

# Phthalic Anhydride

## Study of a Production Process from o-Xylene Oxidation

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**Abstract**— First reported in 1836, phthalic anhydride can be produced from naphthalene, ortho-xylene, and recently from renewable sources. This article focuses on the production process of 75 000 tons per year of phthalic anhydride with a purity of 99.9wt-% obtained from gas-phase oxidation of o-xylene. To this end, the thermodynamics and kinetics of the compounds and reactions involved are studied, followed by the establishment of the process operating conditions. The life cycle analysis of the process offers good prospects, however the financial analysis carried out shows that it would seem difficult to convince investors to lend money for this project. The results obtained are finally compared with processes of the industry. [Open access files.](#)

**Keywords**— Gas-phase phthalic anhydride production process, Ortho-xylene oxidation, *Aspen* modelling, Life cycle assessment, Cost analysis

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### 1 INTRODUCTION

**1** As part of the Integrated Project of the master degree in Chemical and Materials Engineering, a chemical plant to produce phthalic anhydride is studied.

**2** The goal of the project is to reach a production of phthalic anhydride of 75 000 tons per year, with a purity of 99.9wt-%. The production process considered is the gas-phase oxidation of ortho-xylene to phthalic anhydride.

**2** This paper is a summary of the work realised in the framework of this Integrated Project. For the studied process, it is important to have good knowledge of the phthalic anhydride main properties, characteristics, hazards, main uses, and market opportunities. So, these elements are first presented.

**9** The production process, the thermodynamics and the kinetics are described in the second section, as well as the design and the optimisation of the different units, namely the reactor, the distillation column, and the switch condensers. As part of the optimisation, a heat integration is also performed to minimise the process energy consumption. This leads to the modelling of the heat exchangers. The global flowsheet is finally described to give an overview of the optimised process.

**15** As the chemical plant must be as realistic and as cost-effective as possible, a life-cycle assessment study and an economic analysis are performed.

**17** Finally, an extended literature review is presented to compare the results obtained for this process with others found in the literature.

## 2 WHAT IS PHTHALIC ANHYDRIDE?

Phthalic anhydride is an organic compound that corresponds to the anhydride form of phthalic acid. It is also known as isobenzofuran-1,3-dione. Its molecular formula is  $C_6H_4(CO)_2O$  or  $C_8H_4O_3$  [1].

Phthalic anhydride was discovered in 1836 by Auguste Laurent. Its production through the oxidation of naphthalene was developed by the German company BASF in 1872. It was the first anhydride of a carboxylic acid to be commercially used. Since then, other production processes have been developed [2].

### 2.1 Properties

At ambient temperature, phthalic anhydride is a white solid in the form of flakes which has a mild distinctive odour [3]. Its main properties are listed in Table 1.

**Table 1:** Main properties of phthalic anhydride [3] [4]

Property	Value
Molar mass	148.12 <i>g/mol</i>
Boiling point	295°C
Melting point	130.8°C
Flash point	152°C
Critical temperature	518°C
Critical pressure	4.72 <i>MPa</i>
Density (at 20°C)	1.53 <i>g/cm<sup>3</sup></i>
Upper explosive limit	10.5 <i>vol-%</i>
Lower explosive limit	1.7 <i>vol-%</i>

### 2.2 Hazards

In the conception of the plant, the hazardous effects of phthalic anhydride must be considered. Indeed, phthalic anhydride is an explosive and flammable compound. The main feedstock, o-xylene, is also flammable and it was decided during the optimisation of the process to work within the flammability limits (0.9*vol-%* ; 6.7 *vol-%*) of o-xylene. The plant is therefore subject to fire hazard. Moreover, phthalic anhydride is corrosive, irritant and dangerous for health as it may generate cough, sore throat and wheezing, among others.

Precaution is thus required while manipulating, synthesising and stocking this product [1][5].

### 2.3 Main Uses

Phthalic anhydride is commercially important, especially in the plastic industry as it is mainly used as raw materials for the production of phthalate plasticisers, unsaturated polyester resins, and alkyd resins [6].

Plasticisers are the primary use of phthalic anhydride and

consume more than 50% of its total production. They are involved in the manufacture of polymers to increase their flexibility. Unsaturated polyester resins are used in the production of fibreglass-reinforced resins, while alkyd resins are required to manufacture solvent-based coatings [7][8].

Finally, phthalic anhydride is involved in the fields of paints and pharmaceuticals [9].

### 2.4 Market

The global market of phthalic anhydride is important as this component has many applications in various fields. In 2020, the market was valued at \$3.7B and is projected to reach \$5.6B by 2030 [10]. Concerning the selling price of phthalic anhydride, one ton is sold between \$40 000 and \$60 000 [4].

The main companies in the production of phthalic anhydride are, among others, BASF, ExxonMobil Corporation, IG Petrochemicals Limited, Mitsubishi Gas Chemical Company, Aekyung Petrochemical Co. Ltd and LANXESS [10][11]. In Belgium, the main production centre is Ostend Basic Chemicals, located in Ostend.

Due to an important use of plasticisers in this area, the largest market is located in Asia-Pacific and it is the fastest-growing one [10]. Since European governments tend to limit the plastics use, phthalic anhydride will be less used in Europe in the future and the European market is expected to decline.

## 3 PRODUCTION PROCESS

### 3.1 Subject of the Integrated Project

The process studied in this Integrated Project is the gas-phase phthalic anhydride production from air and o-xylene as shown in Figure 1.

The pressure and temperature of air and o-xylene (Ox) flows are adjusted by means of the adequate devices to be identical before entering the reactor. The reactor is a fluidized bed reactor which allows the production of phthalic anhydride (PA) and side products, such as maleic anhydride (MA) and benzoic acid (BA). The effluent of the reactor is cooled down, then enters the switch condensers, a complex set of three condensers operating in alternation. The gases are separated from the anhydrides and the benzoic acid, and sent to off-gas treatment. The three other products are carried to the distillation column to extract the desired phthalic anhydride.

The goal of the project all year long was to study, model, and optimise this process in order to produce at least 75 000 tons per year of phthalic anhydride with the constraint that the final product purity must reach 99.9*wt-%*.

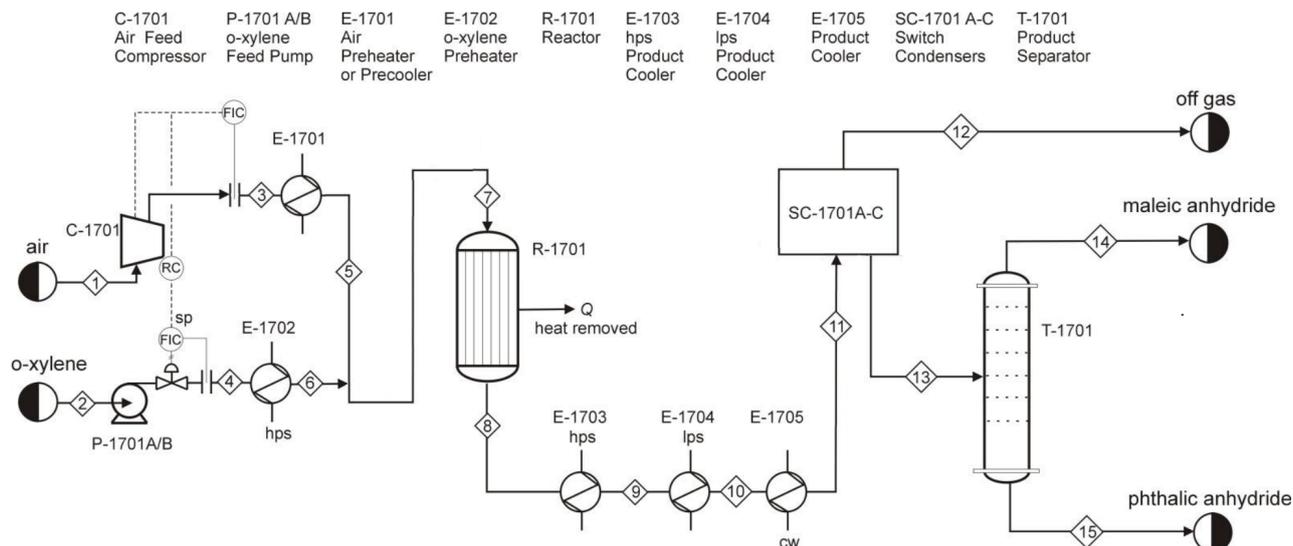


Fig. 1: Initial process flowsheet

### 3.2 Thermodynamics

A critical part of process modelling is the choice of the thermodynamic model, used to represent the liquid and vapour mixtures involved. To determine the most suitable model for both phases, the main characteristics of the process have to be known. The process involves low to moderate pressures ( $< 15 \text{ bar}$ ). In addition, the molecules are mostly polar. The latter entails that the mixtures are non-ideal. Therefore, it is considered that an activity coefficient model is the most suitable for the liquid phase while an equation of state model has to be applied for the vapour phase [12].

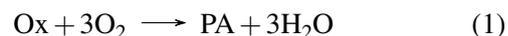
Using the *Aspen* software, the RK-Soave and Peng-Robinson models were tested for the vapour phase while the UNIQUAC and NRTL models were tested for the liquid phase. It was realised that the available databanks do not contain all the binary coefficients necessary to describe the mixtures properly. The *Aspen* software thus considers that the unknown parameters are equal to zero and the results are idealised. Even through screening the literature, the missing parameters were not disclosed in past research.

An alternative to those models could have been predictive models, such as UNIFAC. Unfortunately, some parameters were again missing. Indeed, the functional groups required to represent the anhydride part of the main molecules of interest, phthalic anhydride and maleic anhydride, are not available in the databanks. An additional research in the literature was performed to find information about the anhydride functional group [13] but not all of the interaction parameters could be found, and the UNIFAC model could therefore not be applied.

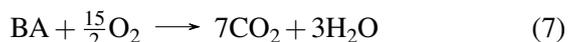
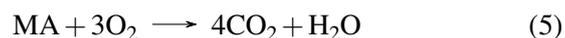
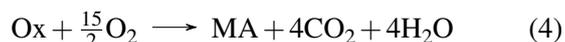
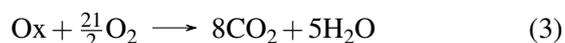
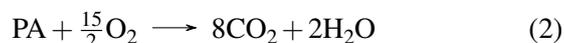
Due to the lack of resources available, the only applicable model for the project is the ideal thermodynamic model.

### 3.3 Kinetics and Catalyst Study

Within the reactor, seven reactions take place [14]. The one of interest is the o-xylene oxidation to phthalic anhydride (abbreviations in Table 11 in the Appendix):



The side reactions are the following:



Based on the Langmuir-Hinshelwood approach, a reaction mechanism is established for each of the reactions 1 to 7 [15][16][17][18]. The rate laws obtained based on those mechanisms are quite complex. To simplify them, it is assumed that the reaction of adsorbed molecules is the limiting step while the other ones are in quasi-equilibrium. Moreover, steady-state approximation for the adsorbed molecules is assumed. Those hypotheses lead to rate laws in the form of Eq. 8:

$$-r_j = k_0 \exp\left(\frac{-E_a}{RT}\right) p_1 p_2 \quad (8)$$

where

- $j$  is the index of the reaction (1 to 7)
- $k_0$  as the units of  $\text{kmol} \cdot \text{m}_{\text{reactor}}^{-3} \cdot \text{h}^{-1} \cdot \text{atm}^{-2}$
- $p_1$  and  $p_2$  are the reactants partial pressures in  $\text{atm}$
- $E_a$  has the units of  $\text{kJ/kmol}$

For each reaction, the values of the activation energies and enthalpies are provided in Table 2. It should be noted that the reaction enthalpies are calculated for the reacting mixture at 240°C and 3 atm. The enthalpies are considered constant for other operating conditions since their variations are negligible.

**Table 2:** Kinetic constants, activation energies and reaction enthalpies

Reaction	$k_0$ [ $\text{kmol}/\text{m}^3 \cdot \text{h} \cdot \text{atm}^2$ ]	$E_a$ [ $\text{kJ}/\text{kmol}$ ]	$\Delta H_r$ [ $\text{kJ}/\text{kmol}$ ]
1	$4.12 \cdot 10^{11}$	112 968	$-1.2 \cdot 10^6$
2	$1.15 \cdot 10^{12}$	129 704	$-3.25 \cdot 10^6$
3	$1.73 \cdot 10^{11}$	119 662	$-4.37 \cdot 10^6$
4	$2.25 \cdot 10^{11}$	116 733	$-2.94 \cdot 10^6$
5	$7.76 \cdot 10^{11}$	127 194	$-1.42 \cdot 10^6$
6	$5.00 \cdot 10^{09}$	112 968	$-1.19 \cdot 10^6$
7	$5.00 \cdot 10^{11}$	123 428	$-3.17 \cdot 10^6$

The formation of phthalic anhydride is favoured by the use of a vanadium catalyst,  $\text{V}_2\text{O}_5$ , which sinters above 400°C. As the reactor is a fluidized bed, the catalyst is made of small spherical particles flowing with the reacting fluid. The study concerning the behaviour of  $\text{V}_2\text{O}_5$  in the reactor showed that the catalyst particles are isothermal and that there are no diffusional limitations. Thus, the system operates in chemical regime.

### 3.4 Reactor

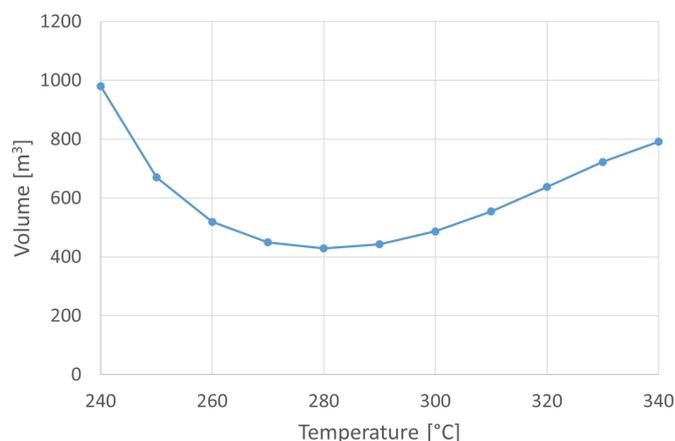
Since the objective is to produce 75 000 tons per year of phthalic anhydride through the oxidation of o-xylene, the reactor is a major part of the design. Two different reactor configurations were considered: staged adiabatic packed bed reactors with inter-stage cooling and an isothermal fluidized bed reactor. Both configurations were first implemented in *Matlab*, then in *Aspen*.

The staging of adiabatic packed bed reactors with inter-stage cooling was discarded due to the exothermicity of the reactions taking place. Indeed, as can be seen in Table 2, the reactions are highly exothermic, especially the combustion ones. In addition, the latter are activated at higher temperatures than the oxidation reactions yielding the products. Therefore, when the temperature increases, additional heat is released which leads to a further increase in the temperature. This behaviour entails a sharp increase in the temperature profile of the reactors. Consequently, the temperature that can be reached within one adiabatic reactor has to be further limited for safety reasons. This leads to an increase in the number of adiabatic packed bed reactors needed to reach the desired production, and thus an increase in the overall investment cost. Therefore, the isothermal fluidized bed reactor is the best configuration from a safety and economic point of view.

This isothermal fluidized bed reactor is modelled in *Matlab* as a plug-flow reactor with 10% of the feed directly by-passed to the outlet of the reactor. By introducing the by-pass, the model is closer to the real behaviour of a fluidized bed. The isothermicity of the reactor is maintained with the help of heat transfer tubes located within the reactor, with *Dowtherm A* as cooling fluid [14].

To model the reactor, the correlation of Wen and Yu [19] (available in the Appendix) is applied to compute the minimum fluidization velocity. This velocity is involved in the definition of the cross-sectional area of the reactor and thus impacts the dimensions of the reactor. In addition, a correlation is given for the pressure drop along the fluidized bed [14] which also impacts the dimensions of the reactor. However, those correlations are not directly available in *Aspen* due to the use of a plug-flow reactor with a by-pass to represent the fluidized bed. Therefore, the optimisation of the reactor has to be performed in *Matlab*. The optimised configuration is then implemented in *Aspen*.

The goal of the optimisation is to minimise the reactor dimensions as well as the inlet flow rate of o-xylene by finding the optimal operating conditions for the reactor. In particular, the working temperature is a crucial parameter which has to be optimised with care due to the competition between the desired reactions yielding the products and the undesired combustion reactions. Figure 2 shows the evolution of the volume as a function of the temperature obtained by varying the inlet flow rate to target a production of 75 000 tons per year of phthalic anhydride while keeping the already optimised parameters constant. Figure 2 shows that a minimum volume is obtained for a specific temperature, equal to 280.5°C. Beyond this optimal temperature, the combustion reactions gain in importance and thus increase the required volume and inlet flow rate to reach the targeted production.



**Fig. 2:** Evolution of the reactor volume as a function of the temperature, keeping everything else constant and varying the inlet flow rate.

Other parameters are also optimised, e.g. the inlet pressure. It is concluded that the most appropriate inlet pressure of the reactor is  $5.7 \text{ atm}$ , based on the calculation of the pressure drop and knowing the optimal separation pressure from the literature [20].

The optimised reactor conditions are summarised in Table 3. Those conditions allow to produce the required 75 000 tons per year of phthalic anhydride.

**Table 3:** Optimised reactor conditions

Parameter	Value
Temperature	$280.5^\circ\text{C}$
Inlet pressure	$5.7 \text{ atm}$
Outlet pressure	$2.18 \text{ atm}$
Pressure drop	$3.52 \text{ atm}$
Fluidization velocity	$1.92 \text{ m/s}$
Total inlet flow rate	$3824 \text{ kmol/h}$
Inlet o-xylene flow rate	$114.73 \text{ kmol/h}$
Inlet o-xylene mole fraction	0.03
Diameter	$4.50 \text{ m}$
Height	$26.98 \text{ m}$
Volume	$428.30 \text{ m}^3$

With this configuration, a molar yield of phthalic anhydride of 67.23% and an o-xylene conversion of 83.05% is obtained.

Those conversion and yield are quite low as compared to the literature (cf. Section 6.2). This is due to the model used to represent the reactor. Indeed, due to the by-pass, 10% of the feedstock can simply not be used. As a result, the available amount of reactants for the reactions is 90% of the input. This corresponds to the maximum yield. Following the modelling, a conversion of 92.2% of those 90% is possible. The overall yield is then of 83.05%.

### 3.5 Separation

After being produced in the reactor, phthalic anhydride must be separated from the other products of the reactor effluent in order to retrieve a final product with the desired purity.

#### Switch Condensers

The role of the switch condensers is to separate the anhydrides and the benzoic acid from the other components.

In reality, the switch condensers are a complex set of three condensers operating in alternation so that the production process can be continuous. The operating process of a condenser is the following: the stream entering the condenser is first cooled to  $130^\circ\text{C}$  by cold oil so that the anhydrides and the benzoic acid desublimates. Then, the gases are expelled and go to the off-gas treatment. After-

wards, the heated oil passes again through the condenser to melt the solids and heat them up to enter the distillation column as liquid. The process continuity is ensured by the fact that the different steps are conducted simultaneously in the condensers but with a time offset. Indeed, while the first condenser is cooled down for the desublimation, the second one is heated up to liquefy the solids, and the third one is brought back to its initial temperature.

In *Aspen*, the switch condensers are modelled as a simple components separator, more precisely using a *Sep* model [14]. This bloc sends all of the light gases, o-xylene, 1% of the phthalic anhydride and 2% of the maleic anhydride to the off-gas treatment. However, this model is oversimplified and does not represent the heat exchanges nor the complex set of operations allowing them to separate the anhydrides and the benzoic acid from the other components. Thus, two additional heat exchangers are added.

The first heat exchanger is used to represent the desublimation step ( $170^\circ\text{C} \rightarrow 130^\circ\text{C}$ ). The gases are then expelled with the *Sep* bloc. Those two units represent the first condenser. The melting and heating of the solids are modelled with the second heat exchanger ( $130^\circ\text{C} \rightarrow 150^\circ\text{C}$ ), corresponding to the second condenser. However, because of the static point of view used in *Aspen*, the dynamic aspect of the switch condensers cannot be implemented [21]. Thus, the third condenser is not considered in the model.

As the *Aspen* model is simplified as compared to reality, the operating conditions are chosen depending on what is found in literature instead of using sensitivity studies. At the entry of the switch condensers operating at atmospheric pressure, a temperature around  $170^\circ\text{C}$  is usually used [20]. The liquid sent to the distillation column is exiting the condensers at  $150^\circ\text{C}$ .

#### Distillation Column

The second separation unit is the distillation tower, used to extract phthalic anhydride with a sufficient purity. The distillation column was first studied using the McCabe-Thiele diagram and then implemented using a *RadFrac* model in *Aspen*. To design the column and choose its internals, an economic analysis is performed, based on the Turton's book methodology [22]. The goal is to find the pair (number of stages; reflux ratio), written  $(N; v)$ , minimising the total costs of the distillation unit.

To avoid extra construction costs related to vacuum operating conditions, it was chosen to operate the distillation column at atmospheric pressure. A distillation tower is composed of a vessel with internals. In this project, two types of internals are considered: sieve trays and structured packings.

The capital cost annuity, the operating costs and the total costs are computed depending on different pairs ( $N; \nu$ ). The number of stages and the reflux ratio are dependent on each other. They vary to meet a constraint: the purity of phthalic anhydride in the bottom stream of the distillation column must be 99.9wt-%. The costs are computed with the *Aspen* data obtained and the Turton's methodology [22]. The results are plotted in Figure 3 depending on the internals.

As expected, the capital cost annuity decreases with the reflux ratio, while the operating costs increase. When the reflux ratio is getting closer to zero, the capital cost annuity tends to increase asymptotically [23].

The aim of the economic analysis is to minimise the total costs. In Figure 3, two minima of the total costs can be seen for each type of internals, an absolute minimum and a local minimum. They are given in Table 4.

**Table 4:** Coordinates of the total costs minima

(a) Local minima coordinates

Internals	$H/D$ [-]	$N$ [-]	$\nu$ [-]	Total Costs [\$/yr]
Sieve Trays	49.47	30	1.2	241 594
Packings	37.97	30	1.2	300 152

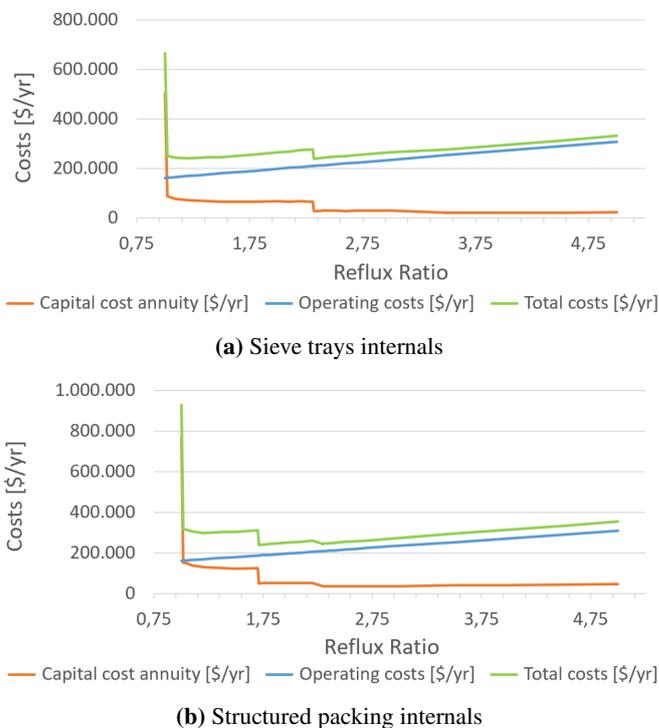
(b) Absolute minima coordinates

Internals	$H/D$ [-]	$N$ [-]	$\nu$ [-]	Total Costs [\$/yr]
Sieve Trays	27.14	19	2.32	239 818
Packings	24.77	23	1.71	239 220

The local minima cannot actually be considered because of the constraints on the height-to-diameter ratio ( $H/D$ ) of the column. This ratio must not be higher than 30 for safety reasons - stresses caused by wind can lead to an unstable column. However, the values of  $H$  and  $D$  are impacted by the choice of internals. Therefore, if the internals chosen lead to  $H/D > 30$ , these internals are considered inappropriate for the column and must not be used. Moreover, if  $25 < H/D < 30$ , cost penalties are applied: the vessel price is doubled. Because of those constraints, it is not possible to use the pairs ( $N; \nu$ ) with a reflux ratio below 1.8 for the sieve trays, or below 1.4 for the packed internals. As a consequence, the local minima have to be discarded from the possible choices.

In Figure 3, the curves of the capital cost annuity should smoothly decrease with the reflux ratio, reach a minimum, then smoothly increase. However, for the sieve trays, a sharp decrease in the capital cost annuity is visible in Figure 3a between the reflux ratios 2.31 and 2.32. The vessel costs penalties explain this jump. Indeed, for  $\nu = 2.31$ , the ratio is  $H/D > 25$ , while for  $\nu = 2.32$ , it is

$H/D < 25$ . Therefore, the constraint on the vessel costs decreases, leading to a significant decrease in the capital costs, and thus a significant decrease in the total costs. A similar behaviour is visible for the packed internals in Figure 3b between the reflux ratios 1.70 and 1.71.



**Fig. 3:** Evolution of the distillation column costs depending on the internals and the reflux ratio

Comparing the two internal types, it can be seen in Table 4 that the absolute minimum is lower for packed internals than for sieve trays internals. However, the difference is only \$600, which is not enough to choose the internals. Indeed, the methodology of calculation induces an error of around 10%. As the difference is only \$600, i.e. smaller than 10%, none of the internals can be preferred in terms of economic aspect.

Nonetheless, operating costs represent approximately 4/5 of the total costs. As their impact is more significant, it is considered more important to minimise the operating costs than the capital cost annuity. Furthermore, the heat fluxes increase linearly with the reflux ratio [23], thus the operating costs of the column (heating and cooling) also increase. Thus, minimising the reflux ratio seems the best economic choice. By limiting the amount of energy required for the column, the possible profits are maximised as the utilities not used by the column devices can be used elsewhere in the process (cf. Heat Integration).

Therefore, packed internals are considered more suitable. Indeed, at the absolute total costs minimum, the operating costs of the packed internals (\$187 928) are lower than the ones of the sieve trays (\$210 624).

The optimised distillation column configuration used to produce the required 75 000 tons of phthalic anhydride per year is given in Table 5. The total costs of the distillation column are \$239 220.

**Table 5:** Optimised distillation column configuration

Parameter	Value
Operating pressure	1 atm
Condenser temperature	203.5°C
Reboiler temperature	284.0°C
Number of stages	23
Reflux ratio	1.71
Internals	Packings
Diameter	0.61 m
Height	15.12 m

### 3.6 Heat Integration

The operating conditions of the main units of the process being set, the process heat integration can be performed.

The goal of a heat integration is to minimise the overall energy consumption of the process. This is done by performing a pinch analysis, which leads to the implementation of a heat exchanger network in which the energy released in one unit is reused in another unit of the process. The heat can also be used to produce a valuable energetic product. Once this is done, the heat exchangers are designed. Their purpose is to bring the reacting fluid to the required operating temperature.

#### Pinch Analysis

The minimal quantities of hot and cold utilities necessary for the process are determined through the pinch analysis. The goal is to find the theoretical minimum energy consumption of hot and cold utilities.

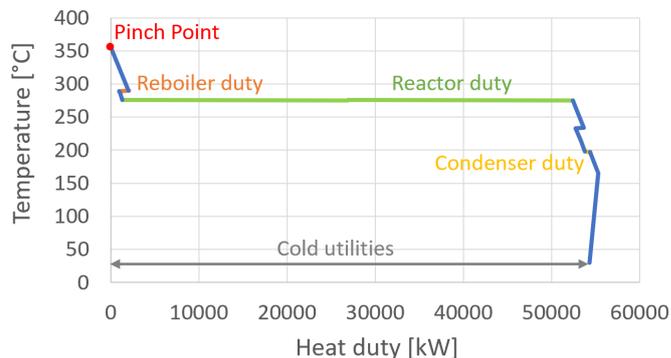
The minimum temperature difference,  $\Delta T_{min}$ , is set to 10°C. In this process, six hot streams and two cold streams are found. One of the cold streams is divided into three to take the phase change into account. Those streams are listed in Table 6.

**Table 6:** Stream table

Unit	Hot stream	Unit	Cold stream
E-1701	H1	E-1702	C1.1
E-1703	H2	E-1702	C1.2
E-1704	H3	E-1702	C1.3
E-1705	H4	Reboiler	C2
Condenser	H5		
Reactor	H6		

Listing the different hot and cold streams of the process allows plotting the Grand Composite Curve, GCC, shown

in Figure 4. The pinch point can be found at the upper extremity of the curve. With an optimal heat recovery system, only cold utilities should be provided to the process.

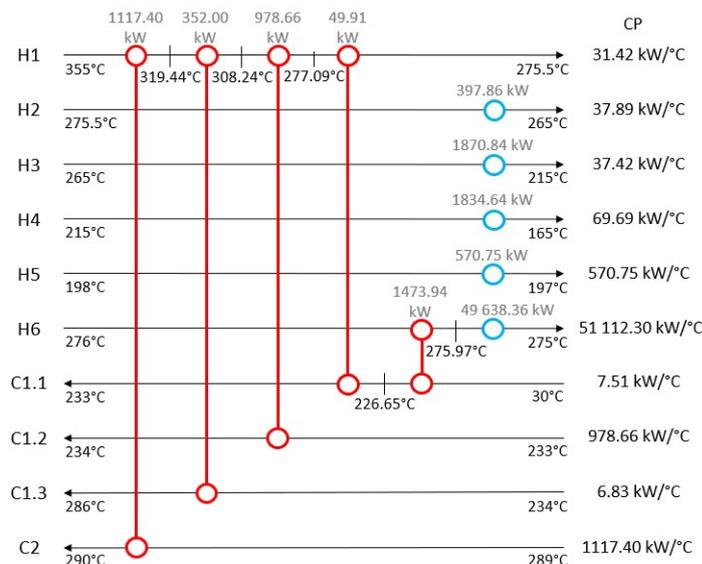


**Fig. 4:** Grand Composite Curve

#### Heat Exchanger Network

The energy recovery system is modelled using a heat exchanger network. As observed previously with the Grand Composite Curve, only cold utilities can be used for the process and no hot utilities can be provided. Indeed, the heat needed by the cold streams in order to reach the required temperatures must be entirely provided by the hot streams.

The heat exchanger network can be found in Figure 5. The red circles represent the heat exchanged between two streams while the blue circles represent the required cold utilities.



**Fig. 5:** Heat exchanger network

Stream H1 does not require any cold utility as the heat exchanges with cold streams are sufficient to ensure that H1 reaches its required temperature. Thus, only five cold utilities are needed for a total of 54 312 kW.

As seen on Figure 5, two heaters are required: one that transfers heat from H1 to the reboiler of the distillation column (H-1701 in Figure 6), and one that transfers some of the heat produced by the reactor to C1.1 (H-1702 in Figure 6). One heat exchanger, E-1701-2, is also used, in which the hot fluid coming from H-1701 is used to heat up the cold fluid coming from H-1702.

The other heat exchangers, E-1703, E-1704 and E-1705, are used to reach 170°C at the inlet of the switch condensers and to produce respectively high-pressure steam (hps), medium-pressure steam (mps) and low-pressure steam (lps) from the heat recovered. Those energetic products can be sold.

### Heat Exchanger Design

Each heat exchanger of the process is modelled using the *EES* and *Aspen* softwares. For each of them, the shell & tube model is considered, the hot fluid passing through the tubes and the cold fluid in the shell.

The design procedure described in the Kakaç reference book [24] is followed for exchanger E-1703. It is chosen to realise the design on *EES* for the "worst-case approximation" and then to implement and rate this design on *Aspen* to obtain more realistic conditions.

The design obtained for E-1703 is given in Table 7, where the hot fluid is the reactor effluent and the cold fluid is high-pressure water, used to produce hps.

The high pressures involved in the heat exchange require the use of high-pressure enclosures, while the corrosiveness of phthalic anhydride induces the use of stainless steel equipment.

### 3.7 Compressors and Pumps

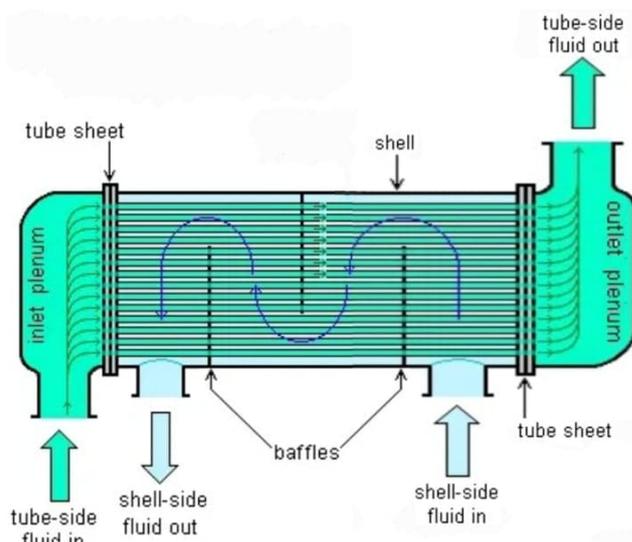
In the process, a two-stage compressor with inter-cooling is used. Indeed, a single-stage compressor cannot be used as the total compression ratio to be achieved through this unit is 7.6, while it should remain between 3 and 5 for a single-stage compressor. The air exiting this unit is at 360°C and 611 kPa. This pressure is slightly higher than the required pressure before entering the reactor since the pressure drops occurring in the following units have to be taken into account.

Similar pressure drops have to be considered for the o-xylene flow. The pressure of this flow exiting the pump is thus of 615.5 kPa, at a temperature of 25.4°C. The isentropic efficiency of this compressor is 60% while it is 80% for the pump.

In the mixer of streams 5 and 6, a pressure drop of 10 kPa is considered, while it is 10 and 15 kPa in the cooler H-1701 and the heater H-1702 respectively.

**Table 7:** Design of E-1703

Tubes		Shell		Baffles	
Pass	1	Pass	1	Spacing	0.362 m
N	1253	N	1	N	3
$D_{out}$	0.019 m	$D_{out}$	0.962 m	Type	Triple
Length	1.82 m	$D_{in}$	0.914 m	Cut	Vertical
Parameter	Hot fluid	Cold fluid			
$\dot{m}$ [kg/h]	119 205	532.5			
$T_{in}$ [°C]	280.6	20			
$T_{out}$ [°C]	270	256.3			
$P_{in}$ [kPa]	220.5	4200			
$P_{out}$ [kPa]	191.4	4197.7			
$\Delta P$ [kPa]	29.1	2.3			
Heat exchanged [kW]		402.8			



**Fig. 7:** Shell & Tube [25]

### 3.8 Final Flowsheet

Each of the optimised units of the process as well as the heat integration are implemented in *Aspen*. This leads to the process flowsheet shown in Figure 6.

Considering a year as 8 000 operating hours, this process produces 75 101 tons of phthalic anhydride per year with a purity of 99.91wt-% from the oxidation of o-xylene. 97 446 tons of o-xylene are purchased per year. Part of this o-xylene also leads to the production of 12 388 tons of maleic anhydride with a purity of 94.24wt-%, which is a valuable co-product of this process.

It can be noticed that 830 tons of phthalic anhydride are lost every year in the separation units. The off-gas which must be treated contains 7.45wt-% of CO<sub>2</sub> and 2.03wt-% of organic components. This fraction of organic components corresponds to 759 tons per year of phthalic anhydride (from the 830 tons), 238 tons of maleic anhydride and 16 618 tons of o-xylene.

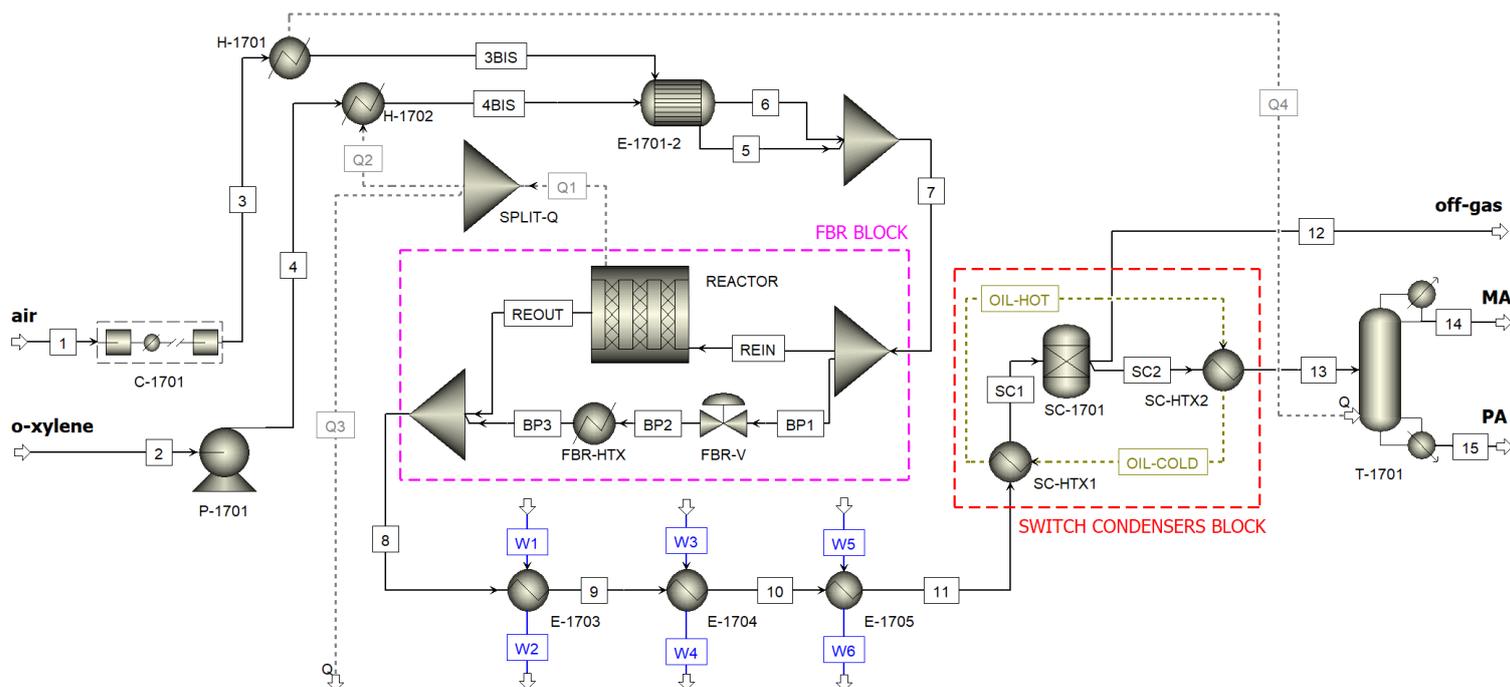


Fig. 6: Final global process flowsheet in Aspen

In addition, the heat integration shows that no heat must be provided to the process. Indeed, the process is self-sufficient in terms of heat due to the high exothermicity of the reactions. The extra heat available is used to produce 529 105 tons of high-pressure steam (hps), 19 824 tons of medium-pressure steam (mps) and 19 768 tons of low-pressure steam (lps) per year.

Finally, the stream tables associated to the final flowsheet can be found in the Appendix (Tables 16 and 17).

## 4 LIFE CYCLE ASSESSMENT

As phthalic anhydride is an important industrial chemical product, especially for the large-scale production of plasticisers used in the production of plastics.

With the significant increase in the global demand for phthalic anhydride, it becomes essential to make production processes more and more environment-friendly. Although the environmental aspect is generally considered less important compared to the economic aspect, it is not only a question of ethics. Indeed, the environmental impact can be materialised financially and influences the profitability of the plant *via* taxes on CO<sub>2</sub> emissions, which will be discussed in the following sections. Therefore, the Life Cycle Assessment (LCA) of the process has to be performed.

In this report, the LCA is realised using a "cradle-to-gate" approach, which only includes the raw materials and the production stage in the life cycle evaluation.

### 4.1 Goal and Scope

The phthalic anhydride production process is mainly based on the partial oxidation of o-xylene, the main raw material, with oxygen obtained directly from air. The energy requirements of the entire process are divided into two contributions: the electricity required to operate the pump, the compressor and the switch condensers, and the cooling/heating energies determined through the pinch analysis.

At the end of the process, off-gas is produced. It must be treated before being discharged into the atmosphere because it contains a small amount of o-xylene, which is harmful for the environment. Moreover, the CO<sub>2</sub> present in this treated off-gas contributes to the global warming indicator. It was decided to treat the off-gas by adsorbing the organic pollutant, o-xylene, on activated carbon. The treatment of the polluted activated carbon is not taken into account in the study.

The goal of the process is to produce 75 000 tons per year of phthalic anhydride while minimising the environmental impacts. In order to compare data, a functional unit of 1 kg of phthalic anhydride, the main product, is chosen. However, maleic anhydride is also taken into account considering its production and its high economic value.

### 4.2 Location Choice

To be competitive on the phthalic anhydride market, the location of production facilities has to be considered. The choice of the location is determined by a trade-off between the environmental and economic aspects. Two lo-

cations stand out: China and Western Europe. In both cases, the local market is studied considering that the products are sold near the plant.

On the one hand, China is considered since Asia Pacific accounts for a major market share of phthalic anhydride - up to 52% in 2019 - and it is expected that the market will continue to rise. The Chinese phthalic anhydride market is driven by a rise in various end-user industries, including building and automotive, where phthalic anhydride is used as raw materials [10][26].

In addition, the feed stream of o-xylene can be purchased from Sinopec (Beijing, China), which is one of the world's largest o-xylene producer [27]. Due to the proximity, it can reduce the environmental impact of o-xylene transport. Regarding electricity, the Chinese electricity is cheaper than the European one, referring to *globalpetrol-prices.com* [28]. The main drawback of building in China is that more than half of Chinese electricity is generated using coal [29], which is an extremely polluting source of energy.

On the other hand, Western Europe is also considered since the energy sources used to generate electricity are more environment-friendly [30], as it can be observed in Figure 8. In addition, European raw materials are cheaper and products prices are higher. Even after taking the European tax on CO<sub>2</sub> emissions into account, building the plant in Europe remains economically more interesting (cf. Cost Analysis section). The tax value is defined as the quantity of CO<sub>2</sub> produced per year in the off-gas multiplied by EU carbon prices per ton [31]. The main drawback of building in Europe is that the market can be saturated.

Therefore, the location has to be established depending on the purpose of the business. Either build in China where the market is more flourishing but with a higher environmental impact, or build in Western Europe for cheaper and greener production but probably with minor market shares.

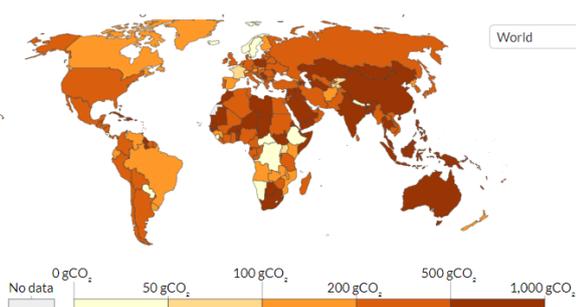


Fig. 8: Carbon intensity of electricity, 2021 [32]

### 4.3 Life Cycle Inventory (LCI)

In this study, the overall emissions, feed and product streams, and flows going through the system are transcribed in terms of functional units. Those variables are illustrated in Tables 12 and 13 in the Appendix, which represent respectively the input and output data of the phthalic anhydride process. Those data are used in the *Simapro* software to compute the figures shown in the following section.

### 4.4 Life Cycle Impact Assessment

The environmental impacts of the process are computed with the *CML-IA* method.

Figures 9, 10, and 11 show the results obtained by the analysis of the process using *Simapro*. This LCA software provides the insights needed to reduce the environmental footprints of products. In this analysis, infrastructure processes and long-term emissions are excluded.

As discussed in the section on the location choice, two production places are considered: China and Western Europe. These two locations are compared in Figure 9, which highlights the life cycle analysis of

- 1 kg of phthalic anhydride produced by the studied process in China,
- 1 kg of phthalic anhydride produced by the studied process in Europe,
- 1 kg of phthalic anhydride produced worldwide - comes from the *Ecoinvent*, a *Simapro* database.

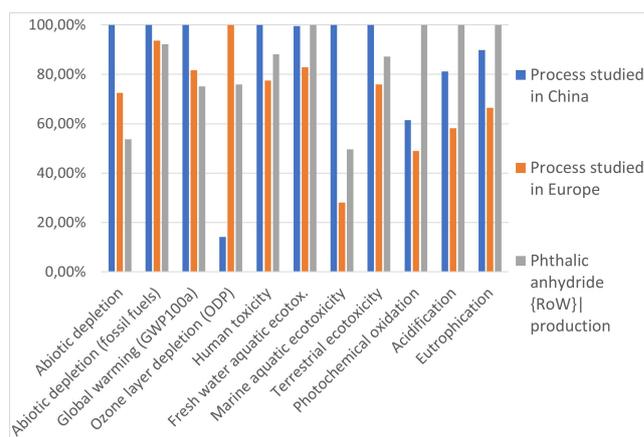


Fig. 9: LCA: Comparison of location

One of the main indicators illustrated in Figure 9 is the global warming potential (GWP). For the studied process, the GWP in China is 19% higher than in Europe, and 25% higher than the one of a standard process. It shows the high environmental impact of the studied process and that measures must be taken to reduce it.

Another important indicator is the abiotic depletion associated to fossil fuels. For the studied process in China, this indicator only differs by 7% compared to the European process, and by 8% compared to a standard process.

More generally, the indicators calculated with the studied process are in the order of magnitude of those calculated with a standard process. Nevertheless, regarding the most important parameters, the studied system in China or in Europe is characterised by slightly higher values. Therefore, the studied process is coherent but has a higher environmental impact.

Figures 10 and 11 represent the LCA for 1 kg of phthalic anhydride produced considering the studied process respectively built in China and in Europe.

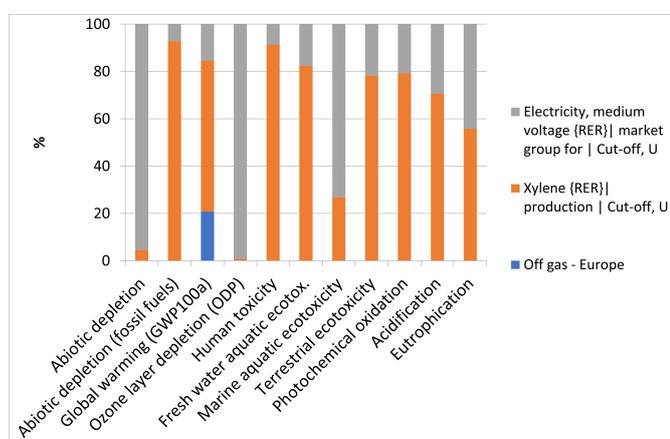


Fig. 10: LCA results in Europe

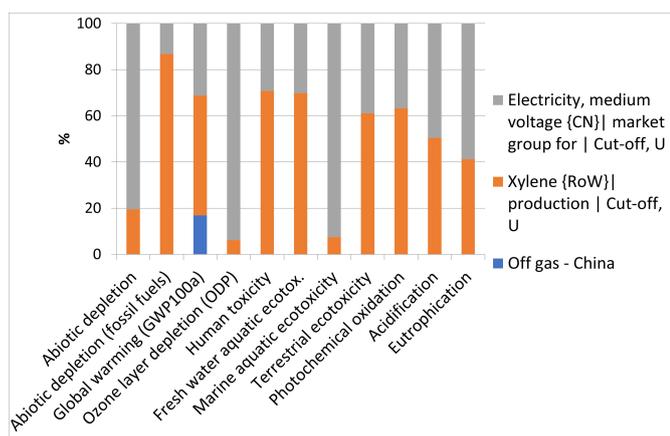


Fig. 11: LCA results in China

The three indicators evaluated in Figures 10 and 11 are the Chinese electricity, the main raw material (o-xylene) and the amount of carbon dioxide contained in the off-gas. As it can be noted, there is no heat indicator as the process is self-sufficient in terms of hot utilities.

By comparing Figures 10 and 11, it can be seen that in both cases the electricity contribution to the environmental impact of the studied process is important, in particu-

lar for the abiotic depletion, the ozone layer depletion, the marine aquatic ecotoxicity and the eutrophication. In addition, regarding the global warming indicator, the electricity part is larger when the process is located in China. As mentioned in the section about the location choice, this can be explained by the fact that the Chinese electricity is mainly produced from coal combustion [33]. Therefore, the relative contribution of o-xylene in the global warming is lower in China due to the larger part of Chinese electricity.

The carbon dioxide contained in the off-gas is only involved in global warming potential. Indeed, the relative part of off-gas is lower in China as the total global warming potential emitted in the Chinese plant is larger.

Table 8 focuses on the global warming potential (GWP) in the process studied in China and in Europe as well as the average data in Europe and in the world, the two latter being provided by the *Ecoinvent* database.

**Table 8:** Global warming potential (GWP) [ $kgCO_2eq.$ ] depending on the location of the plant

	Europe	China	Average data in Europe	Average data in the world
GWP	2.76	3.39	2.20	2.54

Although inventories and yields differ according to the region in the world, Table 8 shows that the global warming impact is much higher in China than in Europe, or even if compared to the average values of phthalic anhydride units in the world. The data of the studied process in Europe seems to be close to the *Ecoinvent* data base. It supports the argument in the *location section* that European processes are more environmentally friendly than those in China.

#### 4.5 Conclusion

Some data and graphs should be interpreted with caution. Indeed, elements had to be neglected or simplified, such as the impact of the treatment of activated carbon used to remove the organic pollutant of the off-gas.

Considering all previous discussions, building the plant in Europe seems to be more interesting than in China as it leads to a more eco-friendly production with a higher profit margin. Unfortunately, the European market is very saturated. Since this last parameter is out of the scope of this project, the location choice can hardly be made and should be subject to a further analysis of the local market.

## 5 COSTS

A crucial step in the design of a process is the cost analysis [34]. Indeed, if the process is not profitable, it

should not be built. In this section, costs are evaluated and analysed. Their computation is divided in two sections: CAPEX and OPEX, respectively, the capital expenditures and the operational expenditures. Then, a cash flow diagram is used to provide a long-term economic view of the plant profitability.

The choice of the plant location is also discussed from an economic point of view.

### 5.1 CAPEX

The CAPEX evaluation is done according to the empirical calculation method from the Turton's book [22]. This method includes the effect of pressure and material choice in the costs computation. In this case, all surfaces in contact with phthalic anhydride should be in 304 stainless steel to avoid corrosion. To be able to eventually improve the process with a recycling loop in the future, it is decided to use 304 stainless steel for all equipment.

The results obtained following the Turton's method are based on the economic situation of 2001, and are then adapted to the 2022 economic situation by increasing the price of the units with respect to the increase in the chemical engineering plant cost index (CEPCI). This index grew from 394.3 in 2001 to 785.9 in April 2022 [35].

There are three unit prices that are not computed based on the Turton's method: the reboiler and condenser of the distillation column, and the switch condensers. The prices of the reboiler and condenser of the column are computed assuming that they represent 10 to 20% of the column costs. Similarly, the switch condensers costs are estimated using assumptions from the literature: it is found that the switch condensers represent approximately 25% of the investment cost of the whole process [36].

### 5.2 OPEX

There are different costs to be considered when evaluating the OPEX.

The two major ones are the utility costs and the raw materials costs. Utility costs are based on the price of the cold water that is used in the heat exchangers and on the price of the electricity that provides energy to the pumps, switch condensers and compressors. The water and steam prices used are available in the Turton [22]. The electricity price is not the same depending on the location considered (cf. Table 9).

The raw materials costs take into account the prices of o-xylene and air, and also include the catalyst price. It is decided to change the catalyst of the reactor each year. Its price is approximated to \$2.25/kg. This price should be refined, but it can be seen in Figure 12 that the price of

the catalyst is negligible as compared to the raw materials price. The raw materials costs are fluctuating with time (cf. Figure 13) and are different depending on the location of the plant (cf. Table 9).

**Table 9:** China and Europe prices

	China	Europe
O-xylene [\$/ton]	1224	875
Phthalic anhydride [\$/ton]	1320	1 143
Maleic anhydride [\$/ton]	2080	1 475
Electricity [\$/kwh]	0.12 [37]	0.1 [38]
Average salary [\$/yr]	20 372 [39]	36 900 [40]
Tax rate [%]	25 [41]	45.6 [38]

On the other hand, other costs also have to be taken into account, e.g. the water-waste treatment and labour cost associated to the employee's salary. According to the Turton's method [22], water-waste treatment cost is \$0.056/ton. Concerning the labour cost, in this work, it is considered that there are three teams working per day. Each operator works 49 weeks per year with five shifts per week. Assuming that the factory operates continuously, a year represents 1 095 shifts. Therefore, 4.5 operators are required for each working position. The number of those working positions  $N_{WP}$  is expressed with Eq. 9:

$$N_{WP} = (6.29 + 31.7P^2 + 0.23N_{NP})^{0.5} \quad (9)$$

where  $P$  and  $N_{NP}$  are respectively the number of particular - 0 in this case - and non-particular processing steps - 13 in this case. For this plant, according to the number of working positions and the number of operators necessary for each of them, a total of 14 operators are required. Then, considering the average salary (see Table 9), the total labour cost can be computed.

The depreciation also has to be evaluated. The depreciation is estimated with the Straight-Line method (Eq. 10):

$$D = FCI \frac{1 - (1 - 0.2)^n}{n} \quad (10)$$

where  $n$  is the operating time of the plant, which is here 10 years, and the FCI is the capital cost.

Finally, the total manufacturing cost can be obtained:

$$COM = \frac{C_{RM} + C_{WT} + C_{UT} + D}{0.81} + \frac{C_{OL}}{0.366} + \frac{FCI}{5.548} \quad (11)$$

The FCI term in this expression stands for the additional costs such as maintenance, small supplies, and so on.

The chemical components prices (cf. Table. 9) for China are based on the February 2022 value given by the *Ceic-data* website [42] while the European prices are based on the October 2019 value of the *Icis* website [43]. Therefore, both cannot be compared. However, the same kind of cost difference between the respective components in

both locations is observed in different sources over the years [42][43][44][45]. The hypothesis is that o-xylene is \$100/ton more expensive in China than in Europe. Moreover, it is considered that both phthalic anhydride and maleic anhydride are sold \$200/ton higher in Europe than in China. Then, for all the following calculations, when considering Europe, the o-xylene, phthalic anhydride and maleic anhydride are respectively considered with the following prices : \$1124/ton, \$1520/ton and \$2280/ton. The ICIS 2019 cost for Europe is then discarded. As prices fluctuate greatly over time, it is not possible to compare two locations without taking into account the variation in price over time.

As France has one of the lowest CO<sub>2</sub> emissions for the production of electricity and one of the cheapest one, it seems preferable to work e.g. in France near the Belgian and German borders. Indeed, if the price of the chemical components in those countries are more interesting, it is easier in terms of transport.

If only the chemical components cost as well as the electricity cost are considered, then Europe is clearly more interesting than China. However, it is also important to take the tax into account. Indeed, the tax rate in Europe is more important than in China. In addition, in Europe, there are measures in place to push towards a more environmentally friendly production and therefore, there is an additional tax on CO<sub>2</sub> production.

### 5.3 Results and Discussion

Based on what is explained previously, the CAPEX (\$55M) and OPEX (China : \$180M/y, Europe : \$174M/y) can be computed, as shown in Figure 12. As it can be observed, the major cost from the OPEX comes from the raw materials and the utilities. For this term, it is interesting to see that the cooling water cost is negligible compared to the electricity cost, which accounts for 99.9998% of the total utility cost. The OPEX varies with the location. In both cases, the labour cost is quite negligible even if it is slightly higher in Europe.

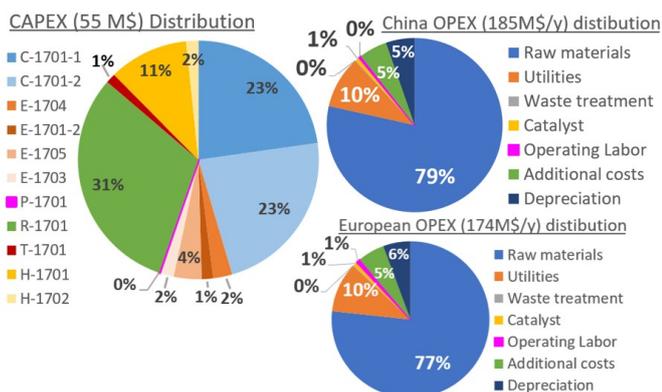


Fig. 12: Costs distribution

On the contrary, the CAPEX is constant as it only depends on the Turton method which does not take the location into account. When compared to the CAPEX, the OPEX is much more important. Indeed, as it is summed up with the capital cost annuity, the OPEX counts for around 94% of the total cost in both cases. The units with the least weight in the CAPEX are the distillation column and the pumps. On the other hand, the compressors are very expensive units as well as the switch condensers.

The revenue can also be studied in the same way. The two major terms of the revenue (resp.  $\approx 80\%$  and  $\approx 20\%$ ) are the phthalic anhydride and maleic anhydride (see Table 9). Moreover, as the process is highly exothermic, the heat excess can be used to produce some high, medium and low-pressure steams. The price of those energetic products is found in the Turton. They are, however, negligible compared to the other revenues. In China, the revenue would be of \$125M/yr while it is estimated to \$140M/yr in Europe.

Now that those costs are known, the profitability analysis can be realised. However, before performing any complex computation, it should be noted that the actual estimated revenue does not balance the OPEX, neither for China nor for Europe. In this case, running the installation even one year would conduct the company to lose money. This is even more important if the plant is in China than in the case it is in Europe. A bigger revenue is then necessary to balance all costs.

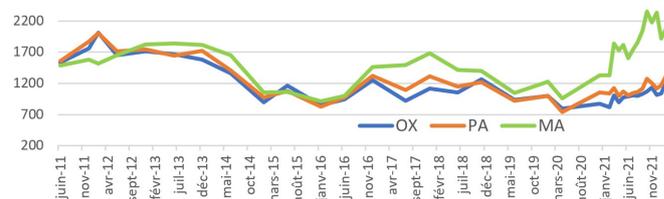


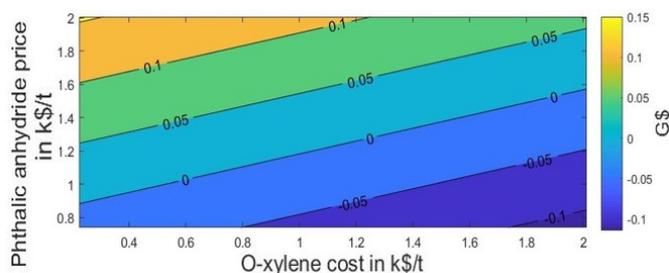
Fig. 13: Chemical components prices in China [\$/ton] [42]

The prices variations (Figure 13) have then been studied. Unfortunately, this kind of data is only available for China. However, it is reasonable to say that the same kind of behaviour would be observed in Europe if only the qualitative aspect is considered.

Since the o-xylene cost ( $\approx 77\%$  of \$174M/yr) is the major impacting chemical components and the phthalic anhydride the second major one ( $\approx 80\%$  of \$140M/yr), the variation of both is studied. The balance between raw materials and products prices is given by Eq. 12 where  $P_i$  stands for the price and  $M_i$  stands for the materials flow.

$$B = P_{OX} \cdot M_{OX} + P_{PA} \cdot M_{PA} + P_{MA} \cdot M_{MA} \quad (12)$$

According to this formula, and by making the different prices vary in between the range exposed in Figure 13, Figure 14 is obtained.



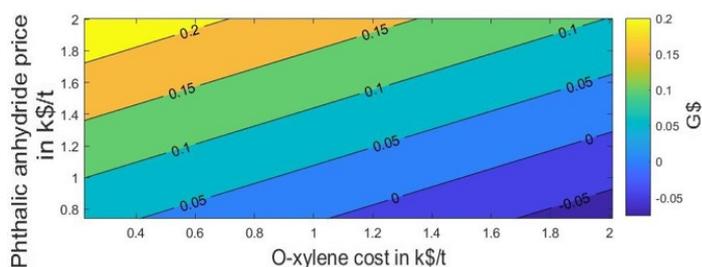
**Fig. 14:** Color scale diagram of the balance of raw materials and products prices in G\$/yr for the plant

Quite logically, with Figure 14, it is noticeable that the balance is maximised when the phthalic anhydride prices are maximised and the o-xylene price is minimised. However, Figure 13 shows that this is never the case in the Chinese market. Indeed, both phthalic anhydride and o-xylene prices are usually quite close to each other. It has been determined that the balance B should be around \$85M/yr for the Chinese market. When associating the results of Figure 13 and Figure 14, this case is never encountered.

Concerning the European market, according to the previous price hypothesis, the difference of price between o-xylene and phthalic anhydride is about \$300/ton and both prices are under \$2000/ton. On the other hand, it was determined that the balance B should be at least of more or less \$80.5M/yr for the European market (this value is obtained considering the CO<sub>2</sub> tax). This combination is more feasible but is still very difficult to achieve.

This is quite astonishing given that some companies currently produce phthalic anhydride using this method. Indeed, the literature review, as exposed later on, shows that those companies have a much higher yield. The installation presented in this report gives a yield of 77.1 wt-% instead of the more or less 114 wt-% found in the literature (a yield of more than 1 is possible as phthalic anhydride weighs more than o-xylene).

It is then interesting to study the prognosis that can be made assuming that the yield is improved and approaches what is currently done. The major costs come from raw materials and utilities. Therefore, the variations that the change in yield generates on the other costs are neglected. Indeed, if the yield increases, the quantity of product to be treated at the reactor outlet increases. The heat exchangers, the switch condensers and even the distillation column would have to be resized and would probably not require the same amount of utilities. This might explain the reasons why in the literature, generally two distillation columns are used. As more products have to be separated, more stages are necessary and so more columns might be needed. This difference compared to literature might also be explained by the fact that, in this work, the switch condensers are idealised.



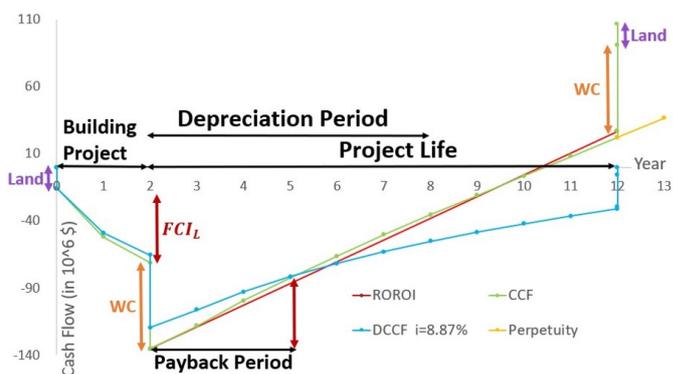
**Fig. 15:** Color scale diagram of the balance of raw materials and products prices in G\$/yr for the yield-modified plant

Then, estimating the new cost evaluation with the correction of the yield, a new balance is obtained (Figure 15).

With the adapted yield, Figure 15 shows that the optimal balance B of \$85M or \$80.5M/yr can be more easily achieved. Indeed, a same combination of price gives a higher balance B.

In order to have a general idea and to see if it is useful to eventually embark on further studies, it is interesting to carry out an economic analysis over time. It is decided to focus on China. Indeed, it is for this market that the most information is available and it is the least advantageous case. So if it is interesting in the end, Europe will be even more.

Considering the most interesting combination presented in Figure 13, the balance only reaches \$80M/yr. However, it is interesting to study the cash flow in this optimal case. Indeed, the break-even for the cash flow is achieved according to the perpetuity method before 8.5 years (cf. Figure 16) of running installation.



**Fig. 16:** Cash-Flow Diagram

The cash flow (CF) is defined by Eq. 13:

$$CF = (R - COM_d - d_k)(1 - t) + d_k - I \quad (13)$$

where R is the revenue,  $COM_d$  the OPEX without depreciation,  $t$  the tax rate (Table 9),  $d_k$  the depreciation at  $k$  year and  $I$  the investment (FCI, land, working capital).

If the cash back method is applied, a discounted rate (also called WACC [46], an acronym for Weighted Average Cost of Capital) of 8.67% (Figure 16) is possible considering the project lifetime is 10 years. The discounted

cash flow (DCF) is determined with respect to Eq. 14:

$$DCF = \frac{CF}{(1 + WACC)^k} \quad (14)$$

In this expression, the WACC is a very important parameter for the company as it will help convince investors and help the company make a choice on the department or work they will invest in. The WACC is defined as follows:

$$WACC = (W_e \cdot C_e) + (W_d \cdot C_d)(1 - t) \quad (15)$$

where  $W_e$  and  $W_d$  are respectively the weightage of equity and debt, and  $C_e$  and  $C_d$  are respectively the cost of equity and debt.

The profitability analysis may be done considering time, cash and interest rates. To do so, the payback period (PBP), the cumulative cash position (CCP or net present value, NPV) and the rate of return on investment (RO-ROI) must be studied. The plant needs 3.15 years after start up to recover the fixed capital investment for the project. The worth of the project at the end of the project life after the complete recovery of the land and working capital cost is of \$106 million. The rate of return on investment is of 0.1919. However, as the CCP depends on the size of the project, the cumulative cash ratio (CCR) is more likely to be used. In this case, it is of 1.7868.

However, this optimal combination is far from the average value :  $P_{Ox} = \$1163/ton$ ,  $P_{PA} = \$1232/ton$ ,  $P_{MA} = \$1596/ton$ ,  $B = \$53M/yr$ . In addition, the optimal combination does not present an interesting WACC. Indeed, when a company needs money, it can borrow from the bank or from investors. Usually, investors will wait for a big interest rate (20%) while the bank will ask for a lower rate (5%). However, this last interest rate strongly depends on the quantity of money brought by investors. If there is no investor, the bank will be less confident and will then increase its rate. In this case, the maximal discounted rate to reach the break-even is of 8.67%, which means it is quite low and investors will have to do an effort. Indeed, a usually targeted discounted rate is between 10 and 20%.

To conclude, from an economic aspect, the plant, as modelled, is not profitable neither in China nor in Europe even if Europe seems a bit more interesting. However, if some improvements are made such as an optimisation of yield, then the plant might be profitable in terms of cost. Indeed, more phthalic anhydride will then be obtained and less  $CO_2$  will be emitted. Moreover, it has to be considered that the coefficients used in all the costs formulas are based on the *Turton* method, which is an American method. By working in China or Europe, those coefficients might have to be adapted.

## 6 LITERATURE REVIEW

### 6.1 Alternative Routes

This section focuses on alternative routes for the production of phthalic anhydride. It is mainly based on the Ullman's encyclopedia [2] and a techno-economic assessment of the production of phthalic anhydride from corn stover [47].

#### *Conventional Process*

Several raw materials routes exist to produce phthalic anhydride and until the 1960s, phthalic anhydride production was based on naphthalene oxidation processes. Since the 90s, most of the phthalic anhydride is obtained from o-xylene. Indeed, o-xylene has several advantages. First of all, a lower theoretical amount of air (two third) is required to oxidise o-xylene as compared to the required amount for the oxidation of naphthalene. Moreover, the heat released during the reaction is  $506 \text{ kJ/mol}$  less than the process using naphthalene.

In addition, the purity of the product obtained with o-xylene is usually higher than the one obtained with naphthalene. Furthermore, a simpler feed system can be used with o-xylene since it is liquid at room temperature. When possible, companies prefer to work with a mix of both o-xylene and naphthalene or at least to be able to switch between both feedstocks [2][48][47].

Those kinds of feedstock are used in various processes, such as the Wacker process, the Alusuisse-Ftalital LAR process, the Nippon Shokubai VGR process, the BASF process and the Rhône-Poulenc process [2]. The three latter ones use the most common method of phthalic anhydride production: the gas-phase o-xylene oxidation on a fixed vanadium oxide catalyst.

Most modern commercial catalysts are based on  $V_2O_5-TiO_2$ . One major change in those different processes is the composition of the catalyst, but there are also other differences [49]. For example, the BASF method uses a tubular reactor instead of a fluidized-bed, and it uses a second reactor to catalytically treat the outlet of the first reactor. This is done to decrease the amount of byproducts and to improve the product quality. Thus, it optimises the yield and decreases the amount of residues and volatile organic compounds. Additionally, the milder operating conditions in the tubular reactor extend the catalyst life. As for the studied process, with this method, there is no need for a liquid condenser before collecting the crude phthalic anhydride in the switch condensers. The plant is designed to ensure a low energy consumption and a high net export of steam and electricity.

Nippon-Shokubai method's characteristic feature is that recycled exhaust gases are added to the mixture of o-

xylene and process air to reduce the oxygen concentration to less than 10 vol% [2]. This was computed in the very first mass balance studied in this project. The main advantage is the possibility to work outside the limits of flammability despite a high o-xylene loading. With their specially developed catalyst system, a good yield is achievable. In this process, naphthalene could be used instead of o-xylene. Both BASF and Nippon-Shokubai methods will be quantitatively discussed later on.

The Rhône-Poulenc process mainly uses o-xylene as raw materials, but the catalyst is capable to process both o-xylene and naphthalene, and even mixtures of both. In this process, the crude product is subjected to a chemical post-treatment before being purified in a two-stage distillation. In the process studied in this project, only one-stage distillation is considered. However, it seems that in most studies uploaded, a two-stage distillation is necessary. This case is discussed in the cost section [2].

Liquid-phase oxidation of o-xylene can also be considered. In this case, a mixture of acetic acid, o-xylene, and a catalyst (mainly Co, Mn, and Br) is introduced in the first vessel of a cascade. In the next vessels, the reaction is completed after being initiated under pressure while the air is injected. The water produced is removed with o-xylene by azeotropic distillation. The isomers of phthalic acid are finally removed from the reaction mixture, and the phthalic anhydride is retrieved by crystallisation. However, as for gas-phase oxidation, the crude product is subject to a pretreatment with special requirements because of the bromine presence [2].

Another way to produce phthalic anhydride is from phthalic acid by simple thermal dehydration [2].

### "Renewable" Process

Nowadays, a "renewable" thinking is ever more asked. New processes and studies are being carried out to develop more environmentally friendly ways of producing phthalic anhydride. The aim is to find non-petroleum derivative feedstocks. In the recent years, the most studied renewable feedstocks are furan and maleic anhydride. Those chemical components can be produced in various renewable ways, e.g. from corn stover or sugars.

An emission assessment for the production of phthalic anhydride from a renewable source [50] states a total emission of  $1024 \text{ kgCO}_2/\text{ton}$  for the global product process. Whereas, according to the same article, for the conventional process, this would be around  $2534 \text{ kgCO}_2/\text{ton}$ . In the case of the phthalic anhydride production from renewable sources, the process is not self-sufficient anymore in terms of hot utilities. However, it seems this route enables producing extra-electricity to sell to the

grid. Finally, it is interesting to study the yield. Overall, with  $104.167 \text{ kg/h}$  of milled corn stover (MCS), the process seems to produce  $7015 \text{ kg/h}$  of phthalic anhydride. The yield is then quite high:  $67.34 \text{ kgPA/kgMCS}$ . [50][51][47][52].

### Separation

A major factor for the efficiency of a phthalic anhydride production plant is the performance of the condensers system. Indeed, this system allows separating phthalic anhydride from the off-gas, i.e. water,  $\text{CO}_2$  and nitrogen. Theoretically, there are different methods to do so. Phthalic anhydride reaction gas could be extracted by absorption into solvents or liquid phthalic anhydride. However, those ways to separate are not exploited commercially. Most commonly, down-flow type switch condensers equipped with finned tubes are alternately heated up or cooled down with a hot or cold heat-transfer medium [2].

## 6.2 Comparison of the Operating Conditions in the Model and the Literature

This section focuses on the comparison between the model operating conditions and the literature. It is mainly based on a *Catalysis Review's* article [53] and *Ulluman's* encyclopedia [2].

It is interesting to compare the present *Aspen* model results to results such as the initial mass balance as well as to results from literature (cf. Table 10) [53][2].

**Table 10:** Model operating parameters from the initial mass balance and the *Aspen* model compared to BASF and Nippon-Shokubai methods

	Inlet reactor Ox concentration [ $\text{g}/\text{m}^3$ ]	PA yield [wt.%]	$T_{\text{reactor}}$ [ $^{\circ}\text{C}$ ]
Initial mass balance	44.5	79.9	/
<i>Aspen</i>	399.6	77.1	280.5
BASF	$\leq 105$	114	360-380
Nippon	$\leq 85$	113	365-375

The difference between the mass balance and the *Aspen* model comes mainly from the fact that, in the first one, a recycling loop is considered while it is not the case for the second one. Moreover, the optimisation of the different units have slightly changed the behaviour of the flows. However, as the same reaction mechanisms were kept, the phthalic anhydride yield is similar in both cases.

When compared to applied models such as BASF or Nippon-Shokubai method (cf. Table 10), it seems that

none of them are near the real feedstock concentration or near the effective phthalic anhydride yield. Even concerning the temperature, it seems that the model considered does not fit to reality. This might come from the thermodynamic model that is used. As explained previously, because of missing data, it is only possible to use the ideal model for the mixtures. However, it does not explain the severe differences. Indeed, in the literature, it is found in several sources that the temperature range of the reactor for the synthesis of phthalic anhydride is between 300 and 400°C and in a pressure range of 1 to 3 *bar*. Thus, as BASF or Nippon-Shokubai methods use a temperature over 360°C they might be working at the atmospheric pressure or at least near to it. In the process described in this report, the reactor is working at an inlet pressure of 5.7 *atm*, thus 5.7741 *bar*. This pressure then seems high.

Finally, in this process, a fluidized bed reactor is used while for BASF, it is a tubular reactor. For the Nippon-Shokubai method, this information is not mentioned. It is concluded that the reactor type also has an impact on the process.

## 7 CONCLUSION

This Integrated Project addresses the phthalic anhydride production process through the gas-phase oxidation of *o*-xylene. The process is composed of several units of major importance: an isothermal fluidized-bed reactor, switch condensers, and a distillation column. The required operation conditions are matched by using compressors, pumps, heaters, and heat exchangers. The heat integration allowed to minimise the energy requirements. The whole process was modelled in *Aspen*.

At the end of the process, 75 101 tons of phthalic anhydride is produced each year, with the desired purity of 99.9wt-%. Moreover, 12 388 tons per year of maleic anhydride is retrieved, with a sufficient purity to be sold. Off-gas is also released and must be treated.

The LCA showed that building the plant in China or in Europe is consistent with standard processes. The electricity produced in Europe is greener than the one produced in China. When looking qualitatively at the costs analysis, a European location of the plant seems to be a better choice than China. However, the final location choice can hardly be made, and is subject to a further analysis of the local market such as its saturation.

According to the economic analysis of the current process, the plant should not be built as the company would not be cost-effective. To make the process environmentally and economically feasible, different improvements can be introduced.

An improvement could be to consider other means of recovery or treatment of these gases, particularly via carbon capture and storage techniques, since the process generates significant quantities of CO<sub>2</sub>. Furthermore, the hot utilities produced and sold could be used, e.g. in turbines to produce some of the electricity needed for units.

The major improvement that could be done is to significantly increase the yield, especially by conducting further studies on the reactor and its operating conditions. To do so, a recycling loop could for example be considered. It would allow recovering the non-converted *o*-xylene. This *o*-xylene would therefore be re-used and the treatment of the off-gas would be diminished. However, separating the *o*-xylene from the off-gas would entail additional separation costs. The first step would therefore be to study the economic interest of such an alternative.

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## 10 APPENDIX

### Abbreviation of the Chemical Components

**Table 11:** Components formulas and symbols

Formula	Component	Symbol
C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	ortho-xylene	Ox
C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> O	phthalic anhydride	PA
C <sub>2</sub> H <sub>2</sub> (CO) <sub>2</sub> O	maleic anhydride	MA
C <sub>6</sub> H <sub>5</sub> (COOH) <sub>2</sub>	benzoic acid	BA
O <sub>2</sub>	oxygen	O <sub>2</sub>
CO <sub>2</sub>	carbon dioxide	CO <sub>2</sub>
H <sub>2</sub> O	water	H <sub>2</sub> O
N <sub>2</sub>	nitrogen	N <sub>2</sub>

### Minimum Fluidization Velocity

The minimum fluidization velocity was calculated from the correlation of Wen and Yu [19] [14] (Eq. 16):

$$(N_{Re})_{mf} = \sqrt{(33.7)^2 + 0.0408 N_{Ga}} - 33.7 \quad (16)$$

$N_{Re}$  is the Particle Reynolds number at the onset of fluidization (Eq. 17) and  $N_{Ga}$  is the Galileo number (Eq. 18):

$$N_{Re} = \frac{d_p \rho_f u_{mf}}{\mu_f} \quad (17)$$

$$N_{Ga} = \frac{d_p^3 \rho_f (\rho_p - \rho_f) g}{\mu_f^2} \quad (18)$$

where  $d_p$  is the catalyst particle size (400  $\mu_m$ ),  $\rho_f$  is the density of the fluid,  $\rho_p$  is the catalyst particle density (2 400  $kg m^{-3}$ ),  $u_{mf}$  is the minimum fluidization velocity,  $g$  is the gravitational acceleration and  $\mu_f$  is the dynamic viscosity of the fluid.

The pressure drop through the fluidized bed is [14]:

$$\Delta p_b = (1 - \epsilon_{mf})(\rho_p - \rho_g)gH_b \quad (19)$$

where  $\epsilon_{mf}$  is the bed void fraction (assumed to be 0.55),  $\rho_g$  is the gas density and  $H_b$  is the height of the bed. The fluidized bed should be operating between 20 to 30 times  $u_{mf}$ . In addition, the pressure drop through distributor plate and exit cyclones is equal to 25% of the bed pressure drop.

Moreover, values of other parameters such as the catalyst bulk density  $\rho_{bulk}$  (1 350  $kg m^{-3}$ ) and the heat transfer coefficient between tube wall and turbulent fluid bed (300  $W m^{-2} K^{-1}$ ) are given in the statement that was provided for the project [14].

### Life Cycle Inventory

Remark: The values in Table 12 do not correspond exactly to the ones of Table 16 because the data included in the LCI was collected before the latest version of the Aspen file.

**Table 12:** Input data inventory

INPUT	Aspen values	Functional Unit
<b>Raw materials</b>	<b>ton/yr</b>	<b>ton/ton of PA</b>
O-xylene	0.117 · 10 <sup>6</sup>	1.047
Air	1.034 · 10 <sup>6</sup>	9.238
<b>Cooling energy</b>	<b>kJ/yr</b>	<b>kJ/ton of PA</b>
Cooling	1560 · 10 <sup>9</sup>	17 · 10 <sup>6</sup>
<b>Electricity</b>	<b>kJ/yr</b>	<b>kJ/ton of PA</b>
Compressor	490 · 10 <sup>9</sup>	5.4 · 10 <sup>6</sup>
Pump	0.072 · 10 <sup>9</sup>	0.794 · 10 <sup>3</sup>
Switch condenser	77 · 10 <sup>9</sup>	66 · 10 <sup>3</sup>
<b>Total of electricity</b>	<b>5.67 · 10<sup>11</sup></b>	<b>5.47 · 10<sup>6</sup></b>

**Table 13:** Output data inventory

OUTPUT	Aspen values ton/yr	Functional Unit ton/ton of PA
<b>Products</b>		
PA	90 707	0.81
MA	14 936	0.19
<b>Emissions</b>		
Off-gas	954 795	8.527
CO <sub>2</sub> in off-gas	64 057	0.572

### Stream Tables

**Table 14:** Utility flows

Stream	T [°C]	P [kPa]	Mass flow [kg/h]
W2	256.1	4197.8	532.5
W4	194.9	1197.2	2478
W6	155.56	496.7	2471

**Table 15:** Energy flows

Stream	Duty [kW]	Stream	Duty [kW]
Q1	51 112	Q3	49 632
Q2	1 480	Q4	1 117

**Table 16:** Stream table of the optimised process

Stream	Phase	T [°C]	P [kPa]	Molar enthalpy [kJ/kmol]	Cp [kJ/kmol.K]	Energy [kW]	Material flow [m <sup>3</sup> /hr]
1	gas	25	80	0	29	0	114 948
2	liquid	25	101.325	-24 510	190	-781	14
3	gas	360	611	9 983	31	10 287	30 678
3bis	gas	325	601	8 898	31	9 170	14
4	liquid	25	615.6	-24 433	190	-779	18
4bis	liquid	223	600.6	22 007	291	701	30 087
5	gas	300	587.6	8 149	30	8 398	625
6	gas	226	587.6	46 232	215.8	1 473	30 490
7	gas	281	577.6	9 292	35.9	9 871	80 501
8	gas	281	220.5	-38 516	35.4	-41 242	90 939
9	gas	270	191.4	-38 892	35.3	-41 645	91 986
10	gas	220	171.8	-40 639	34.6	-43 516	93 480
11	gas	170	151.9	-42 353	34	-45 350	124 907
12	gas	130	101.325	-37 026	31	-38 835	9
13	liquid	150	101.325	-418 816	203.5	-9 190	1
14	liquid	203	101.325	-417 947	190.8	-1 811	3 049
15	liquid	284	101.325	-387 984	224.2	-6 831	7 986

**Table 17:** Stream table of the optimised process (continued) - Mole flows in kmol/h

Stream	Mole flow [kmol/h]	Composition [mol-%]							
		PA	MA	BA	Ox	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>
1	3710	-	-	-	-	21	-	-	79
2	115	-	-	-	100	-	-	-	-
3	3710	-	-	-	-	21	-	-	79
3bis	3710	-	-	-	-	21	-	-	79
4	115	-	-	-	100	-	-	-	-
4bis	115	-	-	-	100	-	-	-	-
5	3710	-	-	-	-	21	-	-	79
6	115	-	-	-	100	-	-	-	-
7	3824	-	-	-	3	20.37	-	-	76.63
8	3854	1.66	0.39	0.02	0.51	8.07	4.76	8.57	76.02
9	3854	1.66	0.39	0.02	0.51	8.07	4.76	8.57	76.02
10	3854	1.66	0.39	0.02	0.51	8.07	4.76	8.57	76.02
11	3854	1.66	0.39	0.02	0.51	8.07	4.76	8.57	76.02
12	3776	0.02	0	-	0.52	8.24	4.85	8.75	77.62
13	79	80.24	18.84	0.92	-	-	-	-	-
14	15.6	0.38	95.40	4.22	-	-	-	-	-
15	63.4	99.89	-	0.11	-	-	-	-	-