table 9 lists some of the component properties obtained from the HYSYS databank together with experimental and predicted data collected from NIST. It can be noted to be some differences between the two sources, some components having greater differences than others. For example, the HYSYS databank and NIST were very consistent for H_2O , O_2 and N_2 whereas the property values for AQ, the solvent and H_2O_2 differs more between the sources. Note that, for the properties with less consistency, NIST gave predicted values and not experimental data. As for the ideal liquid density of AQ, the two values were also at different conditions. However, despite the differences, the HYSYS databank values were assumed to be good enough compared to the NIST experimental data and were therefore

used without adjustments in the simulations.

Table 9: Property validation for the library components.

Property	HYSYS databank	NIST
AQ		
Normal boiling point [°C]	379,9	375,2
Ideal liquid density [kg/m ³]	1272 ^a	1058 ^b
Critical temperature [°C]	626,9	593,9*
Critical pressure [kPa]	3150	3639*
Critical volume [m ³ /kmol]	0,58	0,59*
Acentricity	0,68	0,63
Solvent		
Normal boiling point [°C]	205,1	204,4
Ideal liquid density [kg/m ³]	908,5 ^a	904,1 ^c
Critical temperature [°C]	421,9	416,9*
Critical pressure [kPa]	2830	3101*
Critical volume [m ³ /kmol]	0,49	0,48*
Acentricity	0,37	0,43
H₂O₂		
Normal boiling point [°C]	150,2	153,1
Ideal liquid density [kg/m ³]	1454 ^a	1447 ^d
Critical temperature [°C]	457,0	454,9
Critical pressure [kPa]	21680	22037*
Critical volume [m ³ /kmol]	0,078	0,079*
Acentricity	0,36	0,45
H₂O		
Normal boiling point [°C]	100	100
Ideal liquid density [kg/m ³]	998 ^a	999,1 ^e
Critical temperature [°C]	374,1	374,0
Critical pressure [kPa]	22120	22072
Critical volume [m ³ /kmol]	0,0571	0,060
Acentricity	0,344	0,344
O₂		
Normal boiling point [°C]	-183	-183
Critical temperature [°C]	-118,4	-118,5
Critical pressure [kPa]	5080	5043
Critical volume [m ³ /kmol]	0,073	0,075*
Acentricity	0,019	0,021
N₂		
Normal boiling point [°C]	-195,8	-195,8
Critical temperature [°C]	-147,0	-147,0
Critical pressure [kPa]	3394	3398
Critical volume [m ³ /kmol]	0,090	0,090
Acentricity	0,040	0,037

* predicted value

^a 15°C, 1 atm

^b experimental at 302°C, saturated liquid

^c experimental at 15,5°C, saturated liquid

^d experimental at 15,3°C, saturated liquid

^e experimental at 15°C, saturated liquid

As for the properties of HAQ, HYSYS did not provide any databank values. HYSYS was therefore set to estimation its properties based on the UNIFAC structure. However, this estimation produced some unrealistic results, e.g. the ideal density was estimated to 927,1 kg/m³ but should be comparable to the density of AQ which was given by HYSYS databank as 1272 kg/m³. This large difference is not reasonable since the only difference between the AQ and HAQ molecules are two hydrogen atoms. Due to this a new approach was used, where both AQ and HAQ were defined by UNIFAC structures and NIST was used to estimate the molecules density. This estimation indicated that the liquid density of HAQ should be around 5,5 kg/m³ higher than that of AQ. Hence, the HAQ ideal liquid density was redefined as 1277,5 kg/m³ in HYSYS and a new estimation of the rest of the properties was made based on this density together with the UNIFAC structure. The new set of estimated properties were closer to the values of the AQ properties, hence those were used in the simulations. Both the first set of property estimations and the ones received with the adjusted density are presented in Table 10. In addition to the density, the HAQ heat of formation was changed to the same as of AQ. Otherwise, the oxidation reaction was simulated as endothermic when it should be exothermic. Nevertheless, the HAQ heat of formation was further adapted in the kinetic fitting.

Table 10: Estimated chemical and physical properties for the HAQ.

Property	Initial HYSYS estimation	Adjusted HYSYS estimation
Normal Boiling point [°C]	477,4	375,9
Ideal liquid density [kg/m ³]	927,1	1277,5
Critical temperature [°C]	745,7	656,1
Critical pressure [kPa]	4704	2829
Critical volume [m ³ /kmol]	0,49	0,57
Acentricity	1,00	0,43

4.3 Property package selection

The simulation result does not only depend on reliable physical-chemical data, but it does also depend on a good choice of calculation model, i.e. the property package. For this work, six different property packages were evaluated, both equation of state and activity models were included. If the decision tree in the property package selection guide [18] was followed, the recommendation was to use the activity coefficient model UNIQUAC. The decisions made leading to this were *polar substances - non-electrolyte - pressure below 10 bar - interaction parameters not available - no liquid-liquid equilibrium*. More exact, the guide recommends "UNIFAC and its extensions" but HYSYS does only provide UNIQUAC from this group of models. The other five packages were selected by their descriptions in the HYSYS help tool [17], i.e. PRSV, CPA, Wilson, NRTL and Chien-null.

To evaluate which one of these packages that were to be used in the simulation of the oxidation tower, they all were compared in terms of produced results regarding pure component properties, simulation of the first stage of the calibration tower and simulation of the whole calibration tower. Table 11 presents the results from the evaluation done with respect to chemical and physical component properties. All

data is for saturated liquids of pure components. The simulated property values were compared to experimental data collected from NIST. The experimental data was chosen to be as close to the expected operating conditions as possible, i.e. around 40-50°C. However, this was not possible for all components, especially for AQ, N₂ and O₂. This is not unexpected though, since AQ is a solid at room temperature and N₂ and O₂ are light gasses. The experimental data points that were available for H₂O were many and not always in total agreement, hence an interval of the property value is displayed in the table. Unfortunately, NIST only supplied experimental data for the heat capacity of the solvent and water and hence this property was not included for the other chemicals. Note that, ideally the evaluation should have been done using binary equilibrium data for pairs of the components, but no such experimental data was found.

Table 11: Component properties anticipated by six property packages and from experimental data collected from NIST.

T [°C]	Property	NIST	Chien Null	CPA	NRTL	PRSV	UNIQUAC	Wilson
AQ								
292,7	Density [kg/m ³]	1067	1073	845,2	1073	1073	1073	1073
302,6		1058	1063	838,9	1063	1063	1063	1063
375,9	Vapor pressure [kPa]	99,40	93,69	98,65	93,69	95,24	93,69	93,69
376,9		101,33	95,41	100,7	95,41	97,08	95,41	95,41
Solvent								
25,0	Density [kg/m ³]	902	901	683	901	901	901	901
40,0		888	890	677	890	890	890	890
75,2	Vapor pressure [kPa]	0,87	1,08	1,17	1,08	1,08	1,08	1,08
93,6		3,33	2,61	2,76	2,61	2,61	2,61	2,61
3,4	Heat capacity [J/mol K]	233,6	247,9	235,0	247,3	240,6	247,3	247,3
18,7		235,9	90,6	242,5	254,7	24,8	254,7	254,7
H ₂ O ₂								
3,0	Density [kg/m ³]	1460	1468	1287	1468	1468	1468	1468
19,9		1442	1449	1276	1449	1449	1449	1449
45,4	Vapor pressure [kPa]	1,04	1,01	0,69	1,01	1,00	1,01	1,01
60,0		2,43	2,35	1,69	2,35	2,32	2,35	2,35
H ₂ O								
50,0	Density [kg/m ³]	988,1 - 988,5	988,2	987,2	988,2	988,2	988,2	988,2
60,0		983,1 - 983,4	980,4	980	980,4	980,4	980,4	980,4
50,0	Vapor pressure [kPa]	12,20 - 12,40	12,35	12,25	12,35	12,55	12,35	12,35
60,0		19,88 - 20,00	19,94	19,74	19,94	20,22	19,94	19,94
50,0	Heat capacity [J/mol K]	75,32 - 75,33	76,05	68,59	76,05	72,8	76,05	76050
60,0		75,33 - 75,40	75,86	69,55	75,86	72,91	75,86	75860
O ₂								
-159,5	Vapor pressure [kPa]	691,5	689,7	698,2	689,7	696,7	689,7	689,7
-119,2		4927	4315	error	4849	4938	4849	4849
N ₂								
-157,0	Vapor pressure [kPa]	2074	2059	2044	2059	2072	2059	2059
-151,7		2710	2609	2661	2697	2712	2697	2697

Studying the results in Table 11, it can be seen that the results obtained with the CPA model stands out whereas the other packages produced very similar values. Due to the similar output from Chien Null, NRTL, PRSV, UNIQUAC and Wilson, all these models were used in the next validation step which was to simulate the first stage of the calibration tower.

The results from simulation of the calibration tower's first step are presented in Table 12. Both the results from when water was included in the working solution

feed and not are shown. Starting by comparing the differences when water was included and not, it can be seen that the conversion got slightly lower with water. It can also be noted that more hydrogen peroxide stays in the working solution with water, which is expected due to the hydrogen bonding, and that the outlet gas flow gets larger with water which also is expected. Even though the differences between the simulations with water and those without, it was decided that water should be included in the upcoming simulations to include the water-hydrogen peroxide interactions.

Next step was to compare how the different property packages performed based on the data in Table 12. It can be seen that PRSV was the one that stood out the most by producing much higher conversion than the others (60% instead of 40%). Another important distinction between the property packages is if they assumed two or three phases, i.e. if it assumed one or two liquid phases. Chien Null and NRTL assumed three phases, both with and without the presence of water, and PRSV assumed a second liquid phase when water was added. It is assumed unlikely to be two liquid phases when no water is present, however it may be considered when water is present. After all, water is used as extraction agent to separate the produced hydrogen peroxide from the working solution. Except these differences, the property packages produced pretty similar results.

Table 12: Calibration tower stage one simulation with different property packages.

Parameter	Chien Null		NRTL		PRSV		UNIQUAC		Wilson	
	no water	water	no water	water	no water	Water	no water	water	no water	water
Number of phases	3	3	3	3	2	3	2	2	2	2
Conversion [%]	41,78	41,62	40,04	39,88	61,15	60,70	40,96	40,81	40,96	40,81
T _{in, mix} [°C]	45,68	45,48	45,68	45,48	45,69	44,98	45,68	45,39	45,68	45,39
x _{O₂, liq out}	0,0005	0,0005	0,0005	0,0005	0,0011	0,0011	0,0005	0,0005	0,0005	0,0005
m _{HP, gas out} [kg/h]	16,72	9,65	16,40	9,43	29,57	10,66	4,28	3,43	4,28	3,43
m _{HP, liq out} [kg/h]	745,4	749,4	714,0	717,9	1085,7	1096,5	742,8	741,0	742,8	741,0
m _{HP, tot out} [kg/h]	762,1	759,1	730,4	727,3	1115,3	1107,2	747,0	744,4	747,0	744,4
n _{sol, gas out} [kmole/h]	0,168	0,168	0,169	0,169	0,164	0,170	0,166	0,163	0,168	0,170
Q _{out, gas} [m ³ /h]	1392	1403	1399	1410	1314	1337	1396	1408	1396	1408
Q _{out, liq} [m ³ /h]	206,5	206,4	206,5	206,4	206,1	206,7	206,2	206,0	206,2	206,0

It was decided to disregard the differences between the property packages and include all five in the next step of the validation process. The next test was to simulate the whole calibration tower and compare their performance with the expected values of the water to solvent volume ratio in the off-gas ($\frac{V_{H_2O, gas out}}{V_{sol, gas out}}$) and the concentration of hydrogen peroxide in the off-gas condensate ($C_{HP, gas cond out}$ [g/dm³]). The outcome for these parameters depending on the property package is presented in Table 13. It can be seen that UNIQUAC was the model that was closest to the expected values even though some differences were shown.

Table 13: Calibration tower simulation results.

Parameter	Chien Null	NRTL	PRSV	UNIQUAC	Wilson
$V_{H_2O, gas out}/V_{sol, gas out}$	6,1	6,1	13,2	0,7	4,6
$C_{HP, gas cond out}$ [g/dm ³]	512,4	512,4	270,4	153,8	351,4

Since UNIQUAC produced reasonable outcome in the one stage simulation and showed the results closest to the calibration tower in the whole tower simulation, this package was chosen as the best suited property package for simulation of the oxidation tower. One can possibly conclude that it is reasonable that it was an activity coefficient model that performed best in the simulations. After all, the system is most likely non-ideal due to the interactions between different sized polar and non-polar components.

4.4 Kinetic fitting

The next step in building the simulation tool was to find an expression for the kinetic constant that produce results that fit the expected outcome of the calibration and reference towers. This was done by evaluating the outcome when using different pre-exponential factors and activation energies defining the kinetics in HYSYS. The outcome of the modeling using different expressions for the kinetics was compared in terms of degree of hydrogenation, outlet temperature and outlet oxygen concentration with the expected outcome of the calibration tower. The starting point for this iterative calculations was two kinetic constants found in literature, i.e. Equation (3) by Santacesaria et al. and Equation (4) by Tan et al.

$$k_{ox} = (1,14 \pm 0,08) \cdot 10^{10} \exp\left(\frac{-(59695 \pm 4351)}{R T}\right) \left[\frac{dm^3}{mol s}\right] \quad (3)$$

$$k_{ox} = 2,8773 \cdot 10^{10} \exp\left(\frac{-56760}{R T}\right) \left[\frac{dm^3}{mol s}\right] \quad (4)$$

Figure 10 presents the outcome, in terms of degree of hydrogenation, for when these two equations were used for the kinetic constant in the simulation of the calibration tower together with the expected calibration tower outcome. It can be seen that the kinetic constant from Santacesaria et al. fits better with the expected outcome of the calibration tower compared to the constant from Tan et al. Hence, the constant from Santacesaria et al. is chosen as base to be manipulated for even better fit.

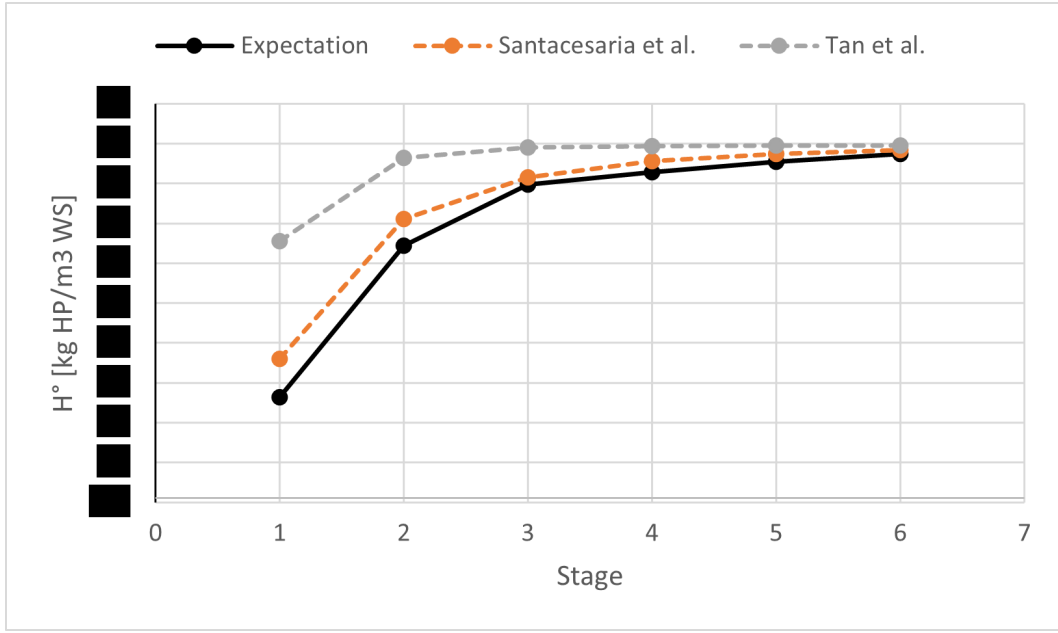


Figure 10: The degree of hydrogenation out of each stage of the calibration tower when two different kinetic constants are used. Santacesaria et al. are referring to Equation (3) and Tan et al. Equation (4). The expected values are from Table 5.

As can be seen in Equation (3), the kinetic constant from Santacesaria et al. is reported with an interval of the pre-exponential factor ($A = (1,14 \pm 0,08) \cdot 10^{10} \text{ dm}^3/\text{mol s}$) and of the activation energy ($E = 59695 \pm 4351 \text{ J/mol}$). In Figure 10, the middle value of both parameters were used (i.e. $A=1,14 \cdot 10^{10} \text{ dm}^3/\text{mol s}$, $E=59695 \text{ J/mol}$). If the highest and lowest value of respective constant are used together with the mid value of the the other, e.g. low A together with mid E , the possible range of degree of hydrogenation that can be generate by this kinetic expression can be outlined. The result of such a study is presented in Figure 11. It can be seen that the pre-exponential factor only had a minor effect on the degree of hydrogenation whereas the activation energy affected it more. It can be concluded that the low pre-exponential factor and mid activation energy provided results closest to the expected values.

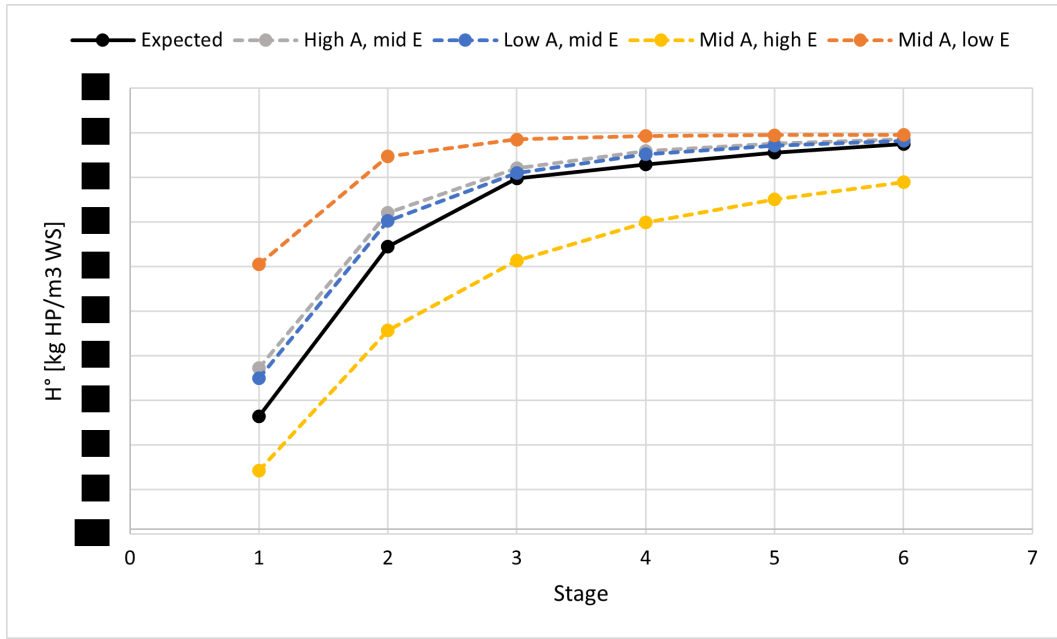


Figure 11: The degree of hydrogenation out of each stage of the calibration tower using different kinetic parameters. The parameter values are based on Equation (3), low $A=1,06 \cdot 10^{10} \text{ dm}^3/\text{mol s}$, mid $A=1,14 \cdot 10^{10} \text{ dm}^3/\text{mol s}$, high $A=1,22 \cdot 10^{10} \text{ dm}^3/\text{mol s}$, low $E=55344 \text{ J/mol}$, mid $E=59695 \text{ J/mol}$ and high $E=64046 \text{ J/mol}$.

The kinetic fitting had until now been done using a heat of reaction of $-136,0 \text{ kJ/mol}$ (corresponding to a heat of formation of HAQ as $-95,20 \text{ kJ/mol}$) generating a temperature increase of $3,2^\circ\text{C}/\text{H}^\circ$. This temperature increase is more than double the expected value, i.e. $1,06^\circ\text{C}/\text{H}^\circ$. To meet the expected temperature increase, the heat of reaction was needed to be lower. However, lowering the heat of reaction will also lower the conversion (see the temperature dependence in Equation (3)). Therefore, the kinetic parameters had to be further adapted simultaneously as the heat of reaction was fitted. A theoretical heat of reaction, which should generate the expected temperature increase of $1,06^\circ\text{C}/\text{H}^\circ$, was calculated to be $-8,726 \text{ kJ/mol}$ (see Appendix B). This heat of reaction corresponds to a heat of formation of HAQ of $-222,5 \text{ kJ/mol}$. When this heat of formation was used instead, together with the low A-mid E kinetic model, a temperature increase of $1,06^\circ\text{C}/\text{H}^\circ$ was received instead. Also the degree of hydrogenation after the sixth stage became too low ($8,6 \text{ kg H}_2\text{O}_2/\text{m}^3 \text{ WS}$) with this heat of reaction. However, despite this, the theoretical heat of reaction and the low A-mid E kinetic parameters were used to simulate the reference towers to see how it preformed in relation the the expected outcome of them. The results from these simulations are presented in Table 14, where the first values are the outcome of the simulations and the ones in parenthesis are the expected values for each parameter and tower. It can be seen that in most cases, the degree of hydrogenation and temperature increase per degree of hydrogenation was lower than expected. The same goes for the outlet temperature and oxygen content in the off-gas. The results for Tower 1 stands out where all parameters except the outlet temperature is higher than expected instead of lower. The oxygen content out of Tower 4 is also higher than expected.

Table 14: Reference towers' simulation results using the low A-mid E kinetic model.

Tower	1	2	3	4	5	6
H° [kg H ₂ O ₂ /m ³ WS]	()	()	()	()	()	()
$^\circ\text{C}/H^\circ$	()	()	()	()	()	()
T_{out} [$^\circ\text{C}$]	()	()	()	()	()	()
$x_{\text{O}_2, \text{out}}$ [%]	()	()	()	()	()	()

Due to the continued too low degree of hydrogenation and temperature increase in the simulations presented in Table 14, it was decided to do another set of iterations to fit both the kinetic expression and the heat of reaction simultaneously. For this, Tower 4 was chosen to be modeled since the results from that tower simulation were most reasonable, i.e. having higher concentration of oxygen out and lower conversion than expected. Some of the simulations made of the reference Tower 4 with different pre-exponential factors, activation energies and heat of formation of HAQ are presented in Table 15.

Table 15: Tower 4 simulation results using different kinetic models and heat of reactions.

Iteration	1	2	3	4
A [dm ³ /mol s]	$1,06 \cdot 10^{10}$	$1,22 \cdot 10^{10}$	$1,22 \cdot 10^{10}$	$1,22 \cdot 10^{10}$
E [J/mol]	59695	59695	55344	55344
$\Delta H_{f, \text{HAQ}}^\circ$ [kJ/mol]	-222,474	-207,474	-202,474	-212,474
ΔH_r° [kJ/mol]	-8,726	-2,3726	-2,3726	-1,8726
H° [kg H ₂ O ₂ /m ³ WS]	9,49	9,53	9,55	9,55
$^\circ\text{C}/H^\circ$	1,0	1,3	1,4	1,2
T_{out} [$^\circ\text{C}$]	55,85	55,48	53,74	53,63
$x_{\text{O}_2, \text{out}}$ [%]	7,79	7,73	7,72	7,72

The iterations presented in Table 15 were altered by rough estimations assuming different values of the pre-exponential factor, activation energy and heat of formation of HAQ. The starting point was the Tower 4 simulation in Table 14. The values used for the heat of formation were intuitively guessed and it was concluded that simulation with a heat of formation value of -212,5 kJ/mol together with the kinetic parameters high A ($1,22 \cdot 10^{10}$ dm³/mol s) and low E (55344 J/mol) generated results that were close enough to the expected outcome of reference Tower 4.

The outcome of the simulations of all the reference towers simulations using this new kinetic model and heat of reaction, are presented in Table 16. It can be seen that the expected degree of hydrogenation and temperature increase were well reproduced by this model. However, the outlet temperature was too low in all towers and so was generally the outlet oxygen concentration as well. It was only in Tower 1 and Tower 4 that the outlet oxygen concentration was too high instead. Nevertheless, this was not assumed to be too important for the simulation model. It was considered that these parameters can be compared as a relative measure in the upcoming simulations.

Table 16: Reference towers' results using the final kinetic model and heat of reaction.

Tower	1	2	3	4	5	6
H^o [kg H ₂ O ₂ /m ³ WS]	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)
$^{\circ}\text{C}/H^o$	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)
T_{out} [$^{\circ}\text{C}$]	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)
$x_{\text{O}_2, \text{out}}$ [%]	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)	■ (■)

4.5 Higher oxygen concentration

The first design and operating alternation investigated with the established model, was changing the gas feed oxygen concentration. The oxygen content was gradually increased from 21% to 100% by decreasing the amount of nitrogen in the feed. The molar flow of oxygen in the inlet was kept constant at ■ kmol/h. For these simulations, the reference Tower 2 was used.

The tower design was adapted to the operation with the new inlet oxygen concentrations by changing the diameter and number of steps. The diameter was scaled so that the tower residence time was kept constant for the liquid and gas, whereas the height of the tower was based on the conversion of HAQ, i.e. as long as the outflow of HAQ did not exceeded 0,2 mol/h (which was the results when the tower was simulated with air) one or more ■ m stage was removed. In addition to this, the pressure drop was also adapted to the new feed composition.

The scaled diameters, when using the higher inlet oxygen concentrations, are displayed in Figure 12a and the corresponding tower volume is presented in Figure 12b. Note the change in the volume-curve at 70% and 95% oxygen inlet concentration. These changes were due to the removal of one 2,2 m stage, i.e. it was first possible to remove one stage when the inlet concentration was 70% or higher and another when the inlet concentration reached 95%. As shown in Figure 12, the oxidation column size could be decreased when the oxygen concentration was increased. It can be seen in Figure 12a that the diameter may be almost halved when increasing the oxygen inlet concentration from 21% to 100%. As seen in Figure 12b, this correspond to a decrease to a quarter of the original tower volume.

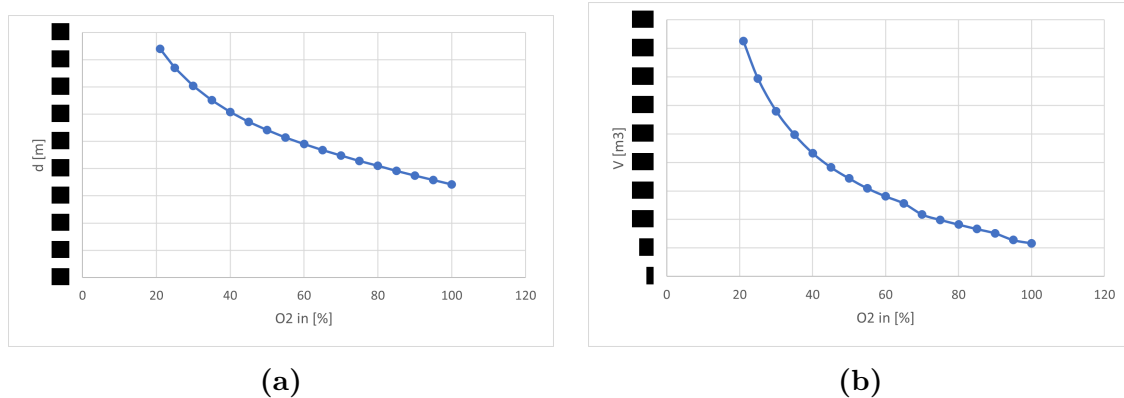


Figure 12: (a) The oxidation tower diameter and (b) total volume when simulated with different inlet oxygen concentrations.

The outlet oxygen concentration is important for the safety of the oxidation tower operation, it should be operated at around 6% (<10%) to avoid risk of fire in the carbon filter used for gas purification (see Section 2.2.4). Figure 13 presents the gaseous outlet oxygen concentration when Tower 2 was simulated with different inlet oxygen concentrations. It can be seen that with a higher inlet concentration, also the outlet oxygen concentration was increased. This may be explained by the lack of diluting nitrogen present for the non-reacted oxygen.

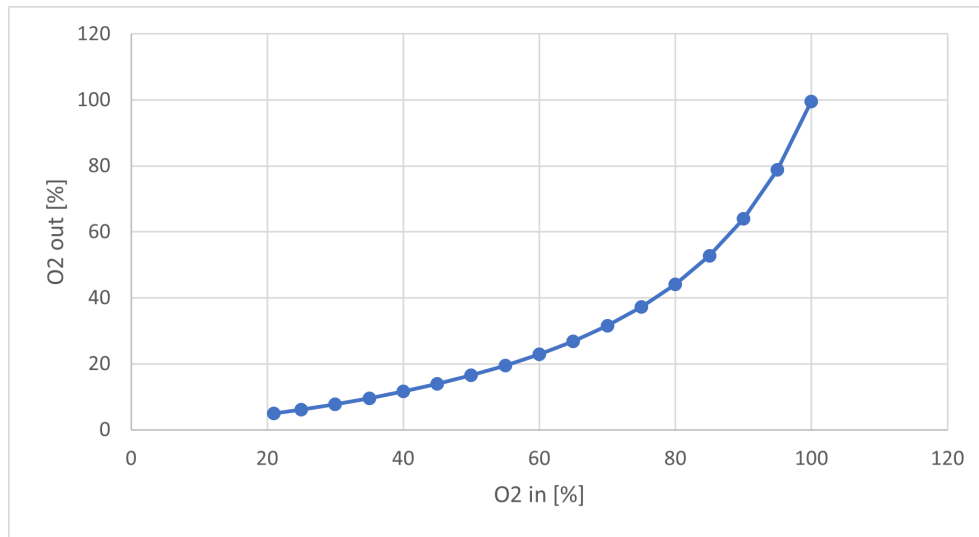


Figure 13: The concentration of oxygen in the off-gas when Tower 2 was simulated with different inlet oxygen concentrations.

A possible way to handle this too high outlet concentration of oxygen in a real tower could be to dilute the off-gas with pure nitrogen gas. Hence, calculations were made of how much nitrogen gas that would be needed to dilute the off-gas to the same oxygen content as when air was used (4,99%). The results from these calculations are presented in Figure 14. It can be seen that the simulation results suggested that already for an inlet concentration of 40% oxygen, almost 400 kmol/h (i.e. around 8300 Nm³/h) of nitrogen would be needed to dilute the off-gas to the oxygen content limit. Note that the the expected outlet oxygen concentration for reference Tower 2 when operated with air was ■■■ % (see Table 16), i.e. the simulation model did not exactly reproduce this expected value. Anyway, the limit used as reference for all optimization simulations was 4,99% oxygen, instead of this. However, it is then important to note that a simulated value higher than 4,99% may not necessarily mean that it would be too high in a real tower, specially since below 10% is the limit for the carbon filters.

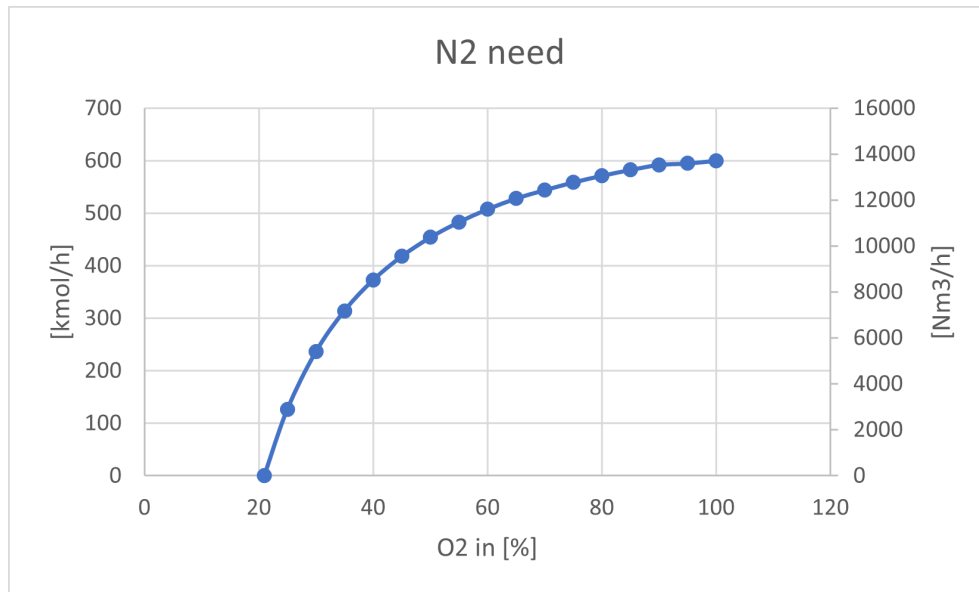


Figure 14: The amount of nitrogen needed to adjust the outlet oxygen concentration to be 4,99% (as it was when the tower was simulated with air) when the tower was simulated with different inlet oxygen concentrations.

In addition to the off-gas oxygen concentration, also the outlet temperature is an important safety parameter. As stated in Section 2.2.4, the temperature should not exceed 54°C to avoid explosions. The outlet temperature depending on the feed oxygen concentration is presented in Figure 15. It can be seen that the simulations did not predict any large difference in outlet temperature, increasing the inlet oxygen concentration to 100% decreased the outlet temperature less than 1°C. This is not unreasonable since the temperature is highly dependent on the conversion of HAQ, and the overall conversion was kept very similar for all the simulations. Note that similarly to the off-gas oxygen concentration, also the outlet temperature generated by the simulations was a bit from the expected value in the base case. Here, the simulated temperature was approximately 4°C lower than the expected temperature (see Table 16). Anyway, judging by the outcome of the simulations, an increase in oxygen concentration should not generate a problem with a too high outlet temperature in a real tower due to the anticipated temperature decrease.

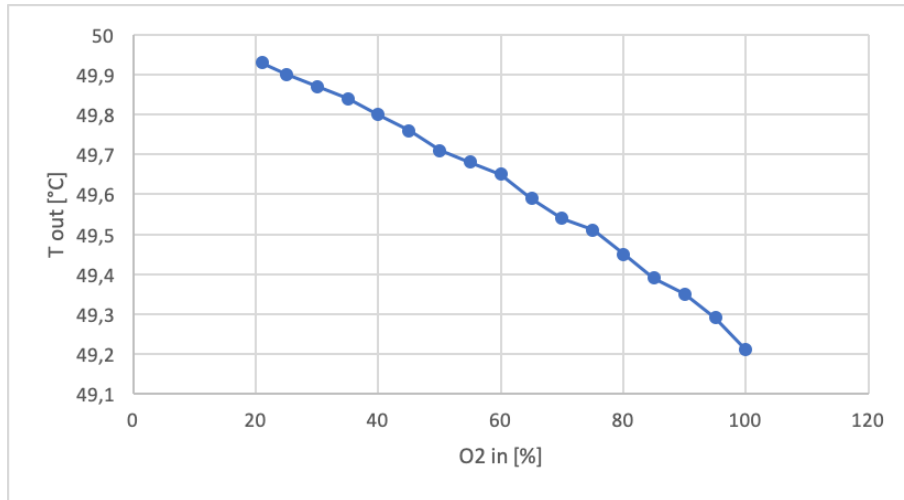


Figure 15: The outlet temperature when Tower 2 was simulated with different inlet oxygen concentrations

The last simulation results reviewed were the outlet pressure, the outcome is presented in Figure 16. It can be seen that the pressure drop was increased for higher inlet oxygen concentrations, i.e. the outlet pressure got lower with a higher oxygen concentrations. This is expected since the liquid and gas mixture in the tower will have a higher density due to the smaller amount of gas present. In Figure 16, it can be noted two small increases in the outlet pressure, one at an oxygen inlet concentration of 70% and one at 95% oxygen in. These increases were due to the removal of one stage, i.e. at these inlet concentrations the tower got shorter and the pressure drop was reasonable lowered. Note that for oxygen concentrations above 85%, the outlet pressure became lower than the atmospheric pressure which may not be a realistic way to operate the tower. In practice, the inlet pressure would be increased to compensate for this increase in pressure drop over the tower.

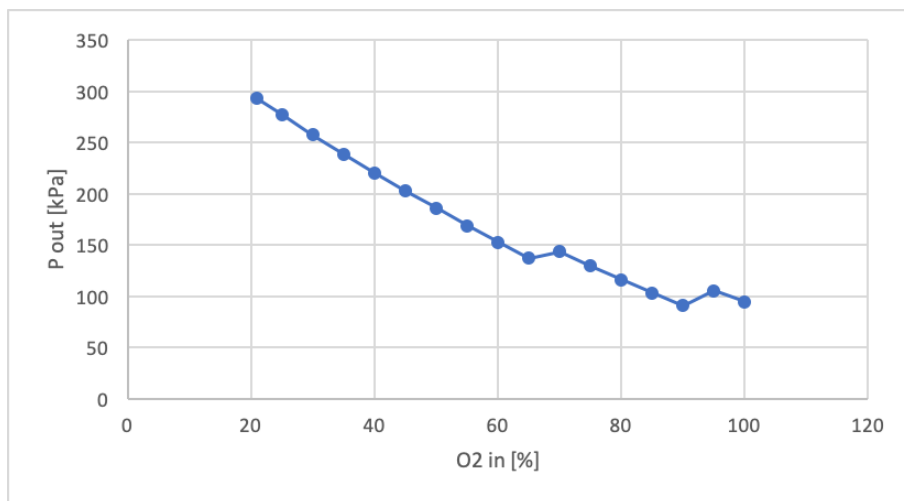


Figure 16: The outlet pressure when Tower 2 was simulated with different inlet oxygen concentrations.

From these simulations, it may be concluded that operation with a higher oxygen concentration would enable the use of a considerably smaller tower. However, it may also be concluded that a higher oxygen concentration seems to result in a too high outlet oxygen concentration already at a moderate increase, generating a safety risk in the operation of the tower. This problem may be overcome by diluting the off-gas by addition of pure nitrogen. Nevertheless, a more cost efficient way to overcome this problem for moderate inlet oxygen increases, would be to decrease the oxygen excess and possibly increase the residence time to enable full conversion. This was investigated in the upcoming simulations.

4.6 Lower oxygen excess

Based on the simulation results from when the inlet oxygen concentrations were increased, it was interesting to construct simulations with a lower oxygen excess to see if the off-gas oxygen concentration could possibly be decreased in that way. The original oxygen excess for Tower 2 was 24,6% in relation to the feed amount of HAQ. There were simulations made with three lower levels of oxygen excess (10%, 18% and 20%) with an oxygen inlet concentration of 60%. For each excess-level the tower was optimized in terms of size using the same methodology as in the previous simulations.

The off-gas oxygen concentrations generated by the simulations with lower oxygen excess are presented in Figure 17a. It can be seen that a lower oxygen excess indeed resulted in a lower off-gas oxygen concentration. However, looking at the conversion of the tower, presented in Figure 17b in terms of molar outflow of HAQ, it can be seen that this was quickly decreased when using a lower oxygen excess. Judging by the simulation results, it is only possible to lower the excess to 20% and still keep the same conversion, i.e. the unconverged HAQ maintaining below the established limit of 0,2 mol/h HAQ out. For an oxygen excess of 20%, the outlet oxygen concentration was decreased 3 percentage points compared to the original operation of the tower. This corresponds to a decrease of around 100 kmol/h (i.e. around 2200 Nm³/h) nitrogen needed to dilute the off-gas concentration to ■ % oxygen.

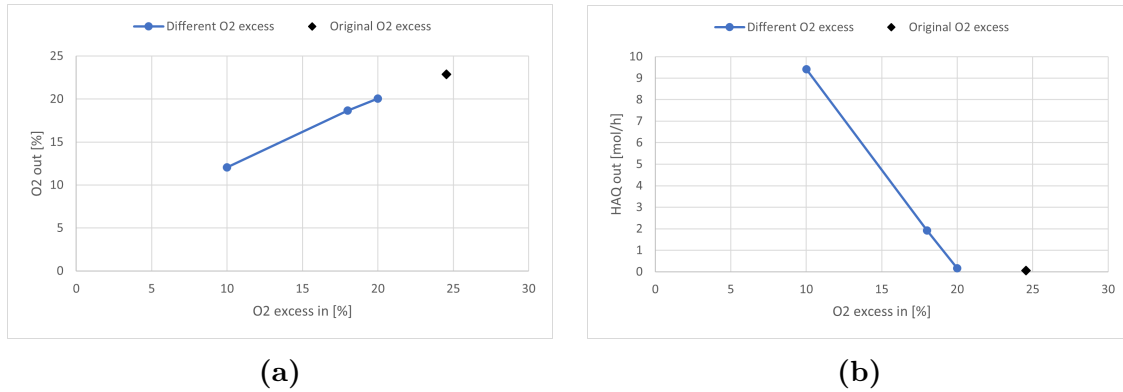


Figure 17: (a) The outlet oxygen concentration and (b) the outlet flow of HAQ when simulating Tower 2 with inlet oxygen concentration of 60% and a lower oxygen excess. The respective values for when the tower was simulated with the original oxygen excess of 24,6% are also marked.

The scaled tower diameters for the different levels of oxygen excess are presented in Figure 18. It can be seen that the diameter was decreased by only 5 cm when the oxygen excess is lowered from 24,6% to 20%.

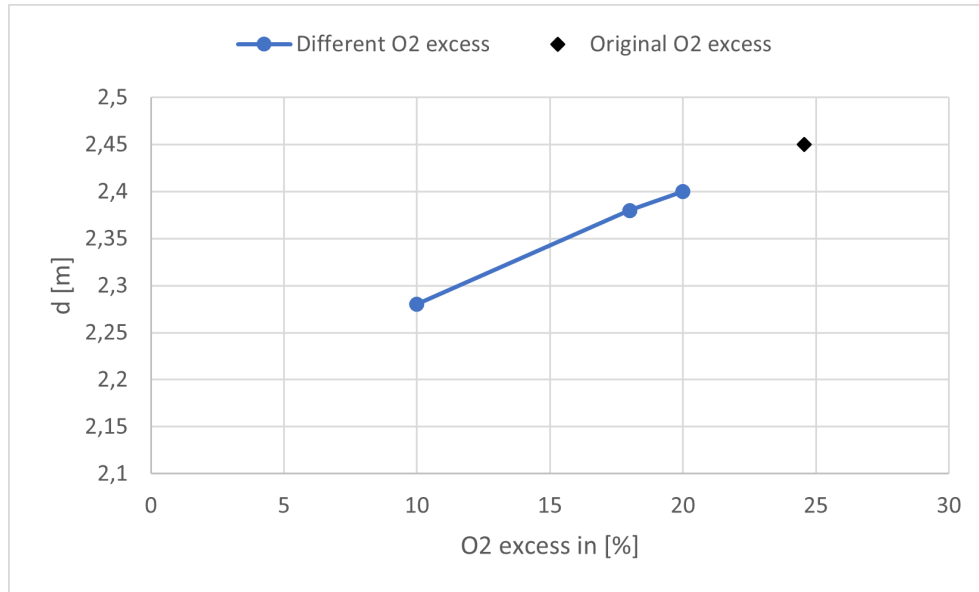


Figure 18: The reference Tower 2 diameter needed when simulated with a inlet oxygen concentration of 60% and a lower inlet oxygen excess. The diameter needed when simulated with the original oxygen excess of 24,6% is also marked.

The last results presented from these simulations is the outlet temperature and pressure presented in Figure 19. In Figure 19a it can be seen that the temperature increased when the oxygen excess was lowered and in Figure 19b it can be seen that the outlet pressure was decreased with a lower oxygen excess. The lower pressure is reasonable since lower oxygen excess implies less gas entering the tower and hence a higher inlet mixture density. The increase in outlet temperature on the other

hand may be explained by a decrease in reaction rate. A lower excess of oxygen lead to a slower absorption of oxygen into the liquid (the gradient and driving force for absorption gets smaller). Hence, the extent of reaction in the first stage was lower which resulted in a less heat removed by the stage one cooler. However, the temperature increase was not that high, lowering the oxygen excess to 10% only resulted in a increase of around 1,5°C.

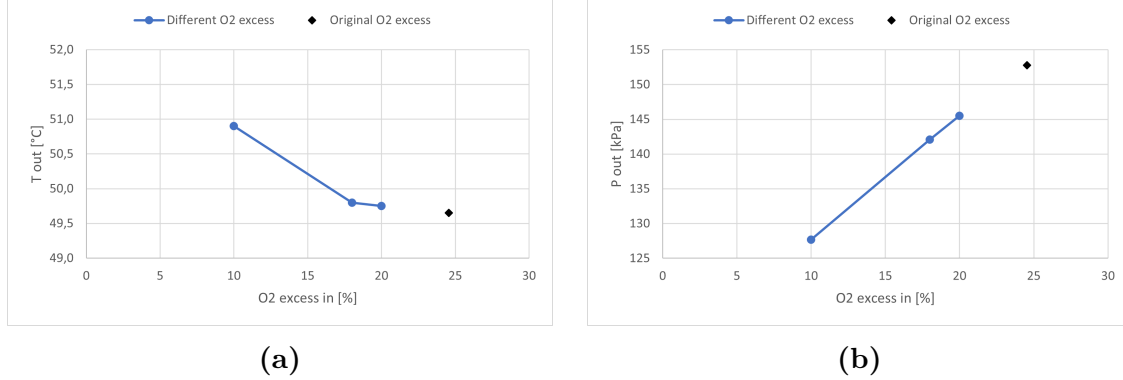


Figure 19: (a) The outlet temperature and (b) the outlet pressure when simulating Tower 2 with a inlet oxygen concentration of 60% and a lower inlet oxygen excess. The respective values for when the tower was simulated with the original oxygen excess of 24,6% are also marked.

Considering the simulations results from the simulations made with a lower oxygen excess, it can be seen that this operating alternative may account for the drawbacks when the inlet oxygen concentration is increased. However, a full study should also have included simulations where the residence time was increased, i.e. increasing the tower volume. This to enable the desired amount of conversion also for lower oxygen excess than 20% with the prospect to lower the outlet oxygen concentration even more.

4.7 Higher operating pressure

Another change in operating conditions that was simulated was the increase of the operating pressure. This was a change anticipated to decrease the tower volume even further, since about 90% of the fluid volume through the tower was composed of gas when operation at the original pressure, and possibly increase the rate of reaction due to a higher driving force for absorption of oxygen into the liquid phase.

For these simulations the reference Tower 2 was used with an oxygen inlet concentration of 35%. The inlet pressure was increased three times by 100 kPa. For each case, the diameter and pressure drop was adapted to the new volumetric flow rates and density, using the same methodology and reference data as for when the inlet oxygen concentration was changed. The adapted diameters for the higher pressure simulations are shown in Figure 20. The first data point is for the base case pressure, i.e. 413,3 kPa, and it can be seen that a higher pressure enabled the use of a smaller tower, still keeping the same fluid residence time.

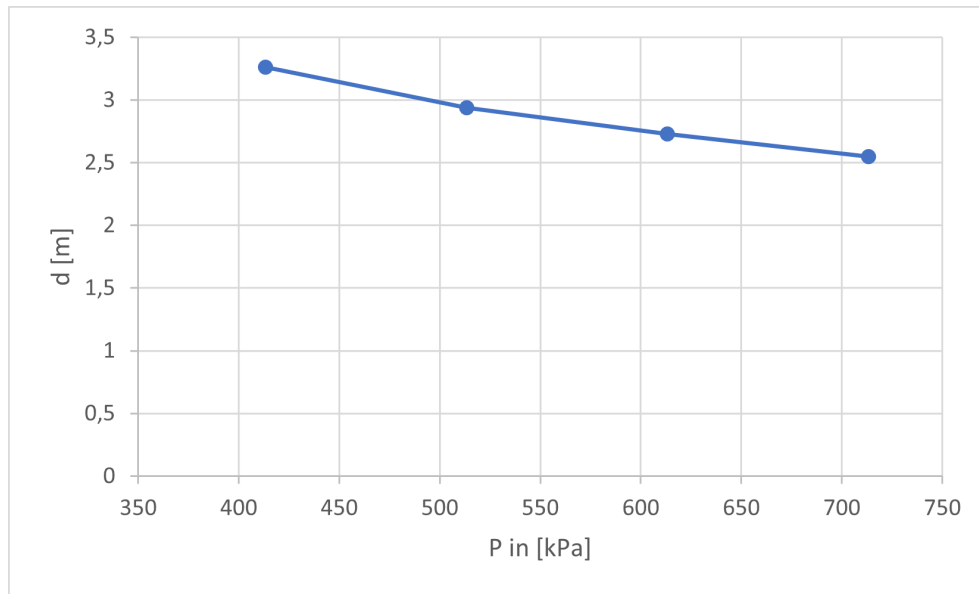


Figure 20: The oxidation Tower 2 diameter needed when it was operated at different inlet pressures and a inlet oxygen concentration of 35%.

To investigate if the higher pressure resulted in a higher rate of reaction, the outlet molar flow of HAQ was observed. The simulation results are presented in Figure 21. It can be observed that a peak of HAQ out was obtained which is assumed to be unreasonable. The reason for this outcome is unknown but one could speculate that it had to do with the solver accuracy. However, if the first point is disregarded, a trend of lower HAQ outlet flow with higher operating pressure can be seen. This could confirm that a higher pressure do increase the rate of reaction even if it is infinitesimal small compared to the tower total conversion.

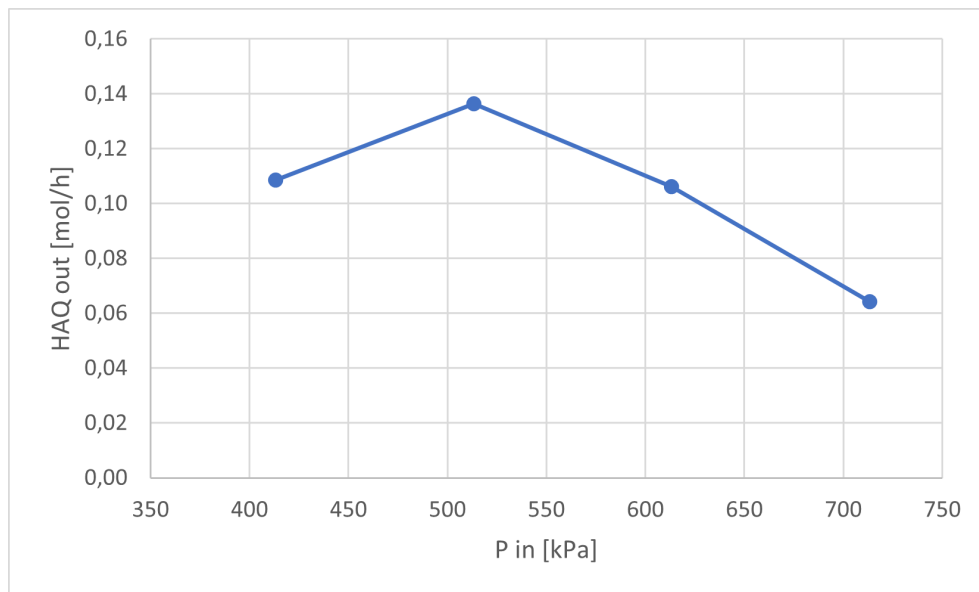


Figure 21: The outlet liquid flow of HAQ when Tower 2 was operated at different inlet pressures and a inlet oxygen concentration of 35%..

Analysing how the higher pressure affects the off-gas oxygen concentration it can be seen in Figure 22 that the oxygen concentration was slightly increased with a higher pressure. Hence, the slightly higher conversion observed in the results presented in Figure 21 did not generate a lower outlet oxygen concentration that may have been expected.

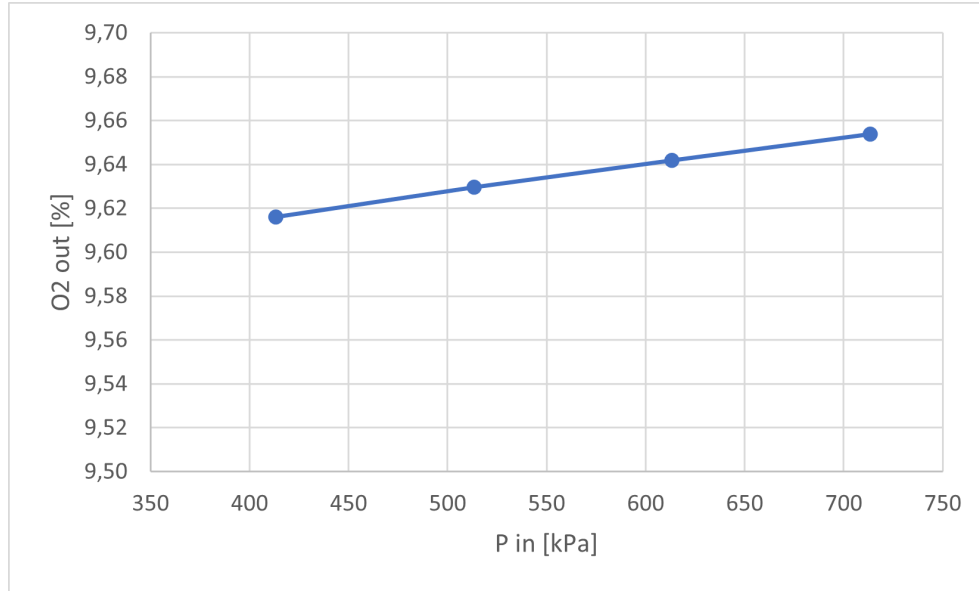


Figure 22: The Tower 2 outlet oxygen concentration when operated with different inlet pressures and a inlet oxygen concentration of 35%..

The outlet temperature and pressure generated by the simulations with higher inlet pressure are presented in Figure 23. As for the simulations when changing the inlet oxygen concentration, the outlet temperature was almost unchanged whereas the outlet pressure instead was increased. The increase in outlet pressure indicates that the pressure drop was not increased as much as the inlet pressure.

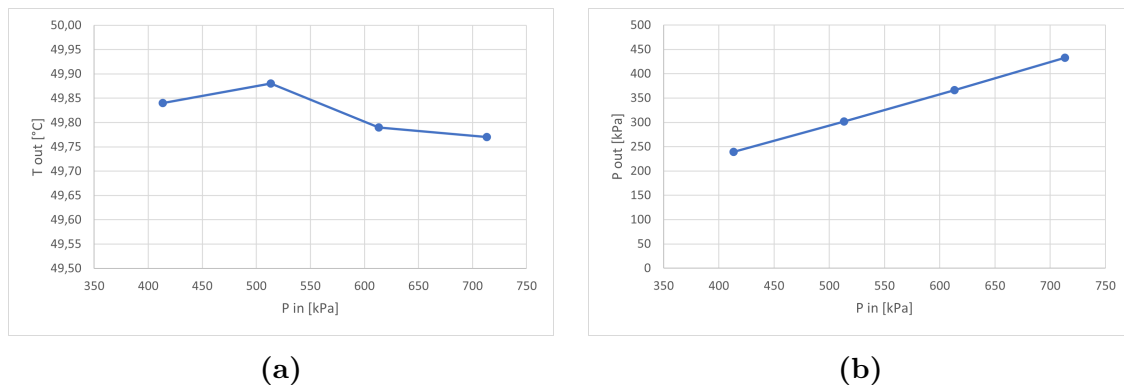


Figure 23: (a) The outlet temperature and (b) the outlet pressure when simulating Tower 2 with higher inlet pressures and a inlet oxygen concentration of 35%..

Operation with higher pressure was also interesting to use with the purpose of

increasing the productivity of a set tower volume. This was investigated using the base operating conditions for Tower 2 operated with air. In these simulations, the original dimensions of the tower was maintained and the decrease in gas volume flow when increasing the pressure was accounted for by increasing the flow rate of the working solution and gas feed. The relation between the working solution and gas feed was held the same as in the original operation of the tower. The pressure was increased in two steps to 513,3 kPa and 613,3 kPa. The outcome of these simulations, in terms of produced amount of hydrogen peroxide, is presented in Figure 24. It can be seen that the production capacity of hydrogen peroxide increased from around $\blacksquare$ kg/h to $\blacksquare$ kg/h when the pressure was increased by 200 kPa. This increase corresponds to an productivity increase of $\blacksquare$ %.

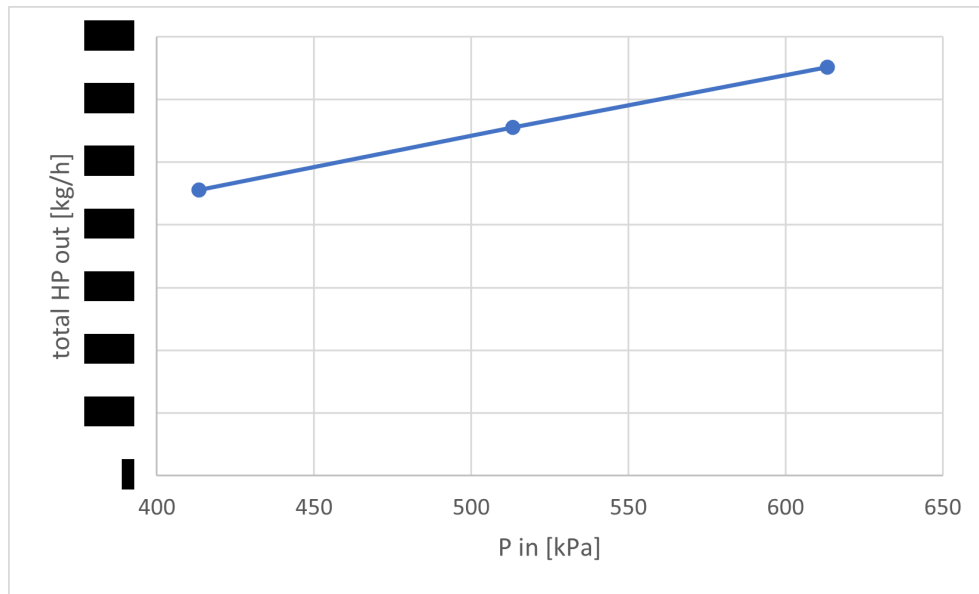


Figure 24: The production capacity of hydrogen peroxide using reference Tower 2, simulated with air and the original dimensions, depending on the operating pressure.

Based on the simulations done with a higher operating pressure, this operating alternative can be used either to get a smaller tower or to increase the productivity in a tower of a certain size. The outlet oxygen concentration was not seen to be affected by the operation with higher pressure which may be surprising. This since it could be assumed that a higher pressure would increase the absorption of oxygen into the liquid. Hence, this part of the results may be questioned. Note that a higher pressure would demand a thicker material in the tower and stronger compressors which may or may not compensate for the higher productivity.

4.8 Lower oxygen excess and higher pressure

The next case simulated was when a lower oxygen excess was combined with a higher operating pressure. This was believed to enable operation of an even smaller oxidation tower with contained levels of HAQ out and off-gas oxygen concentration. This was assumed since the outcome of the two operating alternations separately showed

the opposite trends in HAQ conversion and off-gas oxygen concentration. These simulations were done using reference Tower 2 and an inlet oxygen concentration of 35%. The oxygen excess level was set to 20%, i.e. the excess level that showed the most promising results, and the inlet pressure was increased from 413,3 kPa to 513,3 kPa, 713,3 kPa and 913,3 kPa.

The results in terms of liquid HAQ outflow and off-gas oxygen concentrations are presented in Figure 25. It can be seen in Figure 25a that the minimum conversion of HAQ was fulfilled if the pressure was increased to 913,3 kPa, i.e. the outflow of HAQ was lower than 0,2 mol/h. The results displayed in Figure 25b implies that the outlet oxygen concentration is slightly increased when the pressure is increased. However, comparing with the outlet oxygen concentration generated when the original oxygen excess and pressure were used, the concentration was lowered by more than a percentage point. This corresponds to a decrease in nitrogen need for dilution of the off-gas of almost 100 kmol/h (i.e. around 2200 Nm³/h).

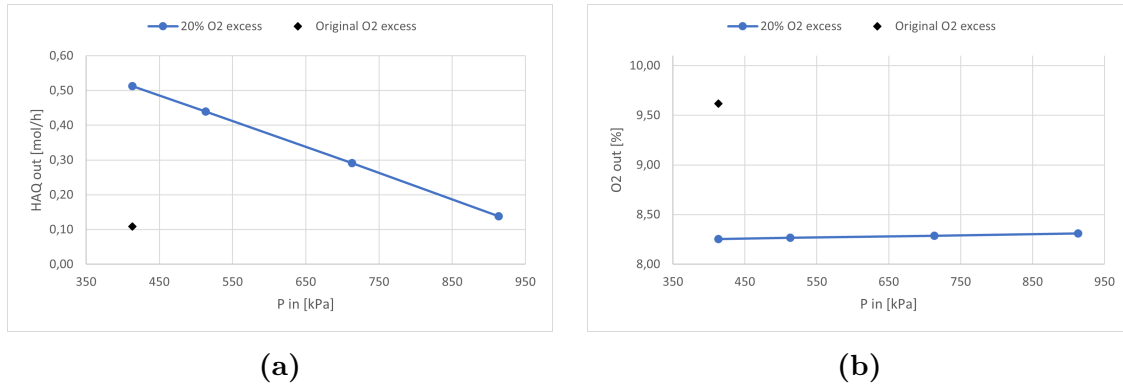


Figure 25: (a) The outflow of HAQ and (b) the off-gas oxygen concentration for when the reference Tower 2 is simulated with an inlet oxygen concentration of 35% and oxygen excess of 20% at different inlet pressures. The respective values for when the tower was simulated with the original pressure and oxygen excess of 24,6% are also marked.

Figure 26 shows how the scaled diameter depended on the higher operating pressure. Also here is the scaled diameter for the original oxygen excess marked. It can be seen that the diameter may be decreased by almost 1 m if the oxygen excess was lowered to 20% and the inlet pressure increased to 913,3 kPa.

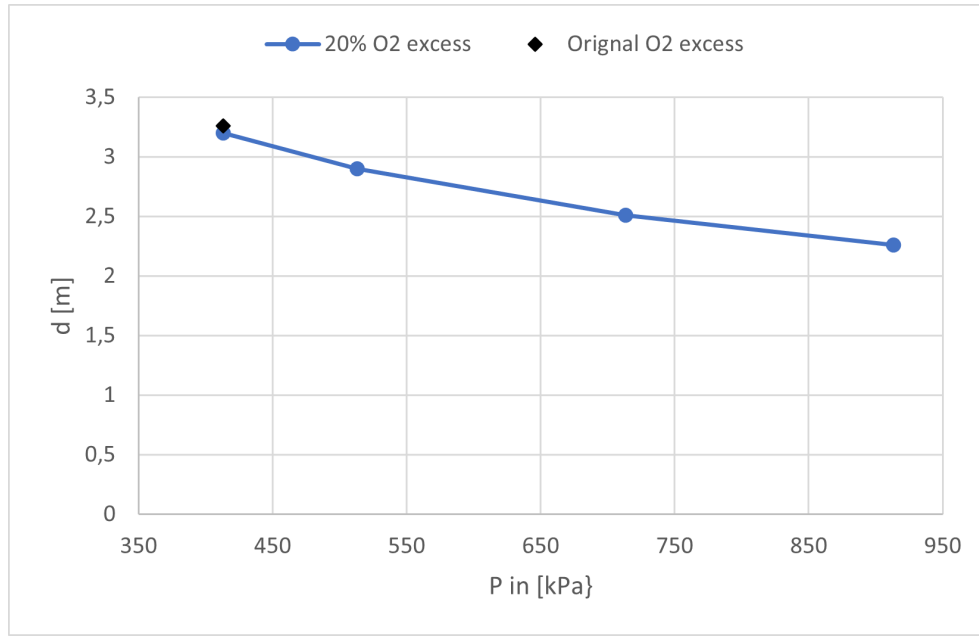


Figure 26: The scaled oxidation tower diameter for simulations of Tower 2 depending on the inlet pressure. The tower was simulated with an inlet oxygen concentration of 35% and oxygen excess of 20%. The diameter generated when the tower was simulated with the original oxygen excess of 24,6% is also marked.

Lastly, the generated outlet temperature and outlet pressure when simulating with an oxygen excess of 20% and increasing the pressure are presented in Figure 27. It can be seen that the temperature was decreased slightly when the pressure was increased whereas the outlet pressure was increased. None of these results are surprising since the same trends were observed when simulations with only higher inlet pressure were made.

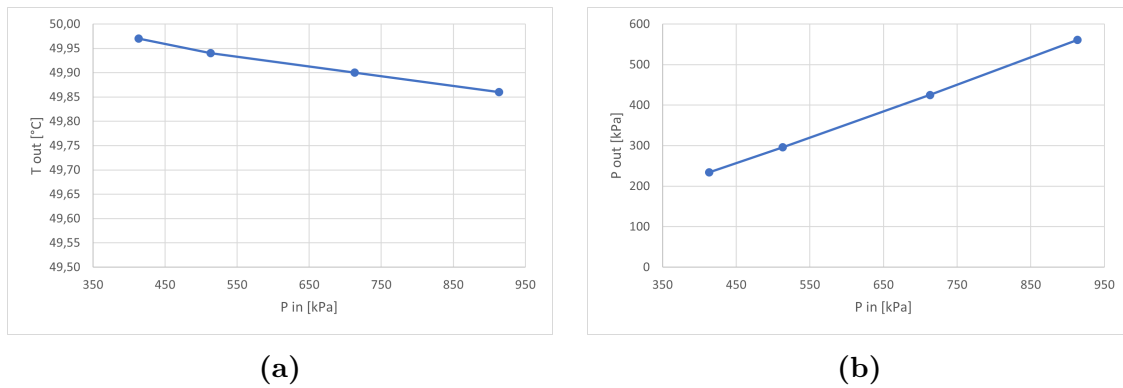


Figure 27: (a) The outlet temperature and (b) the outlet pressure for when the reference Tower 2 was simulated with an inlet oxygen concentration of 35% and oxygen excess of 20% at different inlet pressures. The respective values for when the tower was simulated with the original pressure and oxygen excess of 24,6% are also marked.

From these simulations it may be concluded that the combination of higher pressure and lower oxygen excess makes it possible to reduce the tower size. However, to do so a pressure increase of 500 kPa is needed to maintain the desired conversion of HAQ which may be considered to be too much. Judging by the results presented in Figure 25a, an excess of 20% is too low in the first place to get the desired conversion when using an inlet oxygen concentration of only 35% (the simulations made when only the excess was changed were conducted with an oxygen concentration of 60%). These results may therefore only be used to the conclusion that if the lower oxygen excess does not enable full conversion, a higher pressure can make the last difference in obtaining full conversion.

4.9 Recirculation

The last design alternation made was also with the intention of enabling the use of a higher inlet oxygen concentration, to get a smaller tower, but with a more efficient utilisation of the oxygen sent to the tower, e.i. decreasing the off-gas oxygen concentration and amount. This alternation was the design of a tower with recirculation of a part of the off-gas. This was done for reference Tower 2 with an inlet/fresh feed oxygen concentration of 80%. The results from when 80% and 90% of the off-gas was recirculated are presented in Table 17. The table also includes the results for the base simulation of the tower, i.e. no recirculation. It can be seen that the diameter of the tower increases with increased recirculation amount. It should also be noted that when recirculation was simulated, the full height of the tower was needed to reach the desired conversion, in comparison to the base case where the height could be decreased by 2,2 m. In terms of outlet oxygen concentration it can be noted that it indeed was decreased when recirculation was used. It can also be seen that a drastically lower amount of nitrogen was needed to dilute the off-gas to the used limit of 4,99%. However in terms of profitability, it is possible that the additional equipment and larger tower needed for the recirculation might not make up for the savings in extra nitrogen or decreased fresh feed needed.

Table 17: Simulation results for Tower 2 operated with a gas inlet oxidation concentration of 80% and different recirculation amounts.

Recirculation [%]	0	80	90
d [m]	2,05	2,67	3,21
$x_{O_2, out}$ [%]	44,2	17,0	10,3
N ₂ need [kmol/h]	572	93,5	35,9
N ₂ need [Nm ³ /h]	12815	2096	805

5 Conclusions

This project has resulted in a simulation tool that has been proven to theoretically mimic the expected performance of a hydrogen peroxide oxidation tower. The model has been built using the simulation software HYSYS v12.1 and it has been validated with acceptable result against reference oxidation towers. The simulation tool approximates the oxidation tower design with a number of ideal flash-separators connected in series and uses a kinetic model to simulate the oxidation reaction. The kinetic model consists among other things of a kinetic constant expression presented in Equation (5) and a standard heat of reaction of -18726 J/mol.

$$k_{ox} = 1,22 \cdot 10^{10} \exp\left(\frac{-55344}{R T}\right) \left[\frac{dm^3}{mol s}\right] \quad (5)$$

The simulation tool has been used to investigate how operation with a higher inlet oxygen concentration, lower oxygen excess and higher pressure may affect the performance of the oxidation tower. It has also been used to simulate an oxidation tower with partial recirculation of the off-gas.

The simulations with higher inlet oxygen concentrations suggests that the size of the oxidation tower may be considerably decreased if the oxygen concentration is increased. It does not seem like a higher oxygen concentration will be a hazard in terms of a too high temperature increase than what is adequate. However, with an increased inlet oxygen concentration the outlet oxygen concentration was also increased, e.g. an increase of the oxygen concentration to only 35% gave too high oxygen concentration breaching the safety level of oxygen out of the tower. It is suggested that nitrogen gas may be used to dilute the off-gas to facilitate the safety restrictions in the carbon filters. One other possibility to overcome this has been shown by the simulations to be the operation with a lower oxygen excess.

The outcome from the oxidation tower simulations made with a higher operating pressure indicates that the pressure could be used to either decrease the needed tower volume or increase the productivity in a tower of a certain size. It is also suggested that a higher pressure may be used to enable full conversion when using a lower oxygen excess in the tower. None of the simulations with higher operating pressure indicated that oxygen would be absorbed into the liquid in a greater extent when the pressure is increased which seems surprising.

From the simulations of an oxidation tower with recirculation of the off-gas, the results indicated that this could decrease the outlet oxygen concentration when a higher inlet oxygen concentration is used. However, to keep the same productivity, the simulation results suggests that a larger tower would be needed compared to when no recirculation is used.

In future work, it would be interesting to use the simulation tool to investigate additional design and operating alternatives, e.g. exploring the limit of oxygen concentration versus tower size and oxygen excess and towers with counter-current and cascade flow. It would also be interesting to compare the simulated design and

operating alternatives in terms of economical profitability. This would be to obtain a better measure of which of the designs that may be of interest for even further analysis and possibly real life implementation.

Appendices

The appendices have been removed in this public version of the report.

A Tower setup details

B Calculation of theoretical heat of reaction

References

- [1] Nouryon. Company - a global specialty chemicals leader. <https://www.nouryon.com/company/>. (Accessed: 2022-01-25).
- [2] Nouryon. Eka hp - hydrogen peroxide. <https://www.nouryon.com/products/hydrogen-peroxide/>. (Accessed: 2022-01-25).
- [3] W. Eul, A. Moeller, and N. Steiner. *Hydrogen Peroxide*. John Wiley & Sons, Ltd, 2001.
- [4] Gustaaf Goor, Jürgen Glenneberg, Sylvia Jacobi, Jal Dadabhoy, and Elize Candido. *Hydrogen Peroxide*, pages 1–40. John Wiley & Sons, Ltd, 2019.
- [5] Nouryon. *Hydrogen Peroxide - Product information manual*.
- [6] Jose M. Campos-Martin, Gema Blanco-Brieva, and Jose L. G. Fierro. Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. *Angewandte Chemie International Edition*, 45(42):6962–6984, 2006.
- [7] Leon Gao Adam Held Heike Schlag, Stefan Beraud. Hydrogen Peroxide. IHS Markit, *Chemical Economics Handbook*, August 2021.
- [8] Ronald Hage and Achim Lienke. Applications of transition-metal catalysts to textile and wood-pulp bleaching. *Angewandte Chemie International Edition*, 45(2):206–222, 2006.
- [9] Qinguo Fan. Textile chemistry. *AccessScience*. Last reviewed 2020.
- [10] C W Jones. *Applications of Hydrogen Peroxide and Derivatives*. Royal Society of Chemistry, 1999.
- [11] E. Santacesaria, M. Di Serio, A. Russo, U. Leone, and R. Velotti. Kinetic and catalytic aspects in the hydrogen peroxide production via anthraquinone. *Chemical Engineering Science*, 54(13):2799–2806, 1999.
- [12] Johan Lif. interview, april 2022.
- [13] E. Santacesaria, R. Ferro, S. Ricci, and S. Carra. Kinetic aspects in the oxidation of hydrogenated 2-ethyltetrahydroanthraquinone. *Industrial & Engineering Chemistry Research*, 26(1):155–159, 1987.
- [14] E. Santacesaria and R. Tesser. *The Chemical Reactor from Laboratory to Industrial Plant: A Modern Approach to Chemical Reaction Engineering with Different Case Histories and Exercises*, chapter Kinetics and Transport Phenomena in Multi-phase Reactors, pages 487–553. Springer International Publishing, Cham, 2018.
- [15] J. Tan, L. Du, Y.C. Lu, J.H. Xu, and G.S. Luo. Development of a gas-liquid microstructured system for oxidation of hydrogenated 2-ethyltetrahydroanthraquinone. *Chemical Engineering Journal*, 171(3):1406–1414, 2011.

- [16] Tomonori Nishimi, Takashi Kamachi, Kenji Kato, Tomio Kato, and Kazunari Yoshizawa. Mechanistic study on the production of hydrogen peroxide in the anthraquinone process. *European Journal of Organic Chemistry*, 2011(22):4113–4120, 2011.
- [17] AspenTech. Aspen HYSYS V12.1 Help, April 2021.
- [18] Eric C. Carlson. Don’t gamble with physical properties for simulations. *Chemical Engineering Progress*, pages 35–46, October 1996.
- [19] Erik Bengtsson. SE541158C2 Oxidation column for hydrogen peroxide production. <https://worldwide.espacenet.com/patent/search/family/064268541/publication/SE541158C2?q=pn%3DSE541158C2>, April 2017. (Accessed: 2022-05-09).
- [20] Qingdan Kong, Defu Li, Shudong Wang, Jianguo Zhang, and Tong Zhang. CN101746736A Method for preparing hydrogen peroxide by utilizing microchannel technology. <https://worldwide.espacenet.com/patent/search/family/042474446/publication/CN101746736A?q=pn%3DCN101746736A>, June 2010. (Accessed: 2022-03-02).
- [21] Tan Jing, Luo Guangsheng, and Lv Yangcheng. CN102009961A Oxidation method for preparing hydrogen peroxide by anthraquinone method. <https://worldwide.espacenet.com/patent/search/family/043840321/publication/CN102009961A?q=CN102009961%20A>, April 2011. (Accessed: 2022-03-02).
- [22] Gao Guohua, Yang Keyong, Li Hongbo, and Zong Baoning. CN105271131A Anthraquinone oxidation method for producing hydrogen peroxide. <https://worldwide.espacenet.com/patent/search/family/055141075/publication/CN105271131A?q=CN105271131A>, January 2016. (Accessed: 2022-02-24).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden

www.chalmers.se



CHALMERS
UNIVERSITY OF TECHNOLOGY