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# Simulation and conceptual design of an aniline production process from catalytic hydrogenation of nitrobenzene in ChemCAD®

## *(Simulación y diseño conceptual de un proceso de producción de anilina a partir de la hidrogenación catalítica del nitrobenceno en ChemCAD®)*

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**Abstract:** Aniline is a very important compound in organic chemistry, mainly used to synthesize polyurethane and its precursors. In the present work, the simulation and conceptual design of an aniline production process through the catalytic hydrogenation route of nitrobenzene was carried out using ChemCAD® simulator. The simulated aniline production process consisted of a fired heater, a tubular reactor, several heat exchangers, a phase separator, a decanter, as well as two distillation columns. By means of the simulation, the temperatures, pressures, mass flowrates and enthalpies of the main intermediate and final streams were known, as well as the main operating and design parameters of some equipment. About 1,743 kg/h of aniline with a purity of 99,78 % are produced at the top stream of the second distillation column, while about 49 881 kg/h of hydrogen are obtained as a by-product in the phase separator. In this work a first-of-its-kind ChemCAD® simulation model was obtained in this work, which can be utilized for further optimization studies and tasks involving the increment of aniline purity, yields and productivity.

**Keywords:** aniline, nitrobenzene, ChemCAD®, catalytic hydrogenation, conceptual design.

**Resumen:** La anilina es un compuesto importante en la química orgánica, usado principalmente para sintetizar poliuretano y sus precursores. En el presente trabajo se llevó a cabo la simulación y diseño conceptual de un proceso de producción de anilina a partir de la ruta de la hidrogenación catalítica del nitrobenceno usando el simulador ChemCAD®. El proceso de producción de anilina simulado consistió de un calentador quemador, un reactor tubular, varios intercambiadores de calor, un separador de fases, un decantador así como dos columnas de destilación. Por medio de la simulación se conocieron las temperaturas, presiones, caudales másicos y entalpias de las principales corrientes intermedias y finales, así como los principales parámetros de operación y diseño de algunos equipos. Alrededor de 1 743 kg/h de anilina con una pureza de 99,78 % se producen por la corriente del tope de la segunda columna de destilación, mientras que se obtienen alrededor de 49 881 kg/h de hidrógeno como subproducto en el separador de fases. En este trabajo se obtuvo un modelo de simulación de ChemCAD primero de su tipo, el cual puede utilizarse para estudios posteriores de optimización y tareas que involucren el incremento de la pureza, rendimiento y productividad de la anilina.

**Palabras clave:** anilina, nitrobenceno, ChemCAD®, hidrogenación catalítica, diseño conceptual.

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## 1. INTRODUCTION

Aniline is an organic compound consisting of a phenyl group bonded to an amino group, being a typical aromatic amine. The amino group gives aniline a unique reactivity, making it a very important intermediate compound from an industrial point of view. It is a flammable liquid slightly soluble in water.

Most of the aniline produced is used to manufacture methylene-diphenyl-isocyanate, which is used to prepare polyurethane foams and insulation for refrigerators, freezers and buildings. It is also used in various industries such as polymers, rubber, pigments, agrochemicals, varnishes, explosives and dyes [1].

Aniline production reached 8 million tons per year in 2021, and is expected to reach 10 million tons per year by 2027, which could contribute to the development of more efficient and innovative aniline synthesis production processes [2].

Aniline is produced in both gas and liquid phases. In the case of gas phase production, the catalytic hydrogenation process of nitrobenzene is used at temperatures of 300-475 ºC and pressures of 1-10 bar in fixed-bed multitubular reactors provided with cooling systems due to the highly exothermic nature of the reactions [3]. The production of aniline form catalytic hydrogenation of nitrobenzene in liquid phase has been studied by several authors [4], [5] as well as the conversion of nitrobenzene to aniline by means of a semi-continuous bioelectrochemical system using a microbially catalyzed cathode [6].

There is a report [7] where the production of aniline from nitrobenzene in liquid phase was described. This aniline production process was divided into three main steps: hydrogenation of nitrobenzene, dehydration and purification, obtaining aniline with a purity of 99,95 % in the distillate of the last distillation column. The aniline production capacity of this study was 350,000 MT/year, and the total fixed capital of a plant of this capacity using this production technology was estimated to be around USD $ 200 million in the first quarter of 2015.

The production of aniline by the catalytic hydrogenation route of nitrobenzene has been studied primarily in terms of the catalysts to be applied, specifically mono- and bi-metallic nickel catalyst containing hypercrosslinked polystyrene [2]; $Pd/AlO_3$ catalyst [4], [8]; Pd/layered double hydroxide (LDH) catalyst [9]; $Au/ZrO_2$ catalyst [10]; $Cu/SiO_2$ catalyst [11]; Ni/bentonite catalyst [12] and industrial copper catalyst promoted by chromium and nickel and supported in kieselguhr [13].

The integration of a process using Aspen Plus® simulator and Aspen Dynamics® to simultaneously produced aniline by the hydrogenation of nitrobenzene together with the dehydrogenation of methyl cyclohexane to produce toluene has also been investigated [3]. This study proposed to carry out both reactions coupled in a tubular adiabatic reactor instead of a multi-tubular reactor, thus not needing to complex arrangement of the hydrogenation reaction and the high amounts of hydrogen required preventing the occurrence of irreversible deviations. Furthermore, in [14] the production of syngas from the steam reforming process using the nitrobenzene hydrogenation reaction to produce aniline as a heat source was investigated and simulated in MATLAB®. A coupled recuperative reactor was employed in this study where the steam reforming reactions occur inside the tubes, while the nitrobenzene hydrogenation reaction occurs in the shell. The reactor performance was evaluated and analyzed based on methane conversion, hydrogen yield and nitrobenzene conversion. Also, in [15] the catalytic dehydrogenation reaction of ethylbenzene to produced styrene was coupled with the catalytic hydrogenation of nitrobenzene to produce aniline in a simulated integrated reactor consisting of two fixed beds separated by a hydrogen selective membrane, where both hydrogen and heat are transferred across the surface of the membrane tubes. In this study, both countercurrent and cocurrent operation were investigated and the results obtained by simulation were compared

with the corresponding predictions for an industrial adiabatic fixed-bed reactor operated under the same feed conditions. Other authors [11] studied the catalytic hydrogenation of gas-phase nitrobenzene over $Cu/SiO_2$ catalyst in both a single-stage and two-stage fluidized bed reactor at 513-553 K and atmospheric pressure, obtaining as main result that the nitrobenzene conversion and aniline production selectivity increased in the two-stage fluidized bed reactor compared to those results obtained in the single-stage fluidized bed reactor.

Chemical process simulation consists of the computerized representation of one or multiple interconnected unit operations contained in a given chemical plant. It is applied in different fields of process engineering, either to analyze an existing process (assessment), synthesis of new chemical processes (design), or as training for operators and supervisor. In recent years, it has become a basic tool in the field of chemical engineering, mainly to perform the conceptual design of different chemical, petrochemical and biotechnological processes as an important area for research and development [16].

Among the simulators used today is ChemCAD® (Chemstations Inc.). ChemCAD® is a simulator programmed to perform calculations and simulation of chemical processes commonly found in chemical, petrochemical, pharmaceutical and environmental technology, which provides and alternative for carrying out large-scale continuous process simulations. It contains an extensive database of both pure substances and binary mixtures and several thermodynamic model packages in order to model the chemical process under study in an easy, efficient, feasible way, as well as a palette of equipment usually found in the chemical industry.

This simulator has been extensively used in recent years to carry out the modeling, simulation, optimization and sensitivity analysis of different industrial chemical processes. Among these processes we can mention the design and comparison of different chemical processes for fuel generation using syngas as a feedstock [17]; the conceptual design of an acetone production process form the dehydrogenation of isopropyl alcohol for industrial applications [18]; the simulation of an olive pit pyrolysis plant using a rotary kiln [19]; the implementation of a separation process of an acetol/acetic acid mixture to design the flowsheet [20]; the thermal design of a shell and tube heat exchanger used as a cooler and based on the calculation algorithm of CC-THERM integrated module [21]; and the modeling, simulation and control of a reactive distillation column for the production of ethyl acetate from acetic acid and ethanol [22].

Specifically, the authors of this article have used ChemCAD® simulator to simulate various chemical processes, among which we can mention the production of styrene [23]; acrylic acid [24]; cumene [25]; maleic anhydride [26] and ethylene oxide [27].

It is of interest for an investment company to erect an aniline production plant by means of the catalytic hydrogenation of nitrobenzene, since there is a secure, stable market for this product and the economic, financial and logistic conditions for such a project are available. Therefore, the conceptual design of a plant of this type is desired in order to know its productivity, performance and operation, as one of the first stages of the development of a project in the chemical industry [28].

In this context, in the present work an aniline production process from the gas-phase catalytic hydrogenation of nitrobenzene was simulated using ChemCAD® simulator 7.1.2, in order to know the mass composition, temperature, pressure and enthalpy of the main intermediate and final streams, the productivity of the production process, the operational and design parameters of the main equipment, the operating parameters of the heat exchangers, and the preliminary purchase and installed cost of various equipment.

## 2. MATERIALS AND METHODS

### 2.1. Physicochemical properties of aniline

Table 1 shows the main physicochemical properties of aniline, according to [1]:

**Table 1.** Main physicochemical properties of aniline.

| Property | Value |
|---|---|
| Other names | Aminobenzene, Penylamine |
| Molecular formula | $C_6H_7N$ |
| Molecular weight | 98,16 g/mol |
| Solubility | Miscible in water, ethanol, ethylether, benzene and acetone. |
| Melting point | - 6 ºC |
| Boiling point | 184 ºC |
| Flash point | 76 ºC |
| Density | 1.022 g/mL at 27 ºC |

### 2.2. Description of the aniline production process by catalytic hydrogenation of nitrobenzene

Initially, 2,500 kg/h of liquid nitrobenzene are vaporized to a temperature of 310 ºC using a shell and tube heat exchanger (Preheater 1) against the hot gaseous mixture coming from the tubular reactor, as will be discussed later. In another section of the plant, 50,000 kg/h of hydrogen are preheated (hydrogen/nitrobenzene ratio of 20:1 [14]) from 25 ºC to 310 ºC in a fired heater, to then mix the preheated hydrogen with the vaporized nitrobenzene. A high hydrogen/nitrobenzene ratio is employed to avoid reaction run-away and decontrol [3]. The resulting gaseous mixture, which is at 309 ºC, is compressed to 5 bar in a centrifugal compressor. Because the compressed gaseous stream exiting the compressor is at 750 ºC, it is cooled to 340 ºC in a shell and tube heat exchanger (Cooler 1) that uses cooling water at 2 ºC as the heat exchange agent. The cooled gaseous stream is then sent to the tubular reactor, which is already loaded with Cu/Ni catalyst [3], [14]. In this tubular reactor, a temperature and pressure of 320-340 ºC and 2-5 bar, respectively, are maintained during the course of the chemical reaction, where the temperature control is performed by circulating an special oil as a cooling agent, since the catalytic reaction is highly exothermic. Once the chemical reaction is completed, the hot gas mixture leaving the tubular reactor is sent to a shell and tube heat exchanger (Preheater 1), where it gives part of its heat content to the nitrobenzene feed stream in order to vaporize it. The hot gaseous mixture leaving the Preheater 1, which is at 337 ºC, is sent to another shell and tube heat exchanger (Cooler 2), where its temperature is reduced to 30 ºC by means of cooling water at 2 ºC, to then send this cooled stream to a phase separator, where hydrogen is separated from the liquid phase (aniline, nitrobenzene, water). Subsequently, the liquid phase leaving the phase separator is sent to a decanter where a certain amount of water is separated from the rest of the components (aniline and nitrobenzene). The liquid water is obtained at the bottom stream while the aniline/nitrobenzene/water liquid mixture is obtained at the top stream of this decanter. Both the phase separator and decanter operate at 30 ºC. The top stream coming from the decanter is preheated to 110 ºC in a shell and tube heat exchanger (Preheater 2) which uses saturated steam at 152 ºC and 5 bar as the heating agent, and then this preheated stream is sent to a first sieve tray distillation column (Water Column) to separate the water (top stream) from the aniline/nitrobenzene mixture (bottom stream). The bottom stream of the Water Column, which is at a temperature of 186 ºC, is cooled in a shell and tube heat exchanger (Cooler 3) to 110 ºC, which uses cooling water at 2 ºC. Finally, this stream at 110 ºC is fed to a second sieve tray distillation column (Aniline Column), where aniline is separated from nitrobenzene, thus obtaining about 1,740 kg/h of liquid aniline with a purity of 99,7 % in

the top stream, while about 72 kg/h of liquid nitrobenzene are obtained at the bottom stream with a purity of 43,7 %, being aniline the main impurity found in this stream. Figure 1 shows the flow diagram of the aniline production process described above.

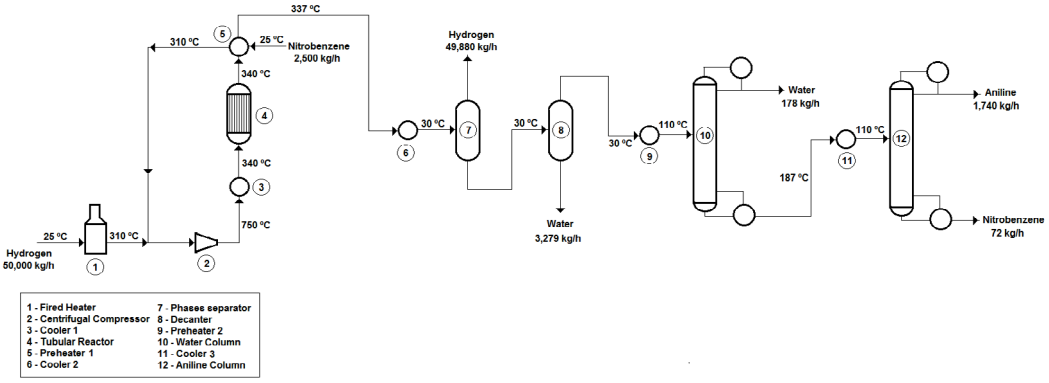
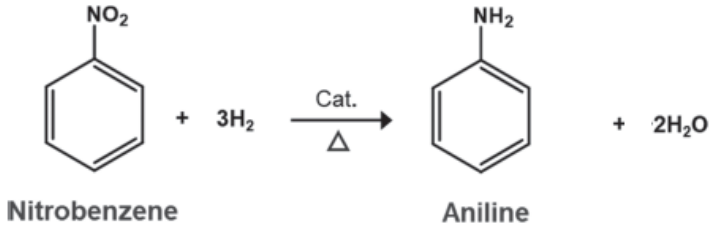



**Figure 1.** Flow diagram of the aniline production process from the catalytic hydrogenation of nitrobenzene.

### 2.3. Chemical reaction occurring in the tubular reactor, and its conversion, kinetics and catalyst properties

According to [8], the reaction of aniline production from the catalytic hydrogenation of nitrobenzene has the following stoichiometry:




(1)

The conversion of this reaction is 97 % [3] with a $\Delta H_{298}$ = - 443.0 kJ/mol [14], [15] while the catalyst used (Cu/Ni) presents the following properties [14], [15]:

- Density: 1,400 kg/m$^3$.
- Diameter of the catalyst particle: 4,7x10$^{-3}$ m.
- Void fraction: 0,46.

The kinetics of the catalytic hydrogenation reaction of nitrobenzene is described by the following rate equation [14], [15]:

$$r' = \frac{k' \cdot K_{NB} \cdot K_{H2} \cdot p'_{NB} \cdot \sqrt{p'_{H2}}}{\left(1 + K_{NB} \cdot p'_{NB} + K_{H2} \cdot \sqrt{p'_{H2}}\right)^2} \quad (2)$$

In this case, the reaction rate constant ($k'$) is defined as:

$$k' = A' \cdot \exp\left(-\frac{E'}{R \cdot T}\right) \quad (3)$$

Where:

$A'$ = 0,186; $E'$ = 10,0 kJ/mol; $K_{H2}$ = 4,427x10$^{-3}$ Pa$^{-0,5}$; $K_{NB}$ = 1,510x10$^{-5}$ Pa$^{-1}$.

### 2.4. Selection of the thermodynamic model

The selected thermodynamic model was PSRK with vapor phase association of Hayden O'Connell, while it was considered the global phase option of vapor/liquid/liquid/solid and the global enthalpy models of latent heat. Finally, the chosen ideal gas heat capacity was DIPPR and the selected steam table was of IAPWS-IF97.

### 2.5. Equipment design parameters

Table 2 shows the design parameters considered for each of the main equipment involved in the simulation of the aniline production process, which were set taking into account the suggestions and recommendations reported in [29], [30], [31], [32] and [33].

**Table 2.** Main design parameters of the equipment included in the aniline production process simulated in ChemCAD®.

| Equipment | Design parameters |
|---|---|
| Fired heater | Type: Vertical, cylindrical.<br>Tube material: Stainless steel 316.<br>Thermal efficiency: 0,75. |
| Compressor | Type: centrifugal.<br>Driver type: Variable speed drive coupling.<br>Motor type: Explosion proof.<br>Motor RPM: 3600. |
| Cooler 1 | Type: Shell and tube.<br>Exchanger type: Fixed head.<br>Material: Stainless steel 316.<br>Area: 30 $m^2$. |
| Preheater 1 | Type: Shell and tube.<br>Exchanger type: U Tube.<br>Material: Stainless Steel 304.<br>Area: 40 $m^2$. |
| Reactor | Type: Tubular, fixed bed.<br>Material: Stainless steel 304.<br>Diameter: 4,0 m.<br>Length: 7,0 m.<br>Tubes: 700 2-inch diameter tubes 5,5 m long. |
| Cooler 2 | Type: Shell and tube.<br>Exchanger type: Fixed head.<br>Material: Stainless steel 304.<br>Area: 30 $m^2$. |
| Phases separator | Type: Cylindrical tank.<br>Material: Carbon steel.<br>Diameter: 2,5 m.<br>Height: 4,0 m. |

| | |
|---|---|
| Decanter | Type: Cylindrical tank.<br>Material: Carbon steel.<br>Diameter: 3,0 m.<br>Height: 5,0 m. |
| Preheater 2 | Type: Shell and tube.<br>Exchanger type: U Tube.<br>Material: Stainless Steel 316.<br>Area: 40 $m^2$. |
| Water column | Type: Cylindrical.<br>Material: Carbon steel.<br>Diameter: 2,0 m.<br>Tray type: Sieve. |
| Cooler 3 | Type: Shell and tube.<br>Exchanger type: Fixed head.<br>Material: Carbon steel.<br>Area: 20 $m^2$. |
| Aniline column | Type: Cylindrical.<br>Material: Carbon steel.<br>Diameter: 1,5 m.<br>Tray type: Sieve. |

## 2.6. Purchase and installed costs of various equipment

The purchase and installed costs of various equipment involved in the simulated production process were determined using the "Costing" option contained in ChemCAD® software. Accordingly, the purchase and installed cost contained in the software was updated to November 2023 using the cost index of Chemical Engineering magazine [34].

Figure 2 shows the flowsheet of the aniline production process by the catalytic hydrogenation route of nitrobenzene simulated in ChemCAD®.

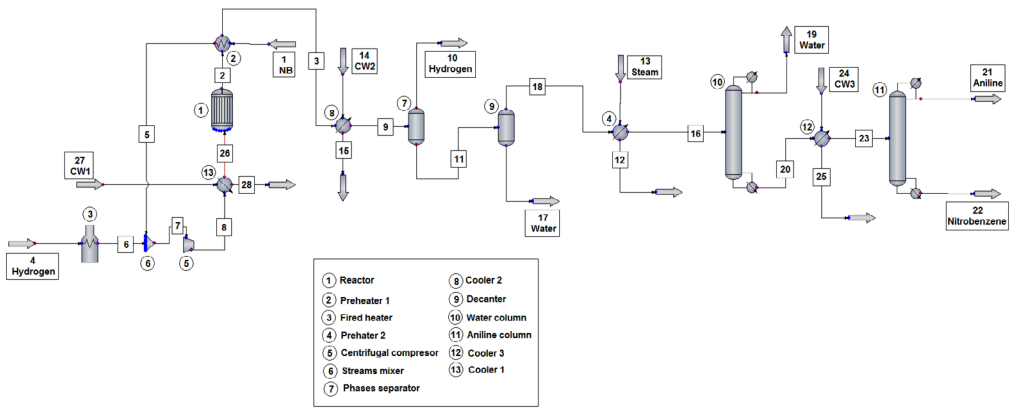



**Figure 2.** Flowsheet of the aniline production process by the catalytic hydrogenation of nitrobenzene obtained by the simulation in ChemCAD®.

## 3. RESULTS AND DISCUSSION

### 3.1. Simulation parameters of the intermediate and final streams

Table 3 displays several parameters of the main intermediate and final streams, which were obtained by simulating the production process in ChemCAD® simulator. For the values of these parameters, according to the stream number, refer to Figure 2.

**Table 3.** Simulated parameters of the main intermediate and final streams.

| **Parameter** | **Stream number (refer to Figure 2)** | | | |
|---|---|---|---|---|
| | **7** | **26** | **2** | **9** |
| Temperature (ºC) | 310,74 | 340 | 340 | 30 |
| Pressure (bar) | 1 | 5 | 5 | 2 |
| Vapor fraction | 1 | 1 | 1 | 0.999 |
| Enthalpy (MJ/h) | 209,413 | 231,370 | 222.042,7 | -4.467,28 |
| | | Mass flowrate (kg/h) | | |
| Nitrobenzene | 2,500 | 2,500 | 74,99 | 74.99 |
| Hydrogen | 50,000 | 50,000 | 49.880,88 | 49,880.88 |
| Aniline | - | - | 1.834,42 | 1.834,42 |
| Water | - | - | 709,71 | 709,71 |
| Total flow (kg/h) | 52,500 | 52,500 | 52,500 | 52,500 |

**Table 3.** Continued…

| **Parameter** | **Stream number (refer to Figure 2)** | | | |
|---|---|---|---|---|
| | **10** | **11** | **17** | **16** |
| Temperature (ºC) | 30 | 30 | 30 | 110 |
| Pressure (bar) | 1 | 1 | 1 | 1 |
| Vapor fraction | 1 | 0 | 0 | 0.184 |
| Enthalpy (MJ/h) | 3.670,13 | -10.601,21 | -8.430,17 | -1.559,54 |
| | | Mass flowrate (kg/h) | | |
| Nitrobenzene | - | 74,99 | - | 74.99 |
| Hydrogen | 49.880,88 | - | - | - |
| Aniline | - | 1.834,42 | - | 1.834,42 |
| Water | - | 709,71 | 532,28 | 177,43 |
| Total flow (kg/h) | 49.880,88 | 2.619,12 | 532,28 | 2.086,84 |

**Table 3.** Final.

| **Parameter** | **Stream number (refer to Figure 2)** | | | |
|---|---|---|---|---|
| | **19** | **20** | **21** | **22** |
| Temperature (ºC) | 99,60 | 187,00 | 186,43 | 194,51 |
| Pressure (bar) | 1 | 1 | 1 | 1 |
| Vapor fraction | 1 | 0 | 0 | 0 |
| Enthalpy (MJ/h) | -2.357,52 | 1.298,46 | 1.206,01 | 92,83 |
| | | Mass flowrate (kg/h) | | |
| Nitrobenzene | - | 74,99 | 3,75 | 71,25 |
| Hydrogen | - | - | - | - |
| Aniline | - | 1.834,42 | 1.742,68 | 91,72 |
| Water | 177,43 | 0,001 | 0,001 | - |
| Total flow (kg/h) | 177,43 | 1.909,41 | 1.746,43 | 162,97 |

According to the results of Table 3, the outlet stream of the tubular reactor (stream 2 in Figure 2) is composed of 3,49 % aniline, being hydrogen the chemical compound with the highest presence in this stream (95,01 %).

Of the 2,500 kg/h of nitrobenzene fed to the tubular reactor, approximately 75 kg/h remained unreacted for a conversion rate of 97 % with respect to this compound, which is consistent with that reported by [3]. In addition, the amount of hydrogen that reacted was 119,12 kg/h and the amount of aniline formed was 1.834,42 kg/h, thus agreeing with the results reported by [35].

In the phase separator, all the hydrogen contained in the inlet stream fed to this equipment (49,880.88 kg/h) is separated at the top stream (stream 10), which can be recovered, purified and conditioned to be recirculated to the aniline production process, or used as raw material in other chemical processes. Thus, it is recommended to carry out further studies to implement steps and operations to recover, purify and condition this important flowrate of hydrogen.

The liquid stream coming from the bottom of the phase separator (stream 11) contains 70,04 % aniline, in addition to water (27,09 %) and nitrobenzene (2,86 %), while 532,28 kg/h of water are discharged from the bottom stream of the decanter (stream 17), for a separation percentage of 75 % regarding this compound in this equipment. This water can be treated and reused in the production plant for the cleaning of equipment, areas and other operations where it is needed.

In the first distillation column (Water Column), almost all the inlet water is separated, which is obtained in the top stream (19) with a flowrate of 177,43 kg//h, while a liquid mixture consisting of aniline (96,07 %) and nitrobenzene (3,93 %) is contained in the bottom stream. The percentage of water separation in this column is almost 100%.

In the second distillation column, the separation of aniline from nitrobenzene is carried out, obtaining 1,742.68 kg/h of aniline with a purity of 99,78 % at the top stream of this equipment (stream 21), being nitrobenzene the main impurity found on this stream. The bottom stream of this Aniline Column (stream 22) is composed of nitrobenzene (43,72 %) and aniline (56,28 %). It is recommended to evaluate the possible recycle of this bottom stream to the aniline production process to recover the quantities of both chemicals, thus improving the productivity and profitability of the simulated plant.

### 3.2. Operating parameters of equipment

Shown below are several operating and design parameters calculated by ChemCAD® simulator for several equipment involved in the simulated aniline production process.

Reactor:

- Calculated heat of reaction: - 464,28 kJ/mol.

Fired heater:

- Heat absorbed: 206,55 GJ/h.

Centrifugal compressor:

- Theoretical power: 245,929 MJ/h.
- Actual power: 327,905 MJ/h.
- Cp/Cv: 1.393.

Cooler 1:

- Log Mean Temperature Difference (LMTD): 486.305 ºC.
- LMTD Correction factor: 0,976.
- Calculated overall heat transfer coefficient: 5,966 W/m$^2$.K.

Preheater 1

- LMTD: 120.463 ºC.

- LMTD Correction factor: 0,987.
- Calculated overall heat transfer coefficient: 120.97 W/m$^2$.K.

Cooler 2:

- LMTD: 106.029 ºC.
- LMTD Correction factor: 1.00.
- Calculated overall heat transfer coefficient: 19,600 W/m$^2$.K.

Preheater 2:

- LMTD: 75.022 ºC.
- LMTD Correction factor: 1.00.
- Calculated overall heat transfer coefficient: 75,47 W/m$^2$.K.

Cooler 3:

- LMTD: 109.989 ºC.
- LMTD Correction factor: 1,00.
- Calculated overall heat transfer coefficient: 42,21 W/m$^2$.K.

Water column:

- Condenser duty: - 500.97 MJ/h.
- Reboiler duty: 1,001.45 MJ/h.
- Minimum stages: 27.
- Reflux ratio, minimum: 1.643.

Aniline column:

- Condenser duty: - 1,877.7 MJ/h
- Reboiler duty: 2,212.41 MJ/h.
- Minimum stages: 10.
- Reflux ratio, minimum: 0,891.

According to the results shown above, the value of calculated heat of reaction in the tubular reactor was – 464,28 kJ/mol, which is very similar to the value reported in [14], [15] for this type of chemical reaction.

The heat absorbed in the fired heater was 206,55 GJ/h, which is within the range reported by [33] for this type of equipment (11-210 GJ/h).

Regarding the calculated overall heat transfer coefficients (U), in case of the Cooler 1 and Cooler 2 the calculated values of U (5,966 W/m$^2$.K and 19,600 W/m$^2$.K, respectively) are higher than the range suggested by [28] of 20-300 W/m$^2$.K for this type of heat exchange service. In the case of Preheater 2, the calculated value of U (75.47 W/m$^2$.K) is within the range reported by [28] of 60-450 W/m$^2$.K. Finally, the calculated value of U for Cooler 3 (42,21 W/m$^2$.K) is within the range described by [28] of 30-300 W/m$^2$.K. In this case, Cooler 2 presents the highest value of U while Cooler 3 has the lowest value of U among all the shell and tube heat exchanger used in the simulation.

The calculated actual power of the centrifugal compressor (327,905 MJ/h $\cong$ 91 MW) is within the range reported by [36] of 75 kW-97 MW for this compressor type, while the theoretical power had a value of 245,929 MJ/h ($\approx$ 68 MW).

The Water Column will have a minimum number of stages of 27, a condenser and reboiler duty of – 500,97 MJ/h and 1,001.45 MJ/h respectively, and a minimum reflux ratio of 1.643. Likewise, the Aniline Column will have a minimum number of stages of 10, a condenser and reboiler duty of - 1,877.7 MJ/h and 2,212.41 MJ/h respectively, and a minimum reflux ratio of 0,891. That is, more stages are needed in the Water Column to separate the water from the aniline/nitrobenzene mixture, requiring in turn a lower duty in the condenser which is due to the fact that the condenser selected in this column was of partial type, while the condenser selected in the Aniline Column was of total type. The Aniline Column required fewer stages because of

the significant difference existing between the boiling points of aniline and nitrobenzene, being aniline more volatile than nitrobenzene.

### 3.3. Heat duty of the heat exchangers

Figure 3 displays the heat duty values calculated by ChemCAD® simulator for each of the heat exchangers used in the production process.

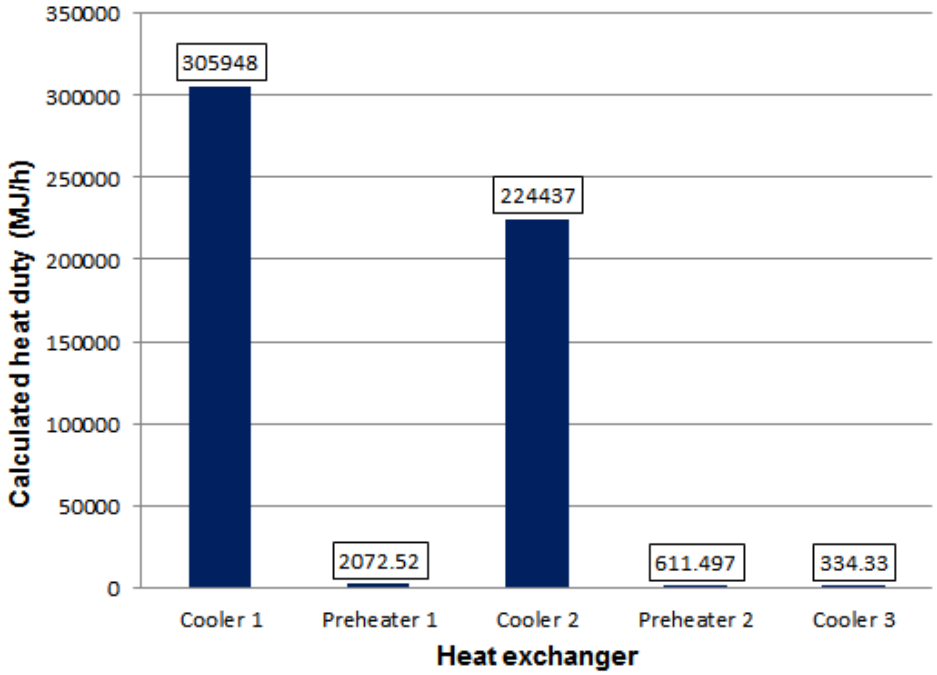



**Figure 3.** Calculated heat duty for each heat exchanger used in the production process.

The heat duty of Cooler 1 has the highest value of all (305,948 MJ/h) mainly because it is in this equipment where the cooling of the nitrobenzene/hydrogen gaseous mixture is carried out from 753 ºC to the reaction temperature (340 ºC), i.e. there is a high temperature difference (ΔT = 413 ºC), in addition to handling a high flowrate of gaseous compounds (52,500 kg/h).

On the other hand, Cooler 2 also has a high heat duty (224,437 MJ/h), which is basically due to the fact that it is the heat exchanger where the gaseous outlet stream of the reactor is cooled from 337 ºC to 30 ºC, i.e. it has the second highest ΔT (307 ºC) while it also handles a gaseous mixture stream composed of several chemicals with a high flowrate.

Finally, Cooler 3 has the lowest value of the heat duty (343.33 MJ/h) because its ΔT is the lowest (77 ºC), i.e. the outlet liquid stream coming from the bottom of the Water Column, composed of aniline and nitrobenzene, is cooled from 187 ºC to 110 ºC before being fed to the Aniline Column. It also should be noted that it is the heat exchanger that handles the lowest flowrate of all the heat exchangers, with 1,909.41 kg/h.

### 3.4. Heat curves of the heat exchangers

Figure 4 presents the heat curves for each of the heat exchangers included in the production process, which were obtained using the "Heat Curves" option included in ChemCAD® simulator.

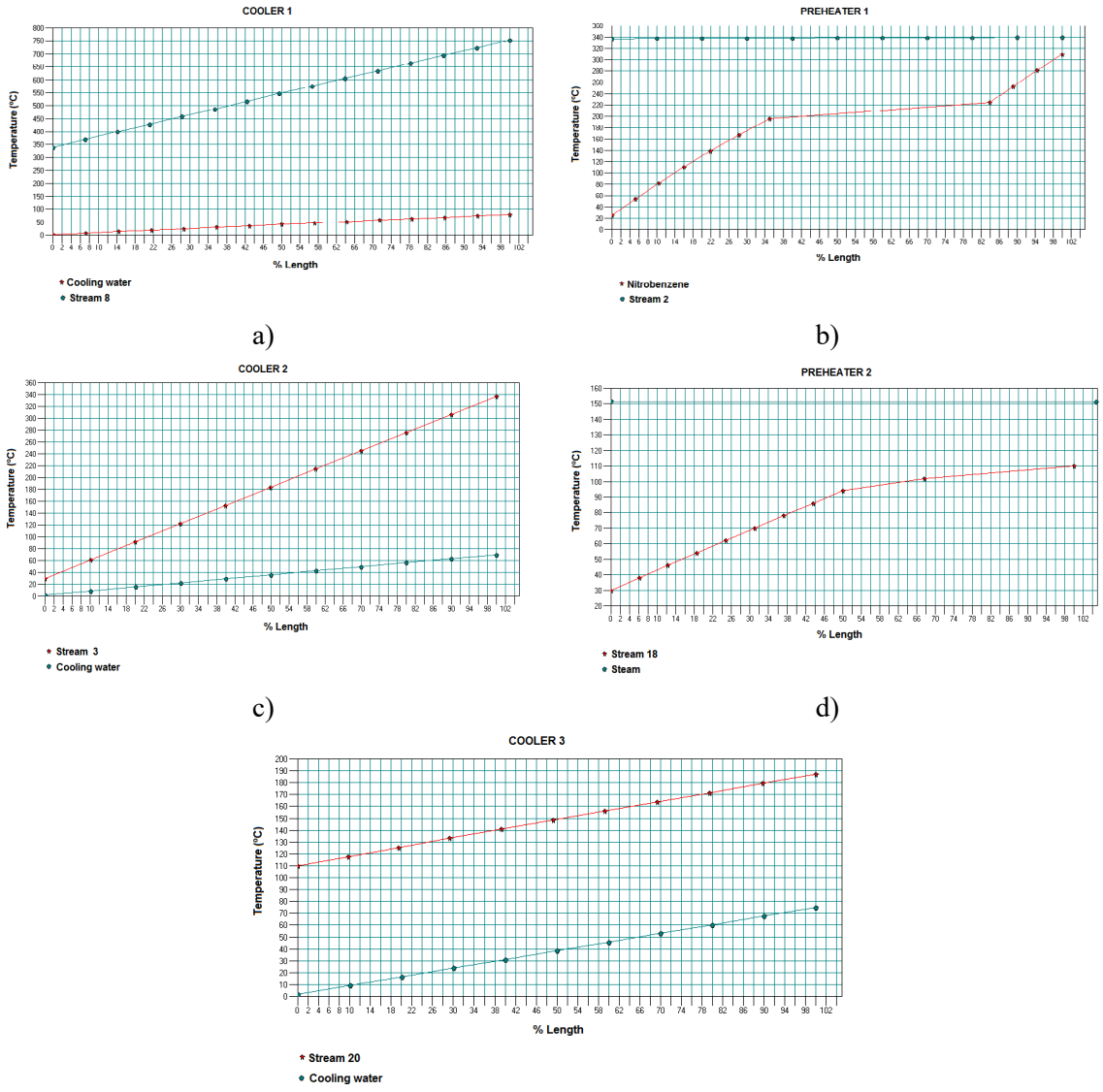



**Figure 4.** Heat curves of all the heat exchangers included in the production process:

a) Cooler 1.
b) Preheater 1.
c) Cooler 2.
d) Preheater 2.
e) Cooler 3.

The heat curve of Cooler 1 (Figure 4a) shows two linear trends for both the cooling water stream and stream 8 (nitrobenzene and hydrogen gaseous mixture). This indicates that both streams do not undergo phase change, i.e. the cooling water is heated from 2 ºC to 80 ºC without vaporization, while the gaseous stream is cooled from 753 ºC to 340 ºC without condensing.

In the case of the heat curve of Preheater 1 (Figure 4b), stream 2 shows a linear behaviour, indicating that this stream cools from 340 to 337 ºC while the nitrobenzene stream shows and ascending linear behaviour up to the 35 % length of the heat exchanger and at a temperature of approximately 195 ºC, to then undergo a phase change (vaporization) between the 35 % and

84 % length of the equipment, to finally gain sensible heat from 225 ºC to 310 ºC. It is worth noting that, according to the simulation results, the nitrobenzene has a vapor fraction equal to zero before being fed to Preheater 1, while its vapor fraction is equal to one at the exit of this heat exchanger, which confirms that this pure nitrobenzene stream is totally vaporized in this heat exchanger.

Considering the heat curve of Cooler 2 (Figure 4c), both stream 3 and cooling water stream present a linear tendency, suggesting that none of these streams undergo phase change in this equipment. Stream 3 is cooled from 340 ºC to 30 ºC without condensing, while the cooling water stream is heated from 2 ºC to 70 ºC without vaporization.

In the heat curve of Preheater 2 (Figure 4d), the stream of saturated steam does not undergo phase change at the temperature and pressure fed to this heat exchanger (152 ºC and 5 bar, respectively), which is corroborated by verifying that the vapor fraction of the inlet and outlet streams of steam to the Preheater 2 is equal to one, that is, it does not condense. Stream 18 is heated from 30 ºC to 100 ºC (up to length 50%) without phase change, and then vaporization occurs for certain fraction of components from 100 ºC to the outlet temperature (110 ºC). This is confirmed by noting that the value of the vapor fraction of the outlet stream of Preheater 2 (stream 16) is 0,18, i.e. a two-phase gas-liquid mixture is obtained at the outlet of this heat exchanger.

Finally, in the heat curve of Cooler 3 the cooling water stream is heated from 2 ºC to 75 ºC without vaporization considering the increasing linear trend of its heat curve, while stream 20 is cooled without occurring condensation from a temperature of 187 ºC to 110 ºC, considering the decreasing linear tendency of the heat curve. This is confirmed by observing that the vapor fraction of both stream 20 and stream 23 is equal to zero.

### 3.5. Purchase and installed cost of various equipment

Table 4 shows the purchase and installed cost of various equipment included in the simulated production process, which were determined using the "Costing" option contained in the ChemCAD® simulator. The total amount of both cost items is also shown. The purchase and installed costs of the reactor, phase separator, decanter and distillation columns were not determined because the simulator does not have this option.

**Table 4.** Purchase and installed cost of several equipment included in the simulated aniline production process.

| Equipment | Purchase cost (USD $) | Installed cost (USD $) |
|---|---|---|
| Fired heater | $6.9719x10^6$ | $9.06347x10^6$ |
| Centrifugal compressor | $3.26058x10^7$ | $4.73061x10^7$ |
| Cooler 1 | 33,282 | 66,564.1 |
| Preheater 1 | 35,368.3 | 70,736.5 |
| Cooler 2 | 26,290.7 | 52,581.4 |
| Preheater 2 | 33,282 | 66,564.1 |
| Cooler 3 | 11,883.4 | 23,766.8 |
| Total | 39,717,806.4 | 56,649,782.9 |
| | ~ 39,720,000 | ~ 56,700,000 |

The equipment with the highest acquisition cost is the centrifugal compressor with USD $ $3.26x10^7$, while the equipment with the lowest cost is Cooler 3 (USD $ 11,883.4). A total amount of USD $ 39.72 million and USD $ 56.70 million will be required to purchase and install the equipment listed in Table 4.

In general, the purchase costs of all the individual equipment included in Table 4 agree with those reported in [29] and are lower than those reported in [28].

## 4. CONCLUSIONS

The simulation and conceptual design of an aniline production process by the catalytic hydrogenation route of nitrobenzene was carried out in this work using ChemCAD® simulator. Through the simulation, the temperature, pressure, mass flowrate, enthalpy and vapor fraction of the main intermediate and final streams of the simulated production process were known, as well as the main operating and design parameters of some equipment, the heat duty and heat curves of the shell and tube heat exchanger used, in addition to the purchase and installed costs of several equipment.

Cooler 1 was the heat exchanger that had the highest calculated heat duty, with 305,948 MJ/h, and a value for the overall heat transfer coefficient (U) of 5,966 $W/m^2.K$, which is higher than the value reported by [28]. Cooler 3 had the lowest value of the heat duty with 343,33 MJ/h and a value for U of 42,21 $W/m^2.K$, which is within the range reported by [28]. In this case, Cooler 2 presented the highest value of U (19,600 $W/m^2.K$) while Cooler 3 had the lowest value of U (42,21 $W/m^2.K$) among all the shell and tube heat exchanger employed in the production process.

The calculated heat of reaction for the tubular reactor (- 464,28 kJ/mol) agrees with what is reported in the literature [14], [15], while the heat absorbed in the fired heater was 206,55 GJ/h, which is within the range reported by [33].

The heat curves obtained in this study show that the two process streams do not undergo phase change in three of the heat exchangers (Cooler 1, Cooler 2 and Cooler 3), which is verified by the linear trend observed for both streams in the corresponding heat curves. On the other hand, the heat curve obtained for Preheater 1 indicates that the nitrobenzene stream experienced total vaporization; while the heat curve obtained for Preheater 2 shows that the Stream 18 undergoes partial vaporization, thus obtaining a two-phase gas-liquid mixture at the heat exchanger's outlet, with a vapor fraction of 0,18 in Stream 16.

The first distillation column (Water Column) had a minimum number of stages of 27, and a heat duty for the condenser and reboiler of – 500,97 MJ/h and 1,001.45 MJ/h respectively. Similarly, the second distillation column (Aniline Column) had a minimum number of stages of 10, while the values of the heat duty for the condenser and reboiler were - 1,877.7 MJ/h and 2,212.41 MJ/h respectively. The Aniline Column needed less number of stages due to relatively significant difference existing between the boiling points of aniline and nitrobenzene, where aniline is more volatile than nitrobenzene.

The purchase and installed cost of certain equipment included in the process flowsheet amounted USD $ 39.72 million and USD $ 56.7 million respectively, being the centrifugal compressor the equipment with the highest calculated purchase cost (USD $ $3.26 \times 10^7$)

The simulated production plant produces 1,742.68 kg/h of aniline with a purity of 99,78 % at the top stream of the second distillation column. Also, 49,880.88 kg/h of hydrogen are obtained at the top stream of the phase separator, which is recommended to be recovered, conditioned and possibly recycled as raw material in the aniline production process. Likewise, the bottom stream of the second distillation column contains 43,72 % nitrobenzene and 56,28 % aniline; therefore it is suggested to recycle this stream to the production process as raw material, to increase its productivity and profitability.

The main contribution of this work is that a simulation model of an aniline production process through the catalytic hydrogenation of nitrobenzene was obtained for the first time using ChemCAD® simulator, which could be utilized for supplementary tasks involving the

increment of aniline yields and throughput, sensitivity analysis and optimization studies of key operating parameters.

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