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Simulation of a phthalic anhydride production process through gaseous catalytic oxidation of o-xylene in ChemCAD® simulator

Simulación de un proceso de producción de anhídrido ftálico mediante la oxidación catalítica gaseosa del o-xileno en el simulador ChemCAD®

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Abstract
Phthalic anhydride (PA) is a key industrial compound, particularly relevant for the large-scale production of plasticizers. This study aimed to develop the conceptual design of a proposed PA production process using the ChemCAD 7.1.2 simulation software, in which maleic anhydride (MA) was identified as the principal byproduct. Several parameters were obtained for the heat exchangers, including heat curves, heat duty, logarithmic mean temperature difference (LMTD), and overall heat transfer coefficient. Additionally, the mass flow rate and composition of the main process streams were determined through simulation, along with their temperature, pressure, and vapor fraction. Design parameters for both distillation columns were also calculated, as well as the heat duty of the catalytic reactor. Finally, the total purchase and installation costs of selected equipment were estimated. The mass flow rate of the bottom stream from the purification column was 10,921.083 kg/h, composed primarily of PA (99.19% purity) and o-xylene (0.80%), while MA was recovered in the top stream with a mass flow rate of 973.342 kg/h and a purity of 83.36%.

Keywords: ChemCAD®; Maleic anhydride; o-Xylene; Phthalic anhydride; Simulation.

Resumen
El anhídrido ftálico (AF) es un compuesto químico industrial importante, especialmente para la producción a gran escala de plastificantes. El propósito de este artículo fue el de llevar a cabo el diseño conceptual de un proceso de producción de AF en el simulador ChemCAD® 7.1.2, donde el anhídrido maleico (AM) fue el principal subproducto producido. Varios parámetros fueron obtenidos para los intercambiadores de calor, tales como las curvas de calor, carga de calor, la DMLT y el coeficiente global de transferencia de calor. También, el caudal másico y composición de las corrientes principales fueron determinadas, incluyendo su temperatura, presión y fracción de vapor. Además, algunos parámetros de diseño fueron calculados para ambas columnas de destilación, así como también el calor intercambiado del reactor catalítico. Finalmente, los costos totales de compra e instalación fueron determinados considerando algunos equipos específicos. El caudal másico de la corriente del fondo de la columna de purificación fue 10 921,083 kg/h, la cual está compuesta principalmente por AF (99,19% de pureza) y o-xileno (0,80%), mientras que el AM es obtenido en al corriente del tope de esta columna con un caudal másico de 973,342 kg/h y una pureza de 83,36%.

Palabras claves: ChemCAD®; Anhídrido maleico; o-Xileno; Anhídrido ftálico; Simulación.

Introduction

Phthalic anhydride (PA) is an organic compound that can be synthesized from precursors such as o-xylene or naphthalene via oxidation in the presence of a catalyst, typically vanadium/titanium oxide. However, some authors [1] have proposed the conceptual design of a PA production process using corn stover, incorporating energy integration strategies, water consumption analysis, and life cycle greenhouse gas emissions assessment.

PA is a crucial chemical intermediate with major applications in the manufacture of plasticizers for PVC, unsaturated polyesters, and alkyd resins used in surface coatings. Its minor applications include polyester polyols, pigments, dyes, sweeteners, and flame retardants [2].

In 1872, BASF developed the naphthalene oxidation process for PA production, marking the beginning of its continuous commercial synthesis. PA was the first commercially used anhydride of a dicarboxylic acid, and its industrial relevance is comparable to that of acetic acid [3].

PA is produced through oxidation reactions occurring at approximately 360–390 ºC from:

- o-xylene, with a reaction enthalpy ranging from 1300 to 1800 kJ/mol and expected yields of 110–112 kg PA per 100 kg o-xylene.
- naphthalene, with a reaction enthalpy between 2100 and 2500 kJ/mol and yields typically not exceeding 98 kg PA per 100 kg naphthalene; carbon dioxide is a co-product.

Until the late 1950s, coal-tar-derived naphthalene remained the preferred feedstock in the United States and Germany. However, a shortage of naphthalene and the growing availability of xylenes from the expanding petrochemical industry led to a shift toward o-xylene. The air oxidation of 90% pure o-xylene to PA was commercialized in 1946. One advantage of o-xylene is its theoretical yield of 1.395 kg PA per kg of feedstock, whereas naphthalene yields a maximum of 1.157 kg/kg due to carbon dioxide losses. Although both feedstocks are viable, o-xylene is predominantly favored. Coal-tar naphthalene is still used in specific contexts, such as when readily available from coke production in steel mills [4].

Over 90% of PA is produced via vapor-phase oxidation of o-xylene over a fixed-bed catalyst. In the 1960s, two types of fixed-bed processes were employed: low-temperature/low space velocity and high-temperature/high space velocity. Advances in catalyst technology enabled higher space velocities under low-temperature conditions while maintaining high yields. Consequently, the low-temperature process, operating below 400 ºC, became the industry standard. A commercially viable plant must achieve a selectivity of at least 75 mol% with an o-xylene feed concentration of 60 g/m³, which exceeds the lower explosion limit of 43 g/m³ [4].

The preference for o-xylene in PA manufacturing is driven by its superior yields, availability, and cost-effectiveness. However, this dependence exposes the process economics to fluctuations in feedstock prices and the volatility of mixed xylenes in global markets. To mitigate this risk, some facilities incorporate o-xylene/naphthalene switching capabilities or xylene separation units [1].

The fixed-bed process utilizes a catalyst composed of vanadium oxide and titanium dioxide, coated onto an inert, non-porous carrier in layers ranging from 0.02 to 2.0 mm in thickness. Ring-shaped supports are preferred over spherical ones to extend catalyst life, reduce reactor pressure drop, and enhance yields [4].

Numerous studies have simulated PA production plants using commercial software. For instance, [5] developed a simulation model of PA production from o-xylene using Aspen Plus, incorporating heat integration and separation processes. Similarly, [6] employed Aspen Plus for steady-state simulation and exported the model to Aspen Dynamics for dynamic simulation and hazard and operability (HAZOP) analysis. In another study, [7] designed and simulated a simplified PA production process using corn stover as feedstock to evaluate scalability. The plant was configured to process 104,167 kg/h of milled corn stover with 20% moisture content. The vapor-liquid equilibrium was modeled using the NRTL method, with gases such as O_2, N_2, CO_2, CH_4, and H_2 treated under Henry's Law. Additionally, [8] assessed the techno-economic feasibility of establishing a PA production facility in Argentina via partial oxidation of o-xylene, identifying an optimal production capacity of 9,000 tons/year.

Other researchers have focused on reactor design and optimization. For example, [9] analyzed thermowell systems for temperature monitoring in fixed-bed catalytic reactors used in the highly exothermic partial oxidation of o-xylene to PA. Particle-resolved computational fluid dynamics (CFD) simulations were conducted for randomly packed spheres in cylindrical tubes with varying tube-to-particle diameter ratios. The presence of thermowells influenced mass and heat transfer, particularly at the reactor core. Likewise, [3] conducted a kinetic study of o-xylene oxidation over a V_2O_5/TiO_2 catalyst in a fluidized bed reactor, enabling accurate kinetic data collection despite the reaction's exothermic nature. In another study, [10] evaluated the performance of highly conductive structured metallic monoliths for PA production, concluding that their use significantly enhances plant productivity. [11] investigated the effect of inlet gas temperature on fixed-bed reactor performance for o-xylene oxidation, using a two-dimensional heterogeneous model across a temperature range of 120 to 450 ºC. [12] demonstrated that PA selectivity can be improved by adjusting operating conditions such as temperature and oxygen partial pressure, based on reactor-scale simulations of industrial units. [13] mathematically analyzed the performance of a fixed-bed tubular reactor for PA production, comparing conversion rates and temperature profiles with data from a petrochemical unit in Iran and pilot plant literature, yielding satisfactory correlations. Finally, [14] proposed a framework integrating ANSYS Fluent with other computing platforms via lock synchronization to extend CFD solvers' applications from modeling and design to control and optimization, selecting PA synthesis due to its industrial relevance and pronounced exothermicity.

Rising energy and feedstock costs have intensified the demand for efficient chemical process design and optimization. Advances in

computational capabilities have facilitated the application of mathematical methods to address these challenges. The development of new processes increasingly relies on high-efficiency synthesis methodologies that prioritize sustainability and performance [15].

Process flow sheet design and optimization are supported by commercial simulation software known as process simulators [16]. Among the most widely used simulators by researchers and engineers for modeling real-world systems are Aspen Plus, SuperPro Designer, UniSim, ProSim Plus, EMSO, ChemCAD, gPROMS, and PRO/II [17].

ChemCAD [18] is an integrated suite developed by Chemstations to enhance productivity and solve complex chemical process models [19]. Its versatility lies in its broad range of thermodynamic models, compatibility with diverse operating conditions, extensive component databases, and user-friendly interface. The simulator is widely adopted in industry due to its comprehensive library of predefined unit operations—including pumps, distillation columns, tanks, heat exchangers, reactors, and compressors—which can be interconnected to model complete chemical facilities. Substances are introduced into the system via feed streams [20].

A chemical company has outlined concrete plans to produce PA via catalytic gaseous oxidation of o-xylene, leveraging the availability of raw materials, budgetary resources, and market demand. To support this initiative, the company requires detailed information on the temperature, pressure, composition, and flow rates of the main process streams, as well as the operating parameters of the equipment involved. Additionally, data on plant yield and throughput are essential. In this context, the present study presents the conceptual design of the proposed PA production process using ChemCAD 7.1.2, aiming to determine the mass and energy balances of the principal streams and assess plant productivity and final PA purity. Key parameters of the heat exchangers, distillation columns, and catalytic reactor were calculated, along with the total purchase and installation costs of selected equipment. The throughput and purity of the byproduct MA were also determined.

Materials and Methods

Physicochemical Properties of Phthalic Anhydride

As reported by [4], the principal physicochemical properties of phthalic anhydride (PA) are summarized in Table 1.

Table 1. Principal physicochemical properties of PA.

Property	Value	Units
Melting point	131	ºC
Boiling point	284.5	ºC
Triple point	131	ºC
Heat of vaporization at 131 ºC	65.3	kJ/mol
Specific gravity at 4 ºC	1.527	-
Specific heat at 90 ºC	422	J/kg.K
Heat of combustion at 25 ºC	- 3,259	kJ/mol
Heat of formation at 25 ºC	- 460	kJ/mol
Heat of sublimation at 131 ºC	88.70	kJ/mol
Heat of fusion at 131 ºC	22.93	kJ/mol

Description of the Proposed Phthalic Anhydride Production Process through Catalytic Oxidation of Gaseous o-Xylene

A stream of dried air, with a total flowrate of approximately 317,240 kg/h and composed of 76.7% nitrogen (243,320 kg/h) and 23.3% oxygen (73,920 kg/h), is compressed from atmospheric pressure (101.325 kPa) to 220 kPa using a centrifugal polytropic compressor. This compressed stream is subsequently heated to 245 ºC in a shell-and-tube heat exchanger (Pre-heater 1) using high-pressure steam available at 254 ºC.

In a separate section of the plant, a liquid stream of pure o-xylene with a flowrate of 11,678 kg/h is pumped through a shell-and-tube heat exchanger (Vaporizer), where its temperature is raised to 245 ºC using the same high-pressure steam, resulting in complete vaporization. The vaporized air and o-xylene streams are then mixed and fed into a fixed-bed catalytic reactor at an inlet temperature of 245 ºC and a pressure of 200 kPa. For safety purposes, the o-xylene concentration is maintained at or below the lower explosive limit of 1 mol%, with the air-to-o-xylene ratio controlled via a ratio controller positioned between the compressor and the pump's control valve.

Within the reactor, o-xylene undergoes oxidation, yielding the target product phthalic anhydride (PA), the byproduct maleic anhydride (MA), and various combustion products. These reactions are highly exothermic, necessitating temperature regulation via a concurrent flow of Dowtherm A through the shell side of the reactor. A pressure drop of 70 kPa is observed inside the reactor due to the passage of reactant gases through catalyst-packed tubes.

The reaction mixture exits the reactor at 353 ºC and 130 kPa and is directed to a shell-and-tube heat exchanger (Cooler 1), where it is cooled to 260 ºC using boiler feed water at 110 ºC. This cooling step generates high-pressure steam at 254 ºC. The mixture is then further cooled to 165 ºC in a second shell-and-tube heat exchanger (Cooler 2), also using boiler feed water at 110 ºC, producing low-pressure steam at 159 ºC. Finally, the stream is cooled to 45 ºC in a third shell-and-

tube heat exchanger (Cooler 3) using cooling water at 30 ºC.

At this stage, the cooled reaction stream is a two-phase mixture and is sent to a set of switch condensers for PA recovery. PA is desublimated as a solid in one condenser using chilled oil, then melted in a second condenser using hot oil, while a third condenser remains on standby. As noted by [21], due to the low partial pressure of PA in the stream, it desublimates rather than condenses. The process stream is cooled using low-temperature oil in tubes to promote desublimation. Once solid PA accumulates on the heat transfer surface, gas flow to the condenser is halted and higher-temperature oil is circulated to melt the solid. This cycle is repeated across three units: one in desublimation mode, one in melting mode, and one on standby. The result is a liquid stream containing condensable components and a vapor stream comprising MA, PA, o-xylene, water, and non-condensables. It is assumed that all light gases remain uncondensed and undissolved, and that 99% of the organics are desublimated and melted. In ChemCAD, the switch condensers are simulated using a component separator, as recommended by [21].

The liquid stream from the switch condensers is depressurized to 70 kPa via a pressure-reducing valve and then heated to 230 ºC in a shell-and-tube heat exchanger (Pre-heater 2) using high-pressure steam. This heated stream is fed into a sieve tray distillation column (Water Column), where a top stream primarily composed of water is separated, and a bottom stream containing mostly PA and MA is collected. The bottom stream is subsequently fed into a second sieve tray distillation column (Purification Column), where PA is recovered at the bottom with a purity of 99.19 wt%, and MA is obtained at the top with a purity of 83.36 wt%. Finally, the bottom stream of the purification column is cooled to 30 ºC in a shell-and-tube heat exchanger (Cooler 4) using chilled water at 5 ºC.

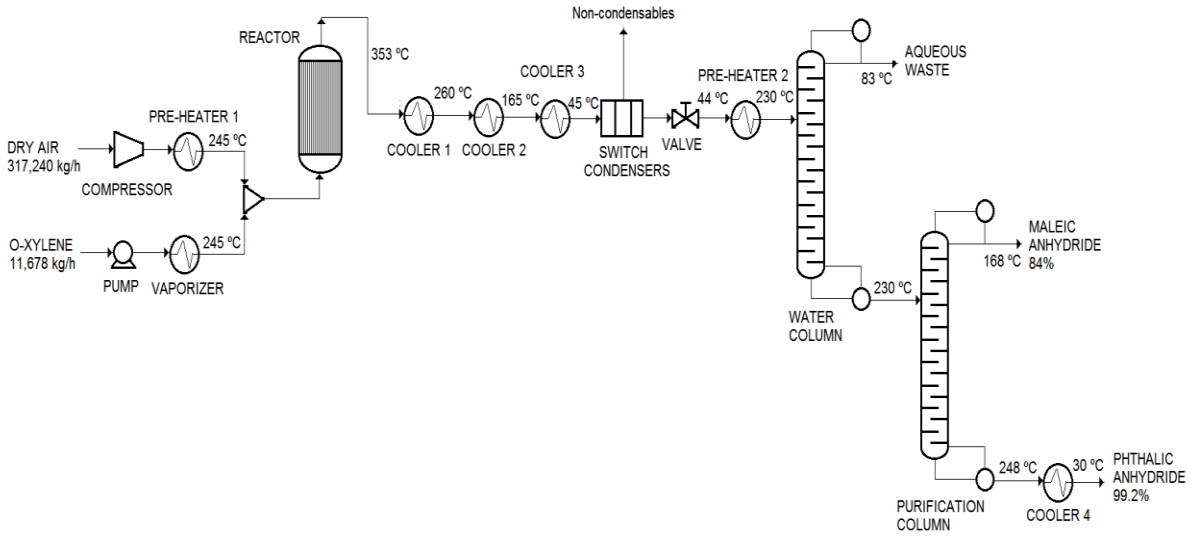

Figure 1. Process flow diagram of the PA production process from the catalytic oxidation of o-xylene.

Reactions

Table 2 presents the stoichiometry and selectivity of the principal reactions occurring within the catalytic reactor, as considered in this study. Table 3 outlines the corresponding reaction kinetics [21].

Table 2. Stoichiometry and selectivity of the reactions occurring in the catalytic reactor.

Number	Reaction	Selectivity
1	Formation of phthalic anhydride: $C_6H_4(CH_3)_2 + 3O_2 \rightarrow C_6H_4(CO)_2O + 3H_2O$	0.70
2	Combustion of phthalic anhydride: $C_6H_4(CO)_2O + \frac{15}{2}O_2 \rightarrow 8CO_2 + 2H_2O$	0.10
3	Complete combustion of o-xylene: $C_6H_4(CH_3)_2 + \frac{21}{2}O_2 \rightarrow 8CO_2 + 5H_2O$	0.15
4	Formation of maleic anhydride: $C_6H_4(CH_3)_2 + \frac{15}{2}O_2 \rightarrow C_2H_2(CO)_2O + 4CO_2 + 4H_2O$	0.10
5	Combustion of maleic anhydride: $C_2H_2(CO)_2O + 3O_2 \rightarrow 4CO_2 + H_2O$	0.08

Table 3. Reaction kinetics of the reactions occurring in the reactor.

Number	Reaction kinetics
1	$r_1 = -\frac{27{,}000}{RT} + 19.837$
2	$r_2 = -\frac{31{,}000}{RT} + 20.86$
3	$r_3 = -\frac{28{,}600}{RT} + 18.97$
4	$r_4 = -\frac{27{,}900}{RT} + 19.23$
5	$r_5 = -\frac{30{,}400}{RT} + 20.47$

Where: R = 1.987 cal·K^{-1}·mol^{-1} T = Temperature in Kelvin

Catalyst

The catalyst employed in this study was vanadium pentoxide (V_2O_5, vanadia) supported on titanium dioxide (TiO_2, anatase) [3][22], with the following physical parameters [21]:

- Catalyst particle diameter: 3 mm
- Catalyst particle density: 1,600 kg/m³
- Void fraction: 0.50

V_2O_5/TiO_2 is a widely used catalyst in various industrial reactions, including the selective oxidation of o-xylene to phthalic anhydride, selective catalytic reduction of NO_x, and selective oxidation of alkanes. The partial oxidation of o-xylene to synthesize phthalic anhydride is a highly exothermic reaction, which leads to the formation of hot spots on the catalyst surface. The yield of phthalic anhydride is strongly influenced by the activity and stability of the catalyst [23].

According to [24], vanadia-anatase supported catalysts used for the oxidation of o-xylene to phthalic anhydride undergo significant deactivation over time. Consequently, the catalyst must be replaced after approximately five years of operation, with the most pronounced decline in activity occurring in the hot spot region. This trend has been observed in catalysts used for 24, 34, 45, and 55 months. During the first 45 months, the catalyst maintains relatively stable activity in the front section of the bed (0–30 cm), whereas the markedly reduced activity observed in catalysts aged 60.5 months beyond the 100 cm region of the bed is likely attributable to reversible deactivation caused by product accumulation on active sites.

Design Parameters of the Equipment

Table 4 presents the design specifications of the shell-and-tube heat exchangers, catalytic reactor, and distillation columns used in the simulation of the phthalic anhydride (PA) production process. These parameters were selected based on recommendations and design criteria reported in [21], [25], [26], [27], and [28].

Table 4. Principal design parameters of the equipment employed in the simulated PA production process.

Equipment	Design parameters
Pre-heater 1	Area: 3,300 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in tubes.
Vaporizer	Area: 450 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in shell.
Cooler 1	Area: 2,600 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in tubes.
Cooler 2	Area: 3,200 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in tubes.
Cooler 3	Area: 2,800 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in shell.
Pre-heater 2	Area: 300 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in tubes.
Cooler 4	Area: 700 m^2 1-2 shell and tube heat exchanger, floating head, and carbon steel. Process stream in shell.
Reactor	Carbon steel construction, 18,000 2-inch diameter tubes each 6 m long. Triangular arrangement, 2-inch pitch. Overall reactor diameter: 7 m. Overall reactor length: 10 m. Co-current flow, process stream in tubes, Dowtherm A in shell.
Water column	Carbon steel, Diameter: 0.95 m, Height 14.5 m, Tray type: Sieve. Trays spacing: 1 ft. (0.3048 m).
Purification column	Carbon steel, Diameter: 0.85 m, Height 8 m, Tray type: Sieve. Trays spacing: 1 ft. (0.3048 m).

Selection of the thermodynamic model

Based on the minimum and maximum temperature and pressure values handled throughout the production process, and using the "Thermodynamics Wizard" feature, the ChemCAD simulator recommended the UNIFAC model for the Global K-Value calculation, incorporating vapor phase association via the Hayden–O'Connell method. For enthalpy calculations, the Peng–Robinson model was selected as the Global Enthalpy Model.

This selection differs from the thermodynamic package proposed by [21] for simulating processes of this nature, which suggested the Soave–Redlich–Kwong (SRK) model for both vapor–liquid equilibrium and enthalpy calculations across all unit operations.

Equipment purchase and installation cost

The purchase and installation costs of selected equipment involved in the proposed production process were estimated using the "Costing" module of the ChemCAD simulator. The Chemical Engineering Plant Cost Index (CEPCI) embedded in the simulator's costing database was updated to March 2023, based on the data reported by [29]. According to the simulator, both purchase and installation costs are calculated using methodologies and reference data published in [30].

It is important to note that the simulator does not provide cost estimation options for the reactor and distillation columns; therefore, their purchase and installation costs were not determined within the scope of this simulation.

Results and discussion

Figure 2 illustrates the process flow diagram obtained from the simulation of the phthalic anhydride (PA) production process using the ChemCAD simulator.

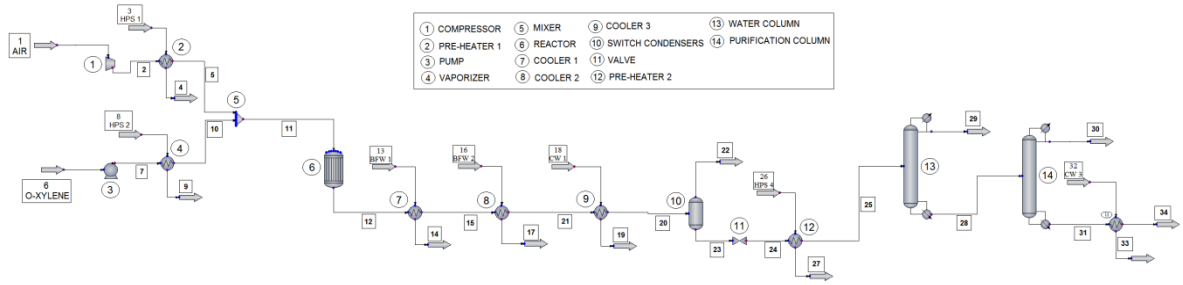

Figure 2. Process flow diagram of the phthalic anhydride (PA) production process via catalytic oxidation of o-xylene, as simulated using ChemCAD®.

Parameters and mass flowrates of the process streams

As a result of the simulation conducted using the ChemCAD® software, the principal parameters of the process streams involved in the phthalic anhydride (PA) production process were determined. These parameters are detailed in Table 5.

Table 5. Main parameters of the process streams involved in the PA production process (refer to Figure 2).

Parameter	Stream number (refer to Figure 2)					
	1	5	6	10	11	12
Temperature (ºC)	25	245	25	245	244.82	353
Pressure (kPa)	101	218	101	290	200	130
Vapor fraction	1	1	0	1	1	1
Component	Mass flowrate (kg/h)					
PA	-	-	-	-	-	11,404.720
MA	-	-	-	-	-	1,078.604
Carbon dioxide	-	-	-	-	-	7,745.515
Nitrogen	243,320	243,320	-	-	243,320	243,320
Oxygen	73,920	73,920	-	-	73,920	58,345
Water	-	-	-	-	-	6,440.158
o-Xylene	-	-	11,678	11,678	11,678	583.900
TOTAL	317,240	317,240	11,678	11,678	328,918	328,917.897

Table 5. Main parameters of the process streams involved in the PA production process (Cont.…)

Parameter	Stream number (refer to Figure 2)				
	15	21	20	22	23
Temperature (ºC)	260	165	45	45	45
Pressure (kPa)	120	110	100	100	100
Vapor fraction	1	1	0.986	0.999	0
Component	Mass flowrate (kg/h)				
PA	11,404.720	11,404.720	11,404.720	570.236	10,834.484
MA	1,078.604	1,078.604	1,078.604	53.930	1,024.674
Carbon dioxide	7,745.515	7,745.515	7,745.515	7,744.740	0.775
Nitrogen	243,320	243,320	243,320	243,295.600	24.40
Oxygen	58,345	58,345	58,345	58,339.150	5.850
Water	6,440.158	6,440.158	6,440.158	2,576.063	3,864.095
o-Xylene	583.900	583.900	583.900	496.315	87.585
TOTAL	328,917.897	328,917.897	328,917.897	313,076.034	15,841.863

Table 5. Main parameters of the process streams involved in the PA production process (Final)

Parameter	Stream number (refer to Figure 2)				
	25	28	29	30	34
Temperature (ºC)	230	230	83.39	168.275	30
Pressure (kPa)	60	52	50	40	42
Vapor fraction	1	0	1	1	0
Component	Mass flowrate (kg/h)				
PA	10,834.484	10,834.484	-	1.083	10,833.401
MA	1,024.674	973.439	51.235	973.342	0.097
Carbon dioxide	0.775	-	0.775	-	-
Nitrogen	24.40	-	24.40	-	-
Oxygen	5.850	-	5.850	-	-
Water	3,864.095	193.205	3,670.890	193.205	-
o-Xylene	87.585	87.585	-	-	87.585
TOTAL	15,841.863	12,088.713	3,753.150	1,167.630	10,921.083

The amounts of oxygen and o-xylene that reacted to generate the various products were 15,575 kg and 11,094.1 kg, respectively, corresponding to 21.07% and 95% of the total quantities fed into the process for each compound. The outlet stream from the tubular catalytic reactor was composed primarily of nitrogen (73.97%), phthalic anhydride (3.47%), and carbon dioxide (2.35%).

In the switch condenser stage, both PA and MA were recovered at a rate of 95%. However, approximately 570 kg/h of PA and 54 kg/h of MA were lost due to venting during this stage, a figure that is considered unacceptable. At this point in the process, carbon dioxide (99.99% removal), nitrogen (99.99%), oxygen (99.99%), water (39.99%), and o-xylene (85%) were separated from the liquid stream and released in gaseous form. The resulting liquid stream was composed mainly of PA (68.39%), water (24.39%), and MA (6.47%). It is therefore recommended to evaluate, design, and implement appropriate recovery systems to reclaim the 496.315 kg/h of o-xylene and the vented PA. These could be recycled into the main process—o-xylene as a high-purity feedstock and PA as a valuable product—thus increasing the overall throughput of the plant.

The most efficient emission control system (96%) for o-xylene-based production involves the combined use of a water scrubber and a thermal incinerator. A thermal incinerator alone achieves approximately 95% efficiency in the combustion of pollutants. Emissions from pretreatment and distillation—such as particulates and hydrocarbons—are typically treated using the same scrubber and/or incinerator systems employed for the main process streams (reactor and condenser), or with scrubbers alone, with comparable efficiency levels [31].

In the water column, the top stream consisted primarily of water (97.81%), while the bottom stream contained mostly PA (89.62%) and MA (8.05%). This bottom stream was subsequently fed into the purification column, where the top stream had a total flowrate of 1,167.63 kg/h and was composed mainly of MA (973.342 kg/h) with a purity of 83.36%, water being the principal impurity (16.55%). Likewise, the bottom stream of the purification column yielded 10,921.083 kg/h, primarily composed of PA (10,833.401 kg/h) with a purity of 99.2%, with o-xylene as the main impurity (0.80%).

Finally, the production yields obtained in this study were 0.927 kg of PA and 0.083 kg of MA per kg of o-xylene. The PA yield is below the value reported by [4], which is 1.395 kg PA/kg o-xylene, and also below the range reported by [1], which is 110–112 kg PA per 100 kg o-xylene. Considering the recovery of the 570 kg/h of PA vented in the switch condensers—through scrubbers or other recovery methods—the PA yield increases to 0.976 kg/kg of o-xylene, which nonetheless remains below the values reported in the consulted literature.

Parameters of the reactor and distillation columns

The design specifications for the two distillation columns employed in the production process are presented in Table 6. These parameters were determined using the ChemCAD® simulator.

Table 6. Design parameters of the two distillation columns calculated by the ChemCAD® simulator.

Parameter	Distillation column 1 (Water column)	Distillation column 2 (Purification column)	Units
Condenser duty	- 22,936.5	- 1,128.37	MJ/h
Reboiler duty	16,134.3	2,236.18	MJ/h
Minimum stages	25	10	-
Feed stage	10	6	-
Reflux ratio, minimum	3.67	0.51	-

The heat duty required to maintain the reactor temperature at 353 ºC was calculated at –153,938 MJ/h, a value that reflects the highly exothermic nature of the catalytic gaseous oxidation of o-xylene to phthalic anhydride and associated byproducts. This substantial energy demand is consistent with findings reported in [3], [11], and [14].

For the water column, the condenser and reboiler duties were –22,936.5 MJ/h and 16,134.3 MJ/h, respectively. In the purification column, these values were –1,128.37 MJ/h and 2,236.18 MJ/h, respectively. The water column required 25 theoretical stages, with the feed introduced at stage 10, while the purification column operated with 10 stages and a feed point at stage 6. The minimum reflux ratios were 3.67 for the water column and 0.51 for the purification column, indicating the relative separation difficulty and energy requirements of each unit.

Heat curves of the heat exchangers

Figure 3 displays the heat curves corresponding to each of the seven shell-and-tube heat exchangers utilized in the phthalic anhydride (PA) production process. These curves were generated using the ChemCAD® simulator.

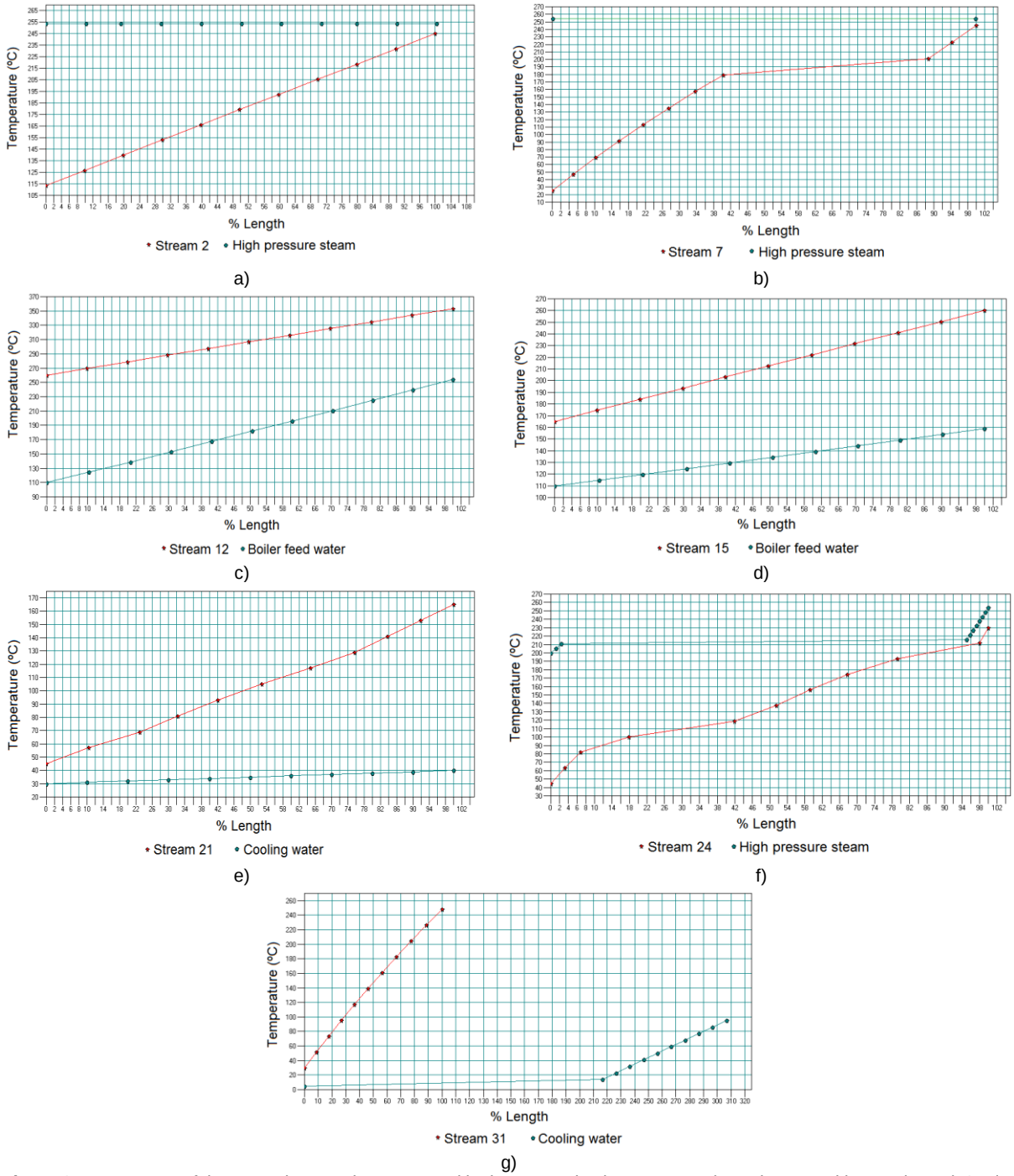

Figure 3. Heat curves of the seven heat exchangers used in the PA production process. a) Pre-heater 1; b) Vaporizer; c) Cooler 1; d) Cooler 2; e) Cooler 3; f) Pre-heater 2; g) Cooler 4.

The heat curve of Pre-heater 1 (Figure 3a) exhibits a linear profile for the high-pressure steam, indicating that the temperature of this auxiliary stream remains constant throughout the entire length of the heat exchanger at 254 °C. In contrast, Stream 2 (compressed air) displays a steadily increasing temperature pattern, evidencing continuous heating until it reaches the target temperature of 245 °C.

Regarding the heat curve of the Vaporizer (Figure 3b), it similarly shows a constant linear profile for the high-pressure steam, maintaining a uniform temperature of 254 °C along the entire exchanger length. Stream 7 (liquid o-xylene) presents an initial linear temperature increase up to approximately 40% of the exchanger length (from 25 °C to 180 °C), followed by a characteristic phase change behavior between 40% and 89% of the equipment length (vaporization). Subsequently, the stream resumes a linear temperature increase from 200 °C to 245 °C between 89% and 100% of the exchanger length, indicating sensible heating

without phase change until the desired temperature is achieved.
In the case of Cooler 1 (Figure 3c), the boiler feed water stream exhibits a linear temperature increase from 110 °C to approximately 254 °C along the entire exchanger length, indicating heating without phase change (sensible heat). Meanwhile, Stream 12 (gaseous outlet from the tubular reactor) shows a linear temperature decrease from 353 °C to 260 °C, confirming cooling without phase transition.
The heat curve of Cooler 2 (Figure 3d) reveals a linear temperature increase for the boiler feed water from 110 °C to approximately 150 °C, indicating sensible heating. Simultaneously, Stream 15 (cooled outlet from Cooler 1) undergoes a linear temperature decrease from 260 °C to 165 °C, reflecting cooling without phase change.
In Cooler 3 (Figure 3e), the cooling water stream displays a linear temperature increase from 30 °C to 40 °C, while Stream 21 (outlet from Cooler 2) shows a linear temperature decrease from 165 °C to 45 °C, both indicative of sensible heat exchange without phase change.
With respect to the heat curve of Pre-heater 2 (Figure 3f), the high-pressure steam exhibits a linear temperature decrease between 100% and 95% of the exchanger length, indicating cooling without phase change. This is followed by a curved temperature profile between 95% and 2% of the exchanger length, suggesting the occurrence of a phase change (condensation). Finally, the steam resumes a linear temperature decrease until reaching approximately 200 °C. In total, this stream cools from 255 °C to around 200 °C, undergoing condensation. The heat curve of Stream 24 (liquid stream from the switch condensers) shows a linear temperature increase up to 7% of the exchanger length (from approximately 45 °C to 82 °C), followed by a non-linear temperature rise between 7% and 98% of the length (from 82 °C to approximately 212 °C), indicative of a phase change (vaporization). The final segment, from 98% to 100% of the exchanger length, presents a linear temperature increase until reaching the target temperature of 230 °C.
Lastly, the heat curve of Cooler 4 (Figure 3g) is not discussed due to an anomalous behavior observed in the cooling water stream, which displays a range of exchanger length from 0% to 310%. This inconsistency is both contradictory and physically implausible, rendering the data invalid for analysis.

Parameters of the heat exchangers

Figure 4 presents the calculated values of heat duty, logarithmic mean temperature difference (LMTD), and overall heat transfer coefficient for each shell-and-tube heat exchanger employed in the phthalic anhydride (PA) production process. These parameters were obtained using the ChemCAD® simulation software.

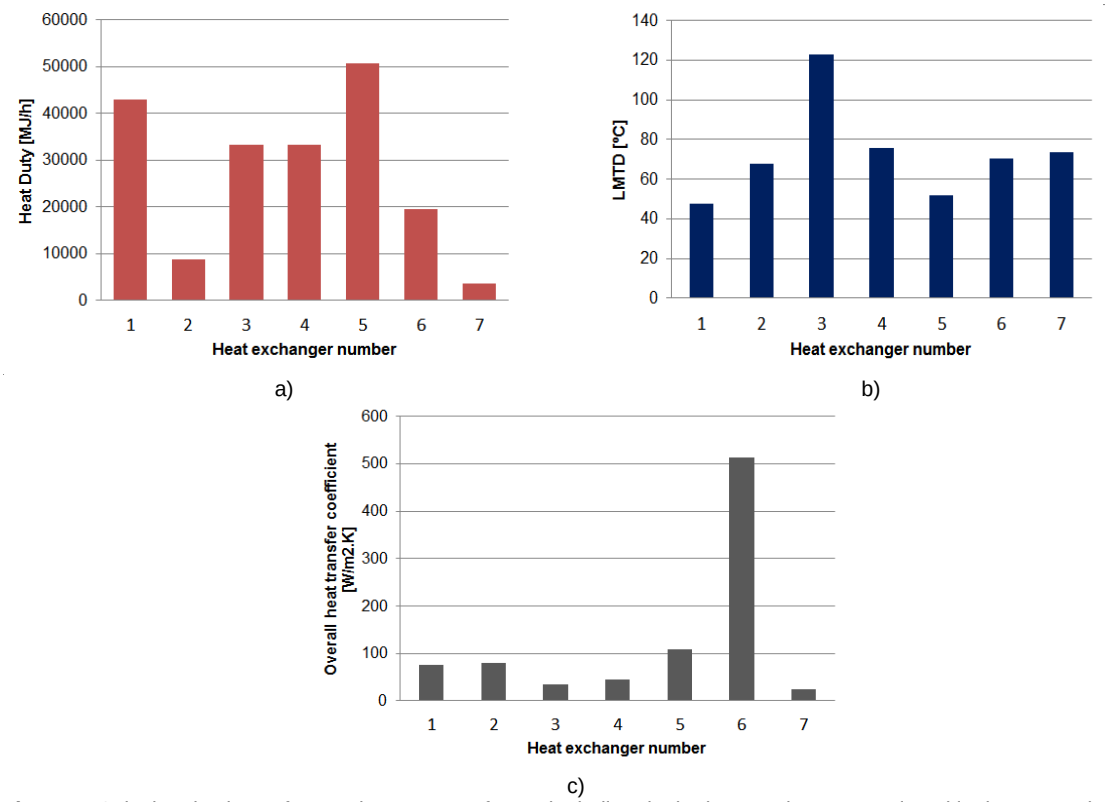

Figure 4. Calculated values of several parameters for each shell and tube heat exchanger employed in the PA production process: a) Heat duty, b) LMTD and c) Overall heat transfer coefficient.

The results presented in Figure 4 indicate that the heat exchanger with the highest heat duty is unit number 5 (Cooler 3), with a value of 50,590.4 MJ/h. This is attributed to the cooling operation performed on the outlet gaseous stream from Cooler 2, which undergoes a temperature reduction from 165 ºC to 45 ºC. The substantial temperature drop of 120 ºC results in the release of a significant amount of thermal energy during the cooling process. Additionally, the volume of gas to be cooled and the specific heat capacities of the stream components likely contribute to the elevated heat duty observed in this unit.

With respect to the logarithmic mean temperature difference (LMTD), the highest value was recorded in heat exchanger number 3 (Cooler 1), at 122.74 ºC. This is primarily due to the fact that this unit is responsible for cooling the gaseous stream exiting the tubular reactor, which reaches the highest temperature in the entire production process (353 ºC). The cooling is achieved using boiler feed water at 110 ºC, resulting in a pronounced temperature gradient across the exchanger.

Finally, the heat exchanger exhibiting the highest overall heat transfer coefficient was unit number 6 (Pre-heater 2), with a value of 513.48 W/m²·K. This unit facilitates both the preheating and vaporization of the outlet stream from the switch condensers, elevating its temperature to a maximum of 230 ºC prior to its introduction into the first distillation column. Consequently, this exchanger demonstrates optimal utilization of the thermal energy provided by the auxiliary service (high-pressure steam at 254 ºC), rendering it the most efficient in terms of heat transfer performance.

Equipment purchase and installation cost

Table 7 presents the estimated purchase and installation costs for the compressor, pump, and all shell-and-tube heat exchangers incorporated into the proposed phthalic anhydride production process. These values were calculated using the ChemCAD® simulator, based on updated data from the Chemical Engineering Plant Cost Index (CEPCI) corresponding to March 2023.

Table 7. Total purchase and installation cost for selected equipment.

Equipment	Purchase cost (USD $)	Installation cost (USD $)
Compressor + Motor + Driver	752,366	978,075
Pre-heater 1	122,543	245,087
Pump	6,695	18,747
Vaporizer	133,347	266,694
Cooler 1	91,368	182,737
Cooler 2	117,936	235,873
Cooler 3	100,016	200,032
Pre-heater 2	90,647	181,294
Cooler 4	378,246	756,492
TOTAL	1,793,164 ~ 1,794,000	3,065,031 ~ 3,066,000

The data presented in Table 7 reveal that the total costs associated with equipment procurement and installation amounted to approximately USD 1,794,000 and USD 3,066,000, respectively.

Conclusions

A conceptual design of a proposed phthalic anhydride (PA) production process via the gaseous catalytic oxidation of o-xylene was developed using the ChemCAD® 7.1.2 simulator, with the objective of determining the temperature, pressure, vapor fraction, mass flow rate, and composition of the main process streams. The principal design parameters of the equipment included in the process flowsheet were presented, along with the stoichiometry and kinetics of the reactions involved. The thermodynamic model employed in this simulation study was UNIFAC with vapor-phase association according to Hayden–O'Connell, while the Peng–Robinson model was selected as the Global Enthalpy Model. Several parameters were determined for the heat exchangers, including heat curves, heat duty, logarithmic mean temperature difference (LMTD), and overall heat transfer coefficient, as well as the heat duty of the catalytic reactor and specific design parameters of both distillation columns. The total purchase and installation costs associated with the specific equipment incorporated into the proposed production process were also estimated. The bottom stream of the purification column exhibits a mass flow rate of 10,921.083 kg/h, with PA as the predominant component, achieving a purity of 99.19%, while maleic anhydride (MA) is recovered in the top stream of the column with a mass flow rate of 973.342 kg/h and a purity of 83.36%. It is recommended to recover, purify, and recycle the gaseous PA and o-xylene vented through the switch condensers in order to enhance plant productivity. The simulation model developed in this study may serve as a basis for further optimization analyses, as well as for evaluating additional process improvements aimed at increasing throughput and enhancing production efficiency.

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