

Bachelor Dissertation

Bachelor of Science in Chemical Engineering

Aspen HYSYS Simulation of Maleic Anhydride
Production from n-Butane via Partial Oxidation

Simulación con Aspen HYSYS de la producción de
Anhídrido Maleico a partir de la oxidación parcial de
n-Butano

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Seville, 2017

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Acknowledgements

Profound thanks to my dissertation supervisor, *Dr. Villanueva* who has been a continuing source of information as well as a solid guide throughout the development of this work.

I am deeply grateful to *my family* whose patience and motivation have always helped me bring out the best of me.

I would like to express deep gratitude to *Luis Miguel C.* who, since freshman year, has been my main peer emotional support and has never let me down; to *Javier N.* who has taught me how to be a great team player and an outstanding friend; to *Jose David J.* for providing me with unfailing support, continuous encouragement and an endless source of inspiration.

To *Debora A.* who has helped me in the past years to care for even the smallest details. I am grateful for her patience, generosity and amazingly precise and considerate editing.

I am also grateful to *David G., Armando C., César P.* and *Marina V.*, among others, who over the years have, with great generosity, in different ways helped me to learn, become a better person and who have been remarkable emotional support.

Xaquelina K. Oliva Kowalsky

Seville, 2017

Abstract

The documentation of the various technologies both current and outdated for the production of maleic anhydride was performed the first place. Afterwards, the modeling and simulation of a maleic anhydride process plant was carried out in this dissertation. Maleic anhydride is produced via n-butane partial oxidation. The software used for the simulation is Aspen HYSYS. Technical data were collected from various sources such as patents and manuals. The chosen technology for the oxidation sections and unreacted n-butane recycle is Dupont's circulating fluidized bed (CFB) which is based on US Patent 4,668,802 and uses VPO catalyst in the CFB reactor. The chosen technology for the recovery section developed by Monsanto has been followed through US Patent 4,188,403.

Throughout the simulation, there have been temperature restrictions concerning liquid mixtures of water and maleic anhydride in order to prevent reactions that lead to maleic acid and fumaric acid. The gaseous mixture and organic solvent interaction are considered as ideal mixtures. The production capacity of the chosen plant is roughly 36,800 metric tons per year. Percentages higher than 99 % concerning product purity and recuperation were obtained as well as reactive losses of about 20 %

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List of symbols and abbreviations

°C	Degrees Celsius
Mt	Million tons
m ³ /h	Cubic meters per hour
kPa	Kilopascals
Torr	Torricelli
K	Degrees Kelvin
m.t.	Metric ton
kt/yr	Kilotons per year
kJ/mole	Kilojoule per mole
m	Meter
mm	Milimeter
bar	Bar
kg	Kilogram
m ² /g	Squared meter per gram
kg/m ³	Kilograms per cubic meter
%n/n	Percent mole
%vol.	Percent volume
%wt.	Percent weight
MAN	Maleic anhydride
FA	Fumaric acid
MA	Maleic acid
UPR	Unsaturated polyester resins
SMA	Styrene-maleic anhydride

MA/AA	Acrylic Acid Maleic Anhydride
THF	Tetrahydrofuran
BDO	1,4-butanediol
VPO	Vanadium-phosphorus-oxygen
CFB	Circulating fluidized bed reactor
SD process	Scientific-Design process
GHSV	Gas hourly space velocity (1/h)

1 INTRODUCTION, BACKGROUND INFORMATION, OBJECTIVES, AND BOUNDARIES

1.1 Background information

1.1.1 Description

Maleic anhydride (MAN) is an organic compound with the chemical formula $C_4H_2O_3$ which main features are two carbonyl groups and a double bond as seen in Figure 1 (1). This chemical is a strong irritant to skin, eyes, and mucous membranes of the upper respiratory system (2). It is also known by other names such as 2,5-furandione, dihydro-2,5-dioxofuran, toxilic anhydride, and cis-butenedioic anhydride (3).

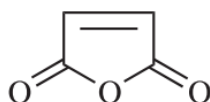


Figure 1 – Structural formula of maleic anhydride (3)

1.1.1.1 Physical properties

At room temperature, this organic compound it is a white crystalline solid with a pungent odor which begins melting at 52.8 °C and boils at 202 °C. However, for handling reasons, during production, it is a liquid or gas (2).

Typical specifications call for a HAZEN color of 20 or less for molten maleic anhydride (4).

This chemical compound is soluble, from greatest to lowest, in acetone, benzene, toluene, o-xylene and kerosene among other organic components (5). However, conditions must be carefully adjusted to avoid isomerization to maleic and fumaric acid (3).

1.1.1.2 Chemical properties

Due to the extremely reactive double bond, maleic anhydride reacts readily (hydrolyzes) with water to form maleic acid (MA) at about 60 °C and fumaric acid (FA) at 100 °C. Fumaric acid crystallizes and is not readily soluble in water. Thermal treatment and catalyst are used to enhance formation of fumaric acid by maleic acid isomerization (3). This reaction is shown in Figure 2.

By limiting the aqueous maleic anhydride acid concentration to 40 % and the temperature to less than 85 °C, fumaric acid will not form in > 0.1 % weight of the reaction mixture.

Maleic acid can be thermally dehydrated from an aqueous solution or through azeotropic distillation to maleic anhydride (3).

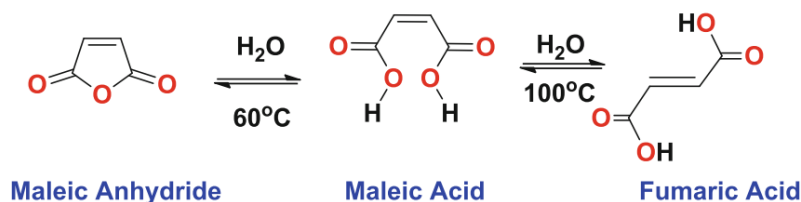


Figure 2 – Reactions from maleic anhydride to maleic acid and fumaric acid (6)

Maleic anhydride is also suitable for homopolymerization and copolymerization forming polymers such as styrene-maleic anhydride (SMA) or Acrylic Acid Maleic Anhydride (MA/AA) (5).

1.1.2 Applications

Unlike maleic acid, the anhydride is a multifunctional chemical intermediate which has great importance in the chemical industry. The global uses of this compound for the year 2009 (Figure 3) are in order of importance: unsaturated polyester resins, butanediol related chemicals and others which include lube oils and additives, maleic copolymers, fumaric and malic acid and agricultural chemicals among other applications.

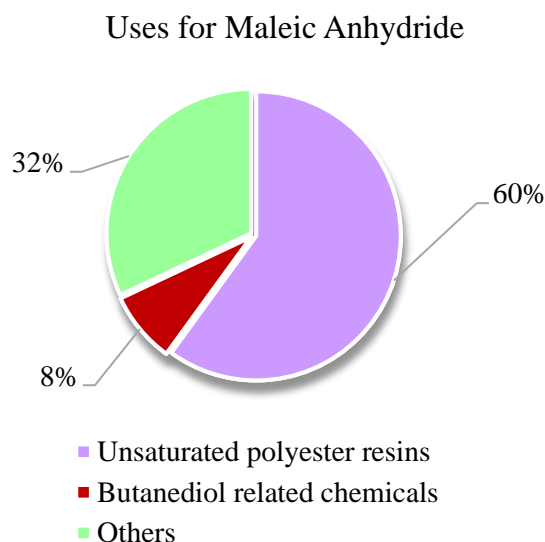


Figure 3 – Maleic Anhydride uses in the United States during the year 2009 (7)

- Unsaturated Polyester Resins (UPR) hold almost two-thirds of the chart. These resins happen to be the major end use of maleic anhydride as feedstock in its production. These laminating resins, which have high structural strength and good dielectric properties are used both in glass-reinforced and in unreinforced applications. The data in the following pie chart (Figure 4) covers the wide range of uses for UPR during the year 2000 including: A third of the chart in construction such as building panels, almost a quarter in other which covers diverse uses; for example, luggage or bathtubs. In third place, marine and transportation industry hold almost the same weight covering aspects such as molded boats and automobile bodies. Corrosion applications cover ten and a half percent and include uses like construction of chemical storage tanks. Lastly, smaller amounts of UPR are used in electrical applications such as radar domes holding not even two percent (1)(2).

Uses for Unsaturated Polyester Resins

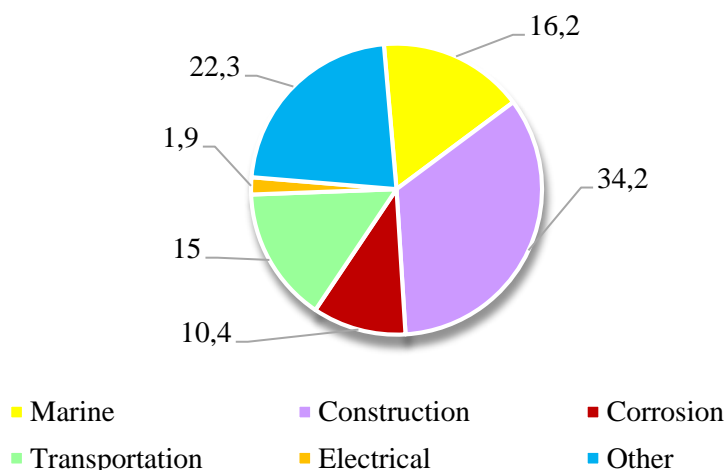


Figure 4 – Uses for Unsaturated Polyester Resins in the United States, 2000 (3)

- Maleic anhydride is a key feedstock in the manufacturing of copolymers since it is a low-cost monomer that adds functionality to traditional petrochemical polymer materials such as binding wood into fiber plastic, inhibiting corrosion, creating protective coatings for wires or even repelling water in sunscreens (8)(7). The aforementioned copolymer, SMA, is used for engineering plastics while MA/AA is used in the detergent industry (1).
- Smaller amounts of MAN are used in agriculture, more specifically in the production of pesticides (captan, malathion) and growth inhibitors (maleic acid hydrazide) (5).
- Maleic anhydride through conversion to fumaric and malic acids, is a vital component of gelling agents, flavor enhancers, and food preservatives. It is also essential to the production of elastane (Spandex) fibers, artificial sweeteners, paper-sizing, water treatments, hardeners for epoxy curing, hairsprays, pharmaceuticals, agricultural chemicals and motor oil additives (8).
- Other end products include lube oils additives, plastics, succinic acid and surface active agents (2).
- After the year 2000, maleic anhydride began to be used as raw material in the production of 1,4-butanediol (BDO), gamma-butyrolactone and tetrahydrofuran (THF). It is important to highlight that nowadays, BDO is one of the world's fastest growing chemicals which is used as raw material in the manufacturing of plastics, elastic fibers and polyurethanes explaining thusly the reason for which this chemical compound does not appear in the pie chart (1).

1.2 Objectives

The purpose of this project is the modeling and simulation of the production process of maleic anhydride via n-butane partial oxidation with Aspen Plus.

The production capacity of the plant is chosen 36,800 cubic meters per year, in other words, about 48,500 metric tons per year of maleic anhydride at a purity of 98% n/n. This capacity is similar to that of a near relatively small scale maleic anhydride production plant (9).

The chosen technology for the oxidation section and unreacted n-butane recycle is Dupont's circulating fluidized bed (CFB) which is based on US Patent 4,668,802 and uses VPO catalyst in the CFB reactor due to the achievement of high selectivities and low risks of explosions.

The chosen technology for the recovery section developed by Monsanto has been followed through US Patent 4,188,403 due to high product recovery and use of thermally stable solvents that do not require multiple stripping

stages in order to be separated from maleic anhydride.

1.3 Boundaries

In this work, it has been avoided, at all times, liquid phase water and maleic anhydride mixtures at temperatures above 60 °C in order to prevent reaction between these two components that leads to maleic acid (60 °C) and fumaric acid (130 °C). It has also been considered the fact that the gaseous mixture interaction with the organic solvent were ideal mixtures.

What occurs inside the CFB reactor has not been taken into account in this work. It has been considered a black box. Therefore, the quantity of catalyst has not been calculated. Aspects such as effluent treatment, raw material pretreatment, economic studies, process control and auxiliary systems are beyond the scope of this work.

2 STATE OF THE ART

This chapter will begin by covering maleic anhydride global economic aspects throughout the early 2000s. Secondly, the main process routes used since 1930 shall be critically discussed. Including outdated processes such as benzene feedstock and newer ones like C4 hydrocarbons. The existence of various technologies depending on the chosen reactor is studied in the third subsection of this chapter.

After analyzing all three different reactors used for maleic anhydride production – fixed bed reactor, fluidized bed reactor and transport bed reactor – the comparison of the main patented technologies has been included. Lastly, this chapter covers the general production process of maleic anhydride indicating its key stages.

2.1 Maleic Anhydride Global Market

As seen in Figure 5, the bar chart illustrates a total MA demand of approximately 1.3 m.t. with a market value of 900MUS \$ for the year 2000. The biggest producers of maleic anhydride in that same year 2000 were Sisas (225,000 t/year), Huntsman (110,000 t/year) and Ashland (63,000 t/year) (10). As for the following years, the global maleic anhydride market in 2005 dropped to about 1.25 m.t. which later increased by 0.45 m.t. in the year 2009.

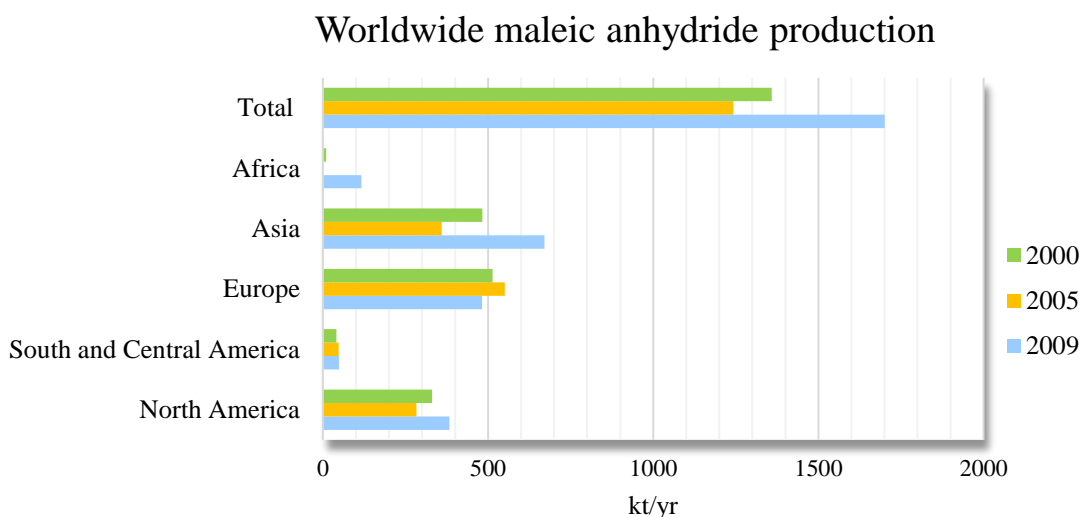


Figure 5 – Worldwide Maleic Anhydride Production for the years 2000, 2005, 2009 (3) (7) (11)

Tight market conditions, as well as rising feedstock butane cost, have driven up MAN prices about 50% during 2004. Supply was also tight in Europe and Asia because high benzene costs had forced benzene-based MAN producers to either shut down plants or cut back production.

Except for Africa which no data has been found, between the years 2005 and 2009, the production of MAN fell slightly in most cases. Tom Fisher, Vice-President Maleic anhydride and commercial licensing at Huntsman, stated: “The demand for UPR has slumped due to the significantly slower housing, auto and marine markets” (7). However, demand for the production of MAN copolymers was projected to grow, specifically for products that aim for a better sustainability profile.

Focusing on a relatively local example for the year 2007, CEPESA’s Gibraltar-San Roque petrochemical plant produced about 5,300 tons of maleic anhydride roughly priced at 2,13 US \$ per ton. Of all petrochemicals produced at said refinery, MAN is ranked third-to-least –meta-xylene and fumaric acid– in terms of production in comparison with benzene (205,000 t) or toluene (125,000 t) (4).

The market was tight until about mid-2007, but the slowdown has made the market predominantly long in 2009. Supply was stable and new entrants were not expected in the US. Although, globally there has been

consolidation with older smaller plants, especially in Europe and Asia (7).

Global MAN demand is expected to grow by at least 4% per year, a little above-forecasted GDO rates. Elvira Greiner, consultant at SRI Consulting (Menlo Park, CA) stated that “As long as the economy does well, demand from UPR and BDO segments should continue to drive MAN demand” (11). Even today, the most important markets are in Europe, The US, and Japan. Overall, it is possible to extrapolate an increase with time in the maleic anhydride global market.

2.2 Process routes

This compound was first prepared in the 1830s but its commercial manufacture did not begin until a century later. The first industrial process was based on benzene oxidation as feedstock and vanadium oxide catalyst in 1933 by the National Aniline and Chemical Co., Inc. In 1962, Denka began producing maleic anhydride by converting n-butenes and a decade later, Monsanto began production by converting n-butane. Nowadays, there are three main ways to produce maleic anhydride industrially as seen in Figure 6 (3).

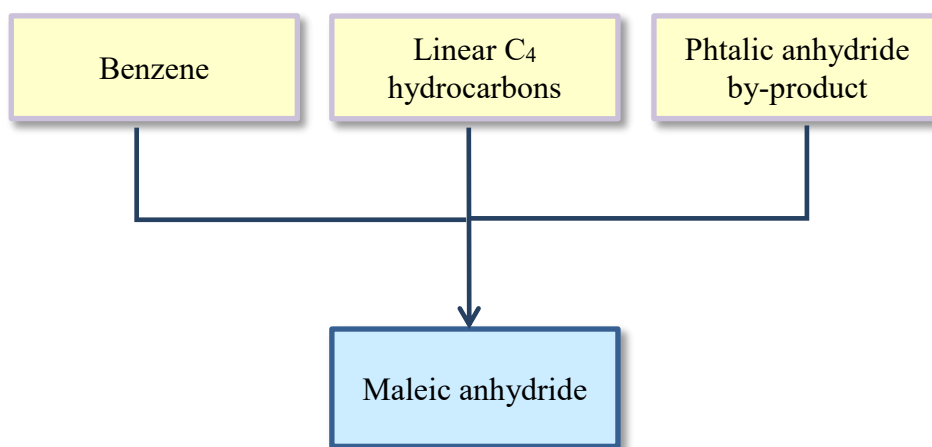
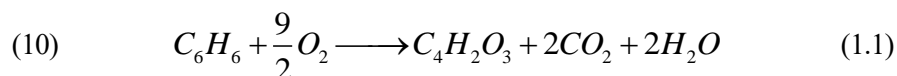


Figure 6 – Maleic anhydride process routes (12)

2.2.1 Benzene oxidation

As mentioned before, the main process route to maleic anhydride was carried out by means of partial catalytic oxidation of benzene in vapor phase:



Benzene, although easily oxidized – very exothermic reaction, -1,848 kJ/mole – to maleic anhydride with high selectivity is an extremely inefficient feedstock due to the excess of carbon atoms between the feedstock and the end product. Therefore, two of carbon atoms of benzene have to be removed by forming carbon dioxide (3) (10).

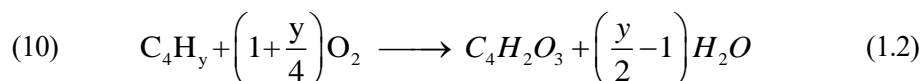
This processing route remains in companies with no alternative feedstock. The technology is quite similar to fixed bed n-butane plants. Thusly, some companies retrofitted their benzene plants to use n-butane (13).

Besides maleic anhydride, the major by-products of benzene oxidation are maleic acid, fumaric acid, carbon monoxide and water. During maleic anhydride manufacture, small amounts of benzoquinone have been found in reaction products, thusly considering it an intermediate product. In addition to benzoquinone, formaldehyde, diphenyl, phenol, and hydroquinone are also reported to be produced in small amounts (14).

2.2.2 Linear C₄ hydrocarbon feedstock

Rapid increases in the price of benzene and the recognition of benzene as a hazardous material made the process obsolete. Therefore, the search for alternative process technology intensified. Since the 1960s, the number of production plants with n-butane as a feedstock has increased steadily. However, early butane-based catalysts were not active and selective enough to allow the conversion of benzene-based plants without significant loss of nameplate capacity. Later advances in catalyst technology, increased regulatory pressures, and continuing cost advantages of butane over benzene have led to a rapid conversion of benzene-to-butane-based plants. Nowadays, the partial oxidation of n-butane is the predominant process route to maleic anhydride (3) (10).

The production of maleic anhydride by means of partial oxidation of a linear C₄ hydrocarbon can be generally expressed by the following reaction:



where the amount of hydrogen in the hydrocarbon y equals 10 for n-butane and 8 for n-butene. This reaction is also very exothermic – -1,236kJ/mole – although it is lower than the benzene feedstock process route. A fraction of the oxygen atoms is incorporated in the hydrocarbon molecule. All but two of the hydrogen atoms in the hydrocarbon have to be removed. This is achieved by means of oxidative dehydrogenation resulting in the formation of water. Most of the provided oxygen atoms are used for this purpose (10) (13).

The nature of by-products is quite different from those of benzene. Among them are the lower monoacids (acetic, acrylic...) and the corresponding aldehydes. Some of these are produced in amounts too small to make an economic recovery possible. In either situation, nitrogen, water, and the carbon oxides are vented to the air after recovery of products and hydrocarbons (14).

N-butane is present in some types of natural gas and in crude oil and can be recovered by distillation. It is also produced by a number of refinery cracking and reforming processes. Cases where maleic anhydride plants are not near n-butane sources, transport costs of the feedstock could be a reason for turning to others which are present at the chemical plant's site. Possible feedstocks could be the various components of C₄ streams obtained by steam cracking (10).

2.2.3 By-product of phthalic anhydride

Besides chemical conversion of suitable hydrocarbons, especially linear C₄ hydrocarbons, maleic anhydride may also be obtained as a by-product of phthalic anhydride production in quantities of about 5 - 6% in relation to the produced phthalic anhydride. During the manufacture of phthalic anhydride from naphthalene and o-xylene, small amounts of maleic and citraconic anhydride, as well as benzoic acid, are coproduced. In some cases, after the removal of phthalic anhydride through condensation, the exhaust gases are scrubbed with water. In many cases, the aqueous solution of maleic acid is recovered in the form of fumaric acid. Since the boiling point of maleic anhydride and citraconic anhydride are 199 °C and 213 °C, respectively, a small amount of citraconic anhydride always accompanies the distilled maleic anhydride, lowering its melting point slightly (10) (14).

2.3 Technologies

Several technologies exist for the production of maleic anhydride which can mainly be classified into three categories depending on the type of reactor that is used: multi-tubular fixed bed, fluidized bed, and transport bed reactors (8).

2.3.1 Multi-tubular fixed bed reactors

Like other highly exothermic oxidation reactions, the partial oxidation of hydrocarbons to maleic anhydride cannot be carried out in a simple fixed bed of catalyst pellets. The catalyst bed must be cooled efficiently to prevent high temperatures which are detrimental to reactor performance and destroy the catalyst. Therefore, multi-tubular reactors are used (10).

Industrial fixed bed reactors normally consist of approximately 30,000 individual tubes which filled with catalyst

pellets. These tubes typically measure between 3.5 to 6 m in length and have inner diameters of about 20 to 35 mm. Molten salt flowing through the shell side is used to cool the tubes as mentioned before. The flow of the molten salt is directed perpendicular to the tubes by baffles for optimum heat transfer from the tube insides to the salt. The heat is removed from the circulating salt bath by generating high-pressure steam. The maximum capacity of a single, multitubular fixed bed reactor is limited to about 20,000 metric tons per year (3) (10).

The hydrocarbons usually enter the reactor from the top and are intensively mixed with a separate air stream by static mixers. The resulting mixture then enters the reactor tubes. Due to the separate feeding of hydrocarbons and oxygen, long residence times with conditions above the explosion limit are avoided. The products leave the reactor at the bottom. Because of this direction of flow, no fluidization can occur and the catalyst pellets remain in their positions. The reactor off-gas must be incinerated to destroy unreacted butane and by-products before being vented to the atmosphere. Typically, the reactions are carried out at temperatures between 350 and 450 °C and at slightly elevated pressures of 2 – 3 bar. For the production of maleic anhydride, these reactors operate at a maximum of 2.5 % n/n of n-butane in the inlet feed. The butane-to-maleic anhydride reaction typically reaches its maximum efficiency (maximum yield) at about 85 % butane conversion (3) (10).

As gases are fed into the reactor tubes, they are generally cooler than the mixed salts in the heat exchanger which leads to a cooling effect of the salt mixture in the heat exchanger. A more significant problem would be the gas temperature in the reactor tubes is greater than the salt mixture in the heat exchanger. Under this scenario, a hot spot can be generated in the catalyst tubes. If not controlled, these hot spots can negatively affect the catalyst life and reactor maintenance thusly decreasing the reactor yield. Operational control of the temperature is challenging because there are normally thousands of tubes and only a few points of temperature measurement. It is important to highlight the fact that hot spots may also lead to possible runaway process conditions. For additional safety, the reactors are equipped with rupture disks at both the reactor inlet and exit areas in case of a runaway event (6).

Although the fixed-bed configuration is well known and has been in practice for several years, it can also be scaled-up very easily. However, limited hydrocarbon inlet concentrations due to explosion hazards, possible hot spots and catalyst instability, as well as its regeneration, have been among the major concerns facing this technology (3) (10).

2.3.1.1 Huntsman

During the early 90's Huntsman Chemical Corporation acquired Monsanto's maleic anhydride business which main feedstock is C₄ hydrocarbon including n-butane or butene. It is important to point out the fact that this process mainly focuses on the recovery and purification stages of maleic anhydride rather than the reaction stage. To better understand this process, a basic process flow diagram has been included in this work – Figure 7– (6).

Using this technology, maleic anhydride is prepared commercially by contacting a feed gas comprising molecular oxygen and the aforementioned C₄ hydrocarbon with a vanadium-phosphorus-oxygen (VPO) catalyst to partially oxidize the hydrocarbon in a fixed bed reactor. The reaction product gas which is produced contains maleic anhydride together with oxidation by-products such as CO, CO₂, water vapor, acrylic and acetic acids and other by-products, explained in previous sections, along with inert gases present in the air when used as a source of molecular oxygen.

Due to increased product yields, the preferred method of recovery comprises selectively absorbing the maleic anhydride in a suitable solvent and subsequently stripping the maleic anhydride from the resulting absorption liquor to obtain crude product.

Maleic anhydride is extracted from the reactor effluent stream using a solvent extraction process. The solvent enters through the top of the column while the extracted gaseous stream is vented through the top and the rich solvent containing maleic anhydride is withdrawn through the bottom. The rich solvent is then introduced into a stripping column which typically operates at below atmospheric pressure and a stream of crude maleic anhydride may be extracted as a gas or a liquid.

In cases where crude maleic anhydride is extracted as a gas, it may be condensed to yield a liquid stream. In other cases, the stripping column is refluxed by condensing an overhead stream and returning a portion of the condensate to the top of the stripping column or may even be totally refluxed.

The solvent enters a reboiler where it is heated by a heat exchanger, afterward, it is cooled, and recycled to

the absorber column. The recycled solvent may also be filtered and stored in a storage tank. In the event of solvent decomposition within the process, fresh solvent may be added to the storage tank.

Effluent reactor components with low boiling points that are extracted into the solvent in the absorber column or produced as byproducts of the extraction process are vented from the stripping column.

Maleic anhydride that exits through the vent line is recovered by solvent extraction in a scrubber at conditions similar to those in the condenser, and the scrubbed solvent stream containing maleic anhydride is returned to the absorber column through a scrubbed solvent line. The low boiling components not removed by the scrubber exit the process through a scrubber vent line. The solvent used for the scrubbing process is fed to the scrubber directly from the solvent storage tank (15)

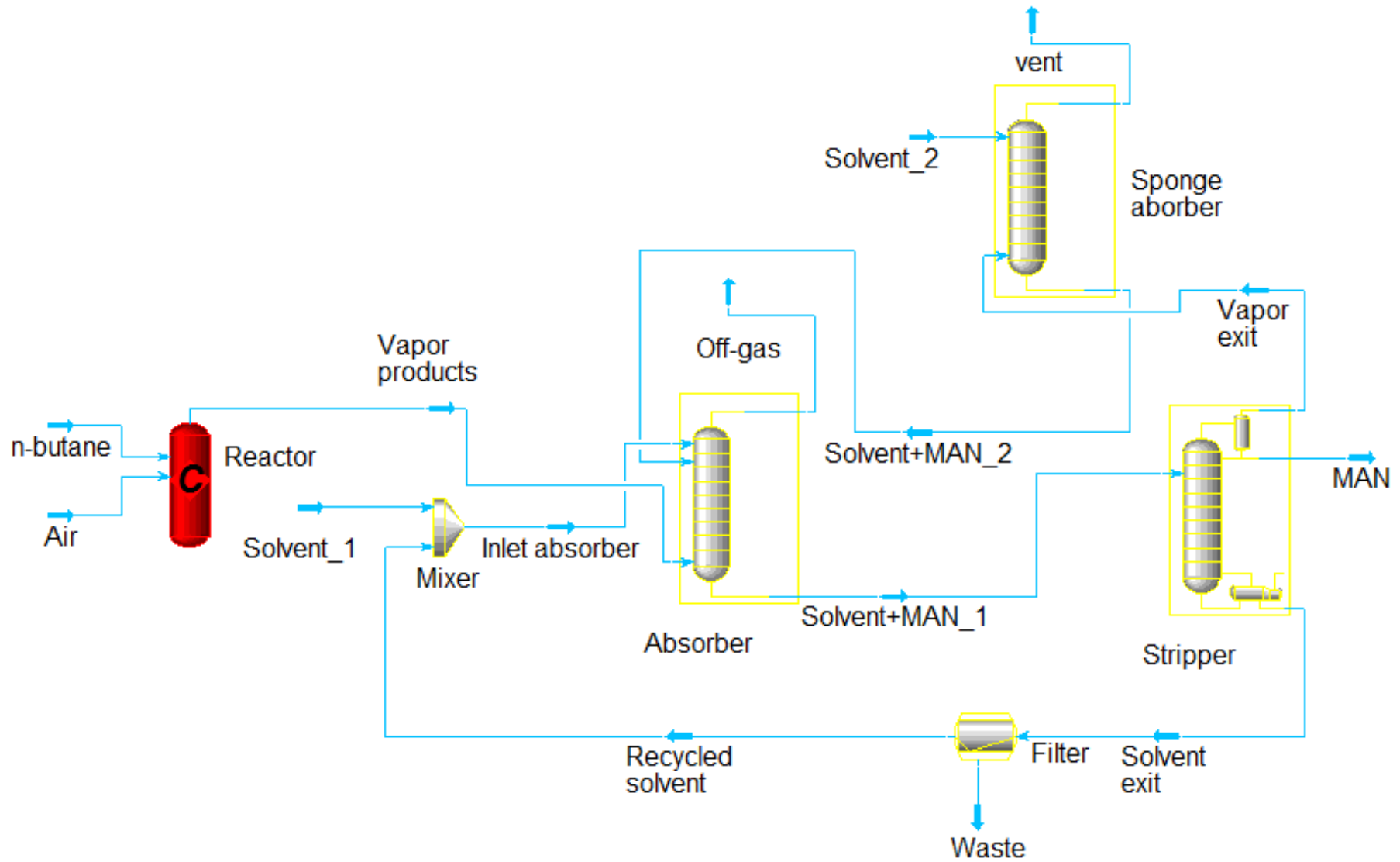


Figure 7 – Huntsman basic process flow diagram for maleic anhydride manufacture (3) (15)

2.3.1.2 Halcon-Scientific Design (HSD)

As mentioned earlier, maleic anhydride production processes were benzene based which afterward converted to C4-based processes. Halcon-Scientific Design is a clear example of a convertible feedstock maleic anhydride manufacturing plant. Figure 8 shows a simplified graphical description of the process.

The feedstock is fed into a compressed air line to be presented into a carbon steel reactor comprised of numerous tubes nominally 3.7 m long and 25 mm in diameter. The hydrocarbon and air are mixed, normally 1.0 to 2.0-mole percent of C4, prior to introduction to the reactor, which houses the catalyst. The reactor is often positioned in an up-flow configuration. The pressure in the operating reactor, ranging from 20 to 50 psi is close to atmospheric requiring only enough pressure to move the gas through the catalyst bed [1800–2800 gas hourly space velocity (GHSV)]. The catalyst is housed in thousands of tubes and surrounded by a heat transfer fluid system as explained earlier. Typically, the catalyst tubes are first packed with an inert material to preheat the gas flow prior to exposure to the catalyst. The reactor heat and heat exchanger are supplied by molten salts. The temperature range of these salts is typically between 390 and 430 °C. These eutectic salt mixtures include salts such as potassium nitrate, sodium nitrate, and sodium nitrite. Many processes recycle this heat in the form of steam generation for additional energy supply.

Upon exiting the reactor, the process stream enters a gas cooler, often made of carbon steel. Partial cooling is applied to the process stream in order to reduce its temperature to just below maleic anhydride's dew point (53–60 °C). The cooled materials then enter a stainless-steel separator, enabling a crude separation between the partially condensed maleic anhydride and other gases and uncondensed vapors. The condensed maleic anhydride is destined for the still pot. It is critical to monitor the temperature at this stage. If the maleic anhydride solidifies, the process can experience blockages coupled to pressure and temperature challenges.

The gas flow continues onto a scrubber unit. The gas flow is contacted with a countercurrent of water to absorb remaining maleic anhydride in the hydrolyzed form of maleic acid. Remaining, unabsorbed overhead gases are exhausted either to the atmosphere or an incinerator. Maleic acid is collected and later pumped to the refiner for further purification processing. In the stainless-steel refiner/condenser batch unit, the maleic acid solution is first dehydrated (azeotropically) with xylenes or toluene. This remaining solution is then combined with the maleic anhydride from the still pot for refining.

The crude maleic anhydride is refined via vacuum distillation. Normally, a forecut at high reflux is removed followed by the collection of product at lower reflux.

The molten maleic anhydride is collected for sale or further converted into briquettes for easier handling. Typical product impurities from such processes include acrylic acid and acetic acid.

The catalyst is vanadium oxide based. The HSD technology allows about 80 % butane conversion with a selectivity of approximately 50 % to maleic anhydride (16). The residual MAN in the stream is scrubbed with an aqueous maleic acid solution. Normally, the solution is brought to 40% of acid. Practically all remaining MAN is recovered by aqueous scrubbing.

The aqueous maleic acid is freed from water by an azeotropic distillation with o-xylene and converted to MAN in the process. The process is designed to minimize thermal isomerization of maleic acid to fumaric acid. MAN from this step and from direct condensation are combined and refiner by distillation (6).

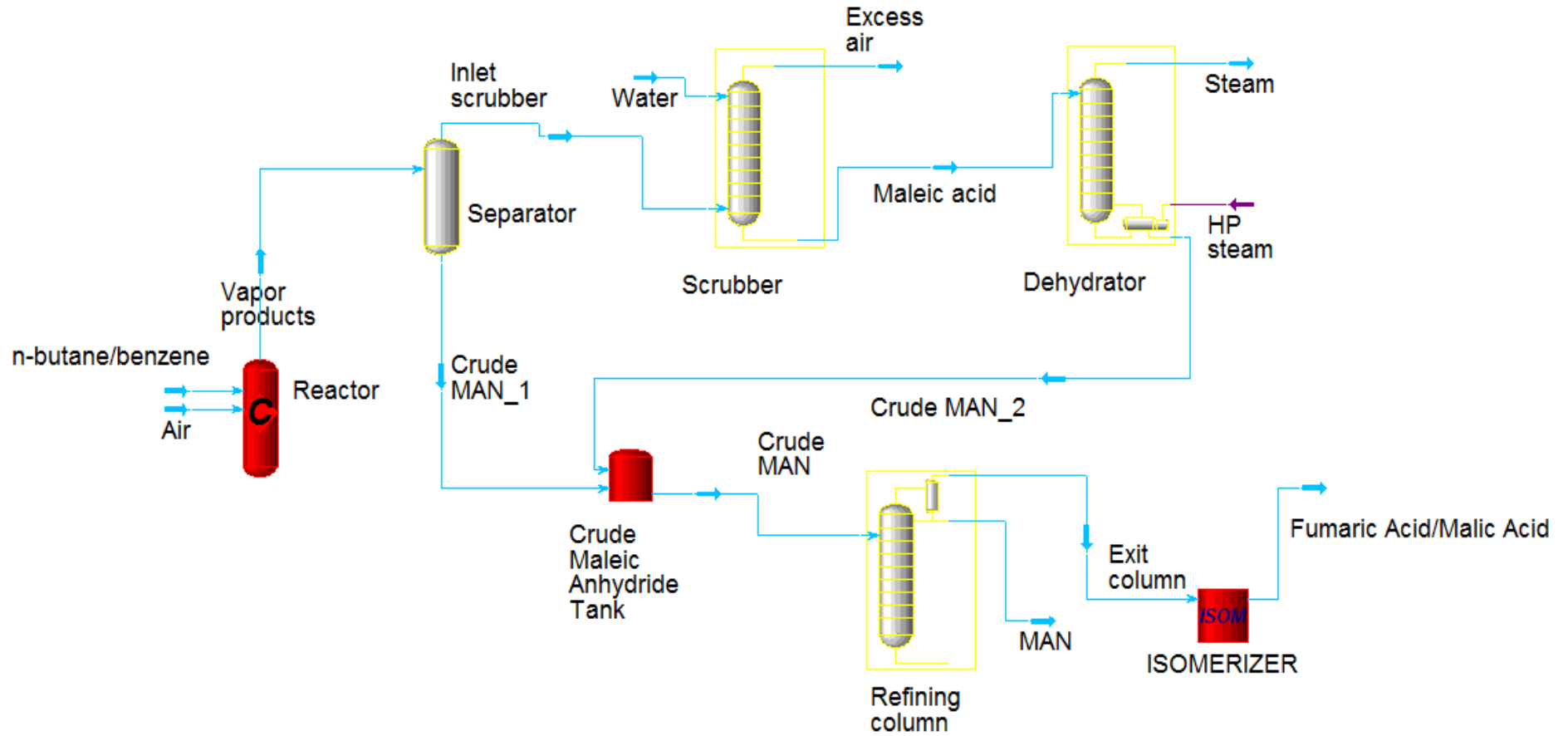


Figure 8 – Halcon-Scientific Design process for maleic anhydride (14) (6)

2.3.1.3 Ruhrol-Lurgi

A process flow diagram – Figure 9 – is provided for this outdated technology which used a mixture of benzene and preheated air passing through a multi-tubular fixed bed reactor cooled by a circulating salt bath. Maleic anhydride was recovered as a solid and liquid in switch condensers. After the condensers were switched, the exiting stream was melted for refining by batch distillation. Recovery was 90%, the remaining 10% maleic anhydride being removed in a two-stage scrubber with water and dilute alkali.

Unconverted benzene was recovered from the exhaust gases in an activated carbon unit. The benzene so obtained was returned to the feedstock. These recovery steps, all combined, made the exhaust gases dust and odor free.

The MA recovered in the scrubber was converted to fumaric acid making the process somewhat dependent on demand balance between MA and fumaric acid (14).

2.3.1.4 Ruhrol-Bayer

This process, as shown in Figure 10, is another example of an outdated technology which derived from the basic Ruhrol process and also used benzene as main feedstock. The recovery system is similar to Scientific Design in which part of the effluent is recovered as molten MAN and the other part as an aqueous maleic acid solution. The latter is dehydrated by azeotropic distillation with xylenes. Benzene in the exhaust gases is removed in absorbers, making it odor free (14).

2.3.1.5 SAVA

A SAVA diagram is represented in Figure 11. This process used an air-benzene mixture (3 %wt benzene) fed to a tubular reactor inside which, the tubes were loaded with a vanadium complex catalyst on extruded cylinders or spheres of alumina. A molten salt bath was used to maintain the temperature of about 355 – 375 °C. The recovery system is also quite similar to the SD process (14).

2.3.1.6 BASF

This process uses n-butene and butadiene mixtures as raw material in fixed bed tubular reactor containing approximately 10,000 tubes housing vanadium based catalyst. The effluent gases from the reactor are cooled and then scrubbed with an aqueous maleic acid solution. Film evaporators are used for the concentration of maleic acid solution and dehydration to MAN. This latter is purified by continuous rectification. This process is shown in Figure 12. In order to eliminate pollution problems, a waste gas incinerator is used (14).

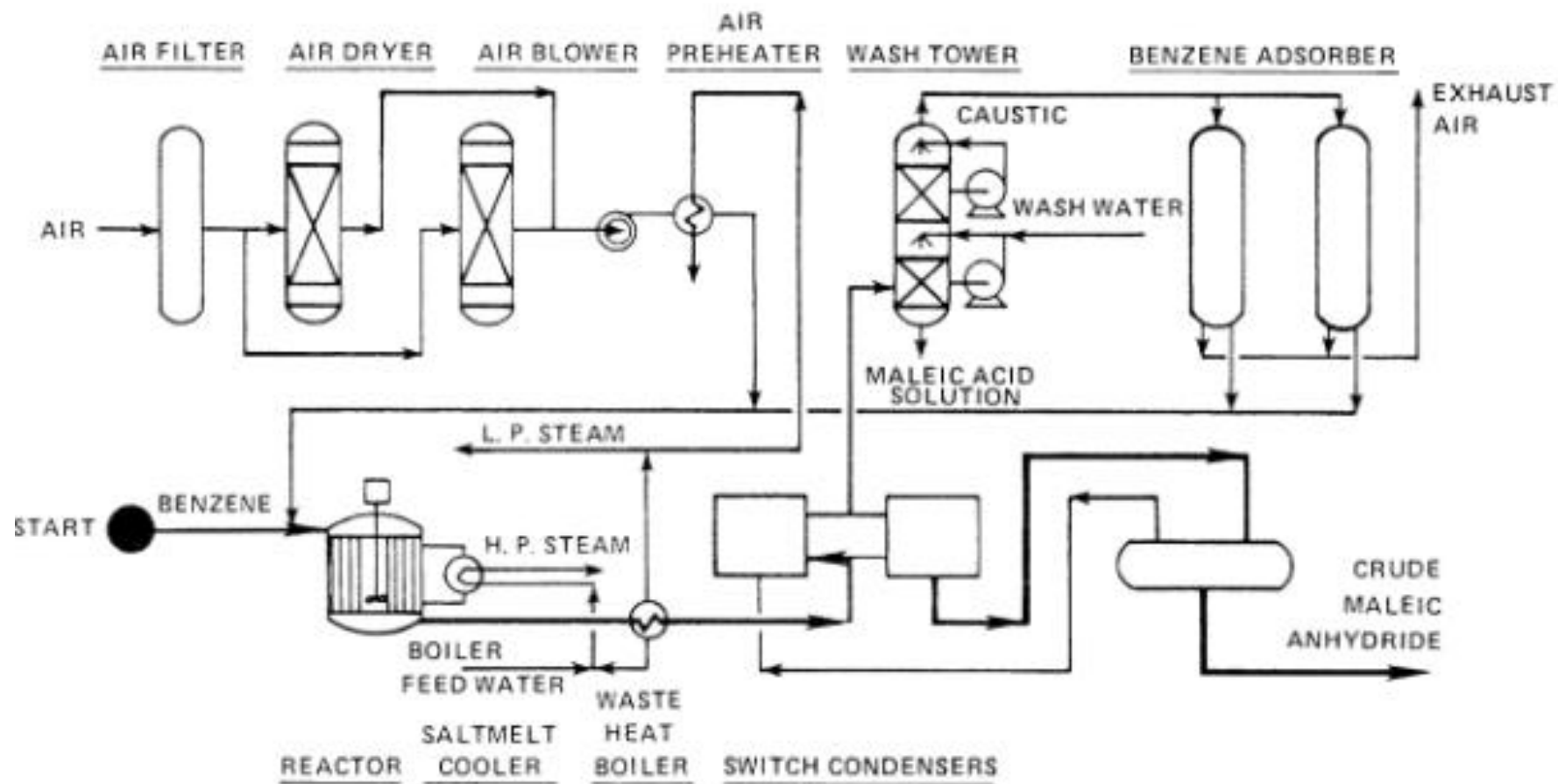


Figure 9 – Ruhrol-Lurgi maleic anhydride production process (14)

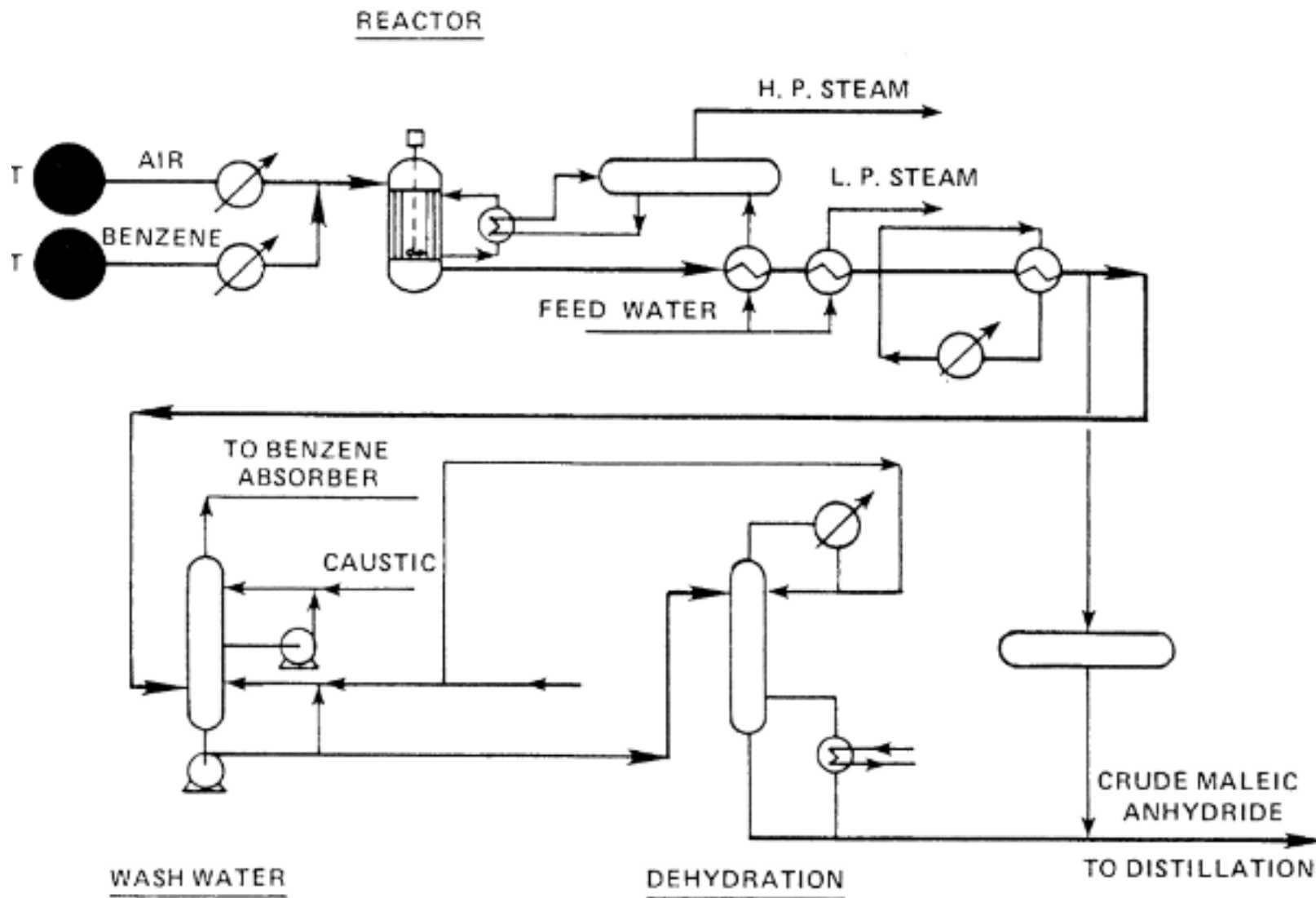


Figure 10 – Ruhrol-Bayer maleic anhydride production process (14)

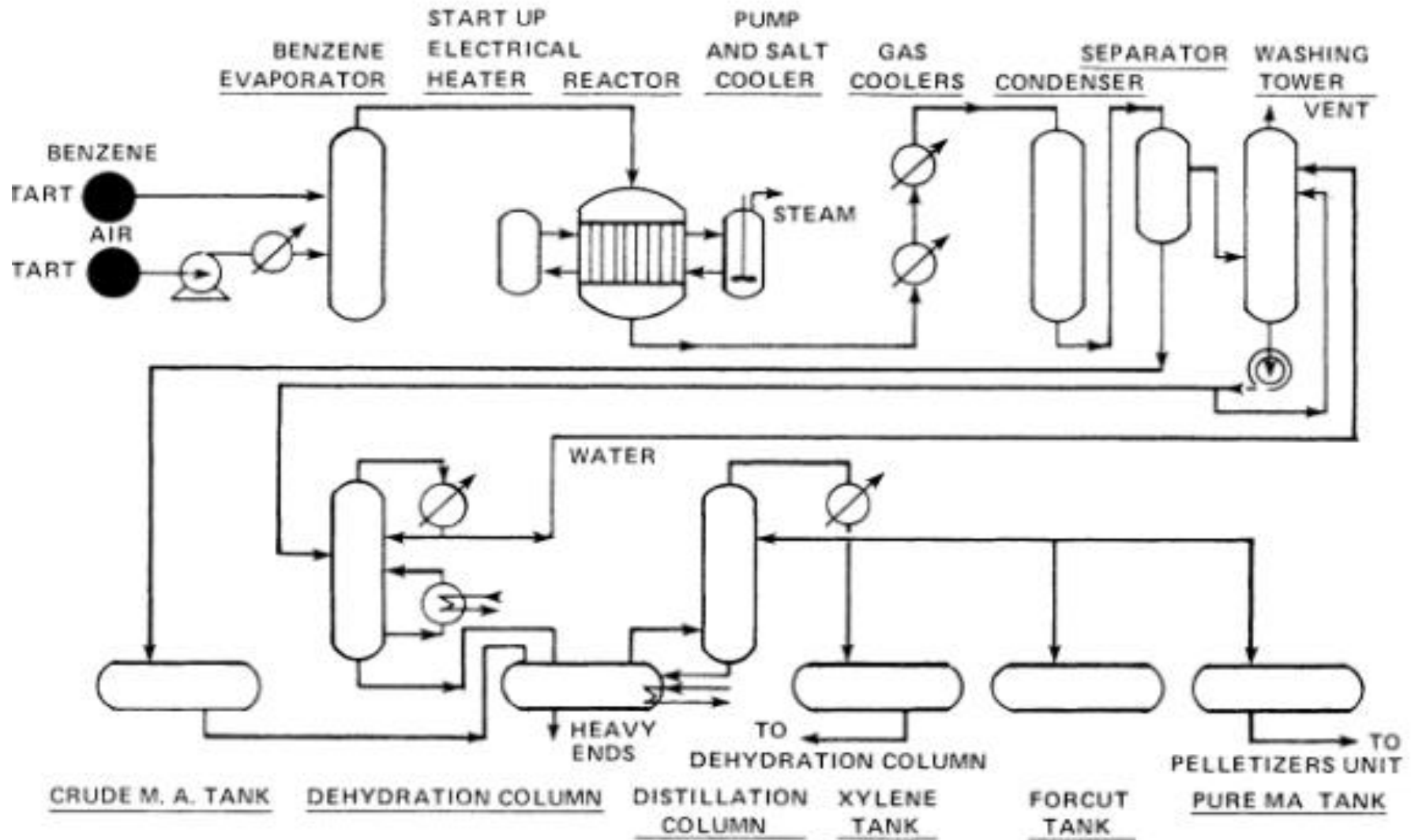


Figure 11 – SAVA process flow diagram for maleic anhydride production (14)

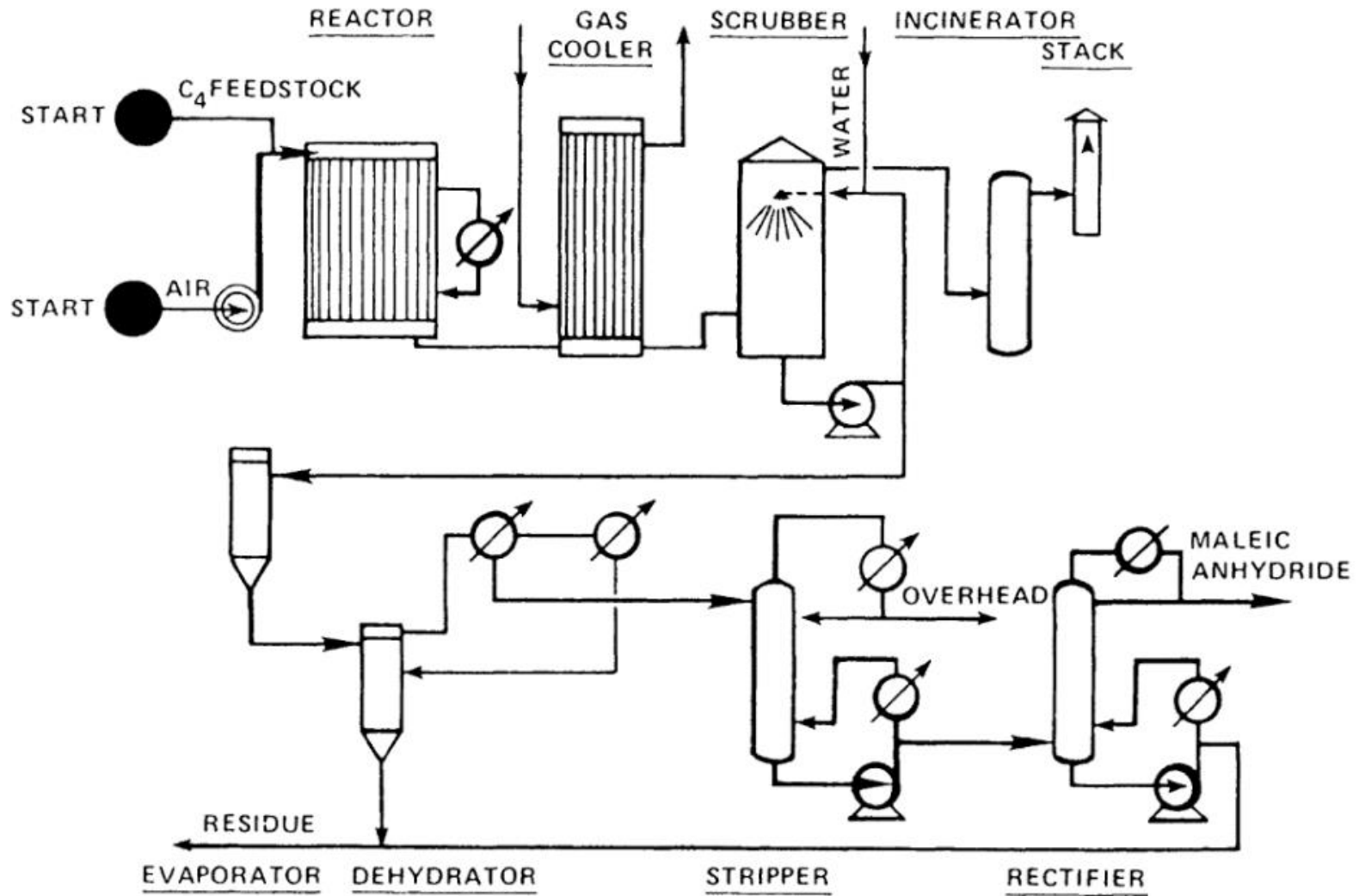


Figure 12 – BASF maleic anhydride process flow diagram (14)

2.3.2 Fluidized bed reactors

As mentioned before, the production of maleic anhydride is highly exothermic therefore this type of reactor also requires efficient heat removal by cooling coils located inside the fluidized bed and generating high-pressure steam inside the coils. The rapid mixing of the catalyst particles in the fluidized bed prevents local hot spots, therefore, achieving a uniform temperature throughout the bed with precise temperature control. Yield losses associated with said hot spots are avoided thusly increasing the catalyst life. The use of fine catalyst particles results in better utilization of the particle surface and in reduced temperature and concentration gradients within the particles. However, due to an abruptly changing motion of the particles, thermal and even chemical stresses may cause attrition resulting in loss of catalyst (3) (10).

Loading and unloading of the catalysts are much easier in the fluidized bed systems compared to fixed-bed systems. These reactors are scalable to very large diameter allowing economies of scale and capacities ranging about 40,000 metric tons per year proving lower investment particularly for a large-scale (17).

In this case, vaporized hydrocarbons are injected directly into the fluidized catalyst bed and the air is fed from the bottom of the reactor flowing upwards with velocities high enough to allow fluidization thusly keeping in suspension the catalyst powder. The product stream contains both gases and undesirable solids which are removed by using either cyclones, filters, or a combination. Afterward, the product gas stream must be cooled before being sent to the collection and refining system.

Like fixed bed reactors, the reactions are typically carried out at temperatures below 450 °C at pressures ranging between 2 and 4 bar. The n-butane fraction in the inlet feed is about 4 – 5% n/n. to produce maleic anhydride. The heat capacity of the catalyst and the rapid heat transfer by the movement of the particles prevents the formation of a flame front, therefore, allowing noticeably higher hydrocarbon concentrations compared to fixed-bed reactor technologies. Conversion levels are usually above 80% and molar yields of maleic anhydride range between 50% and 55% (3) (10).

Recapping, the main advantages of this type of reactor are:

- High heat transfer coefficient.
- Ease of temperature control and elimination of hot spots.
- High C-4 concentrations in the feed.

However, there are also disadvantages that must be pointed out:

- Possible catalyst losses due to attrition.
- Yield losses associated with back mixing in the reactor.
- Some scale-up uncertainties due to the changes in reactor size making it difficult to predict the reactor's performance including poorer gas-solid contact, longer gas residence time distribution and increased back mixing.

2.3.2.1 Mitsubishi

A process diagram has been attached for a better understanding of this technology – Figure 13. This process came into use in 1970 by former Mitsubishi Kasei – currently Mitsubishi Chemical Corporation (18) – process uses crude C₄ fraction from a naphtha cracker as a feed hence can use n-butane or n-butene containing butadiene and isobutylene. In the reactor section, the C-4 fraction is fed with air into the reactor for conversion to maleic anhydride in contact with the fluidized catalyst. The heat of reaction is removed by cooling coils in the reactor generating high pressure (430-710 psi) steam. The reacted gas containing maleic anhydride is absorbed by water in a quench tower so that an aqueous solution of maleic acid is formed. Off-gas from the quench tower, containing a small number of byproducts, is incinerated in the waste gas combustion chamber generating more high-pressure steam. In the dehydration/purification section, maleic acid is concentrated and dehydrated by a process which operates effectively in a short time. The crude maleic anhydride is purified by simple distillation to meet required specifications. The process is considered feasible and economical, especially when cheap and rich C-4 hydrocarbons are available from a naphtha cracker and when a large amount of surplus high-pressure steam can be used at the same site (14)(17).

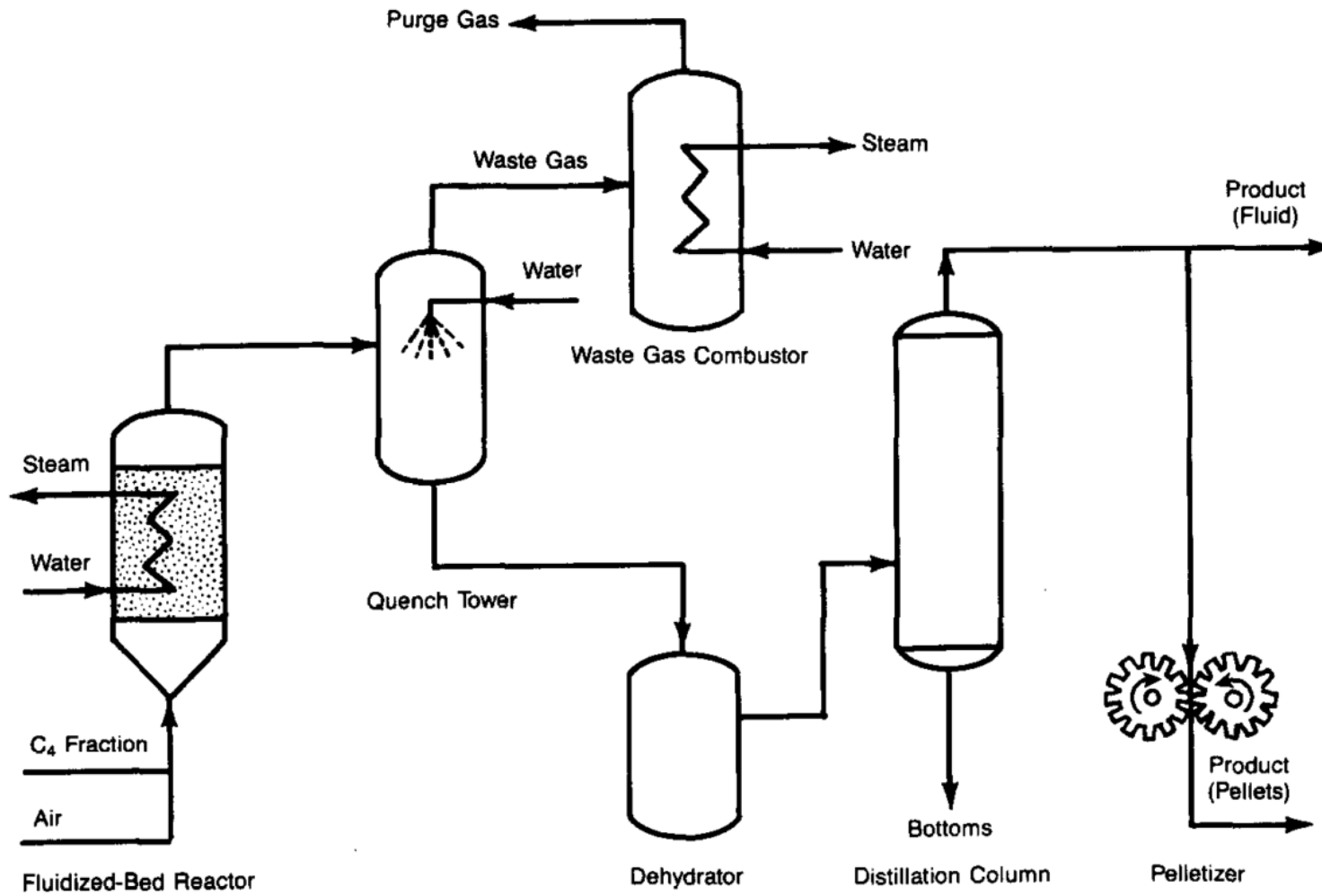


Figure 13 – Mitsubishi maleic anhydride process flow diagram (17)

2.3.2.2 ALMA

In early 1984, Alusuisse Italia/Lummus Crest (ALMA) implemented a maleic anhydride process involving a fluid-bed reactor. A flow diagram of the ALMA Process is shown in Figure 14. In this reactor configuration, C₄ and air are fed separately to the fluidized bed reactor to give about 4 molar percent n-butane concentration. The reactor is typically operated at 360 – 460 °C. The heat generated during the oxidative process is removed from the reactor via steam coils that are in intimate contact with the fluidized solid materials. An interesting component of this process is the ability to change catalyst during operation by intermittently adding a virgin catalyst to maintain stable activities and particle size distributions.

Partitioning of the solids is achieved by cyclone and filter separation. Once separated, the product gas stream is cooled prior to the collection and refining stages. As in the fixed-bed processes, any tail gases are incinerated prior to venting.

The process employs solvent adsorption using an organic solvent to selectively remove maleic anhydride from the cooled reactor effluent. Typically, the solvent is a cycloaliphatic acid dialkyl ester such as dibutylhexahydrophthalate which have a higher boiling point than maleic anhydride. The exclusion of water eliminates byproduct formation experienced with an aqueous recovery system. It allows the entire maleic anhydride production to be separated from the reactor effluent in a single absorption step.

From there, the maleic anhydride solvent mixture is pumped to the stripper where crude maleic anhydride is separated as distillate. This material is fed to the light ends column where small amounts of impure light ends are removed and incinerated. The remaining materials are fed to the product column where the maleic anhydride product is recovered as distillate and residuals are pumped back to the stripper. There is also a solvent purification loop to prevent the buildup of impurities in the solvent. Process impurities typically consist of carbon monoxide and acetic and acrylic acids (3) (6).

2.3.2.3 Badger

Badger developed their process with Denka Chemical Corporation. A flow diagram of the Badger Process is shown in Figure 15. In which, a substantial fraction of maleic anhydride is condensed and recovered as a liquid by cooling the reactor effluent while the rest of the product is absorbed in water as maleic acid.

The acid is dehydrated to anhydride preferably using a water-entraining agent such as xylene. This process has claimed that the fluidized bed catalytic oxidation of n-butane using the Badger Process produces maleic anhydride at good yields with reduced utilities requirements and with a substantially lowered capital investment. This is attributed to discovery and development of attrition resistant catalyst whose performance does not change with time, together with an optimum fluidized bed reactor design (17).

2.3.2.4 BP-UCB

In 1987, BP acquired Sohio outright and made it the cornerstone of a new national operation, BP America. Sohio developed the oxidation catalyst system while UCB operated the recovery and purification system. A flow diagram of this process is shown in Figure 17. This process claims that the catalyst gives over 50 % yield of maleic anhydride on a once-through basis. As with the Badger Process, up to about 50% of the maleic anhydride is continuously condensed out by cooling the effluent gases below the dew point of the maleic anhydride, but above the dew point of water. The specially designed condenser never needs to be put out of service for washing. The remaining product is absorbed in water as maleic acid.

This process chooses not to use any organic solvent as an entrainer for the dehydration step. Instead, the crude maleic acid solution is first evaporated under vacuum, and afterward thermally transformed to anhydride in a dehydration reactor specially developed to reduce the isomerization of maleic acid to fumaric acid (17) (19).

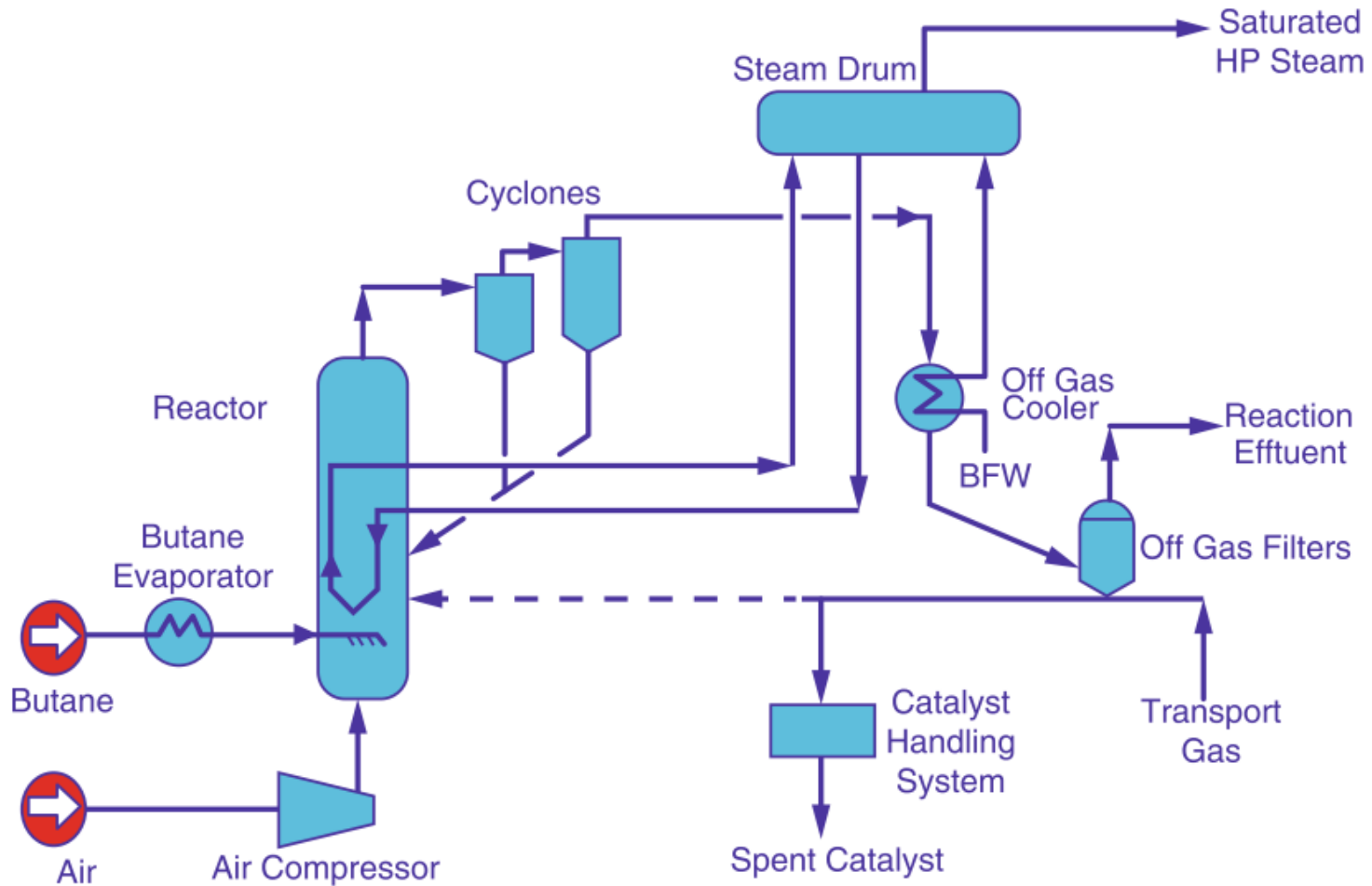


Figure 14 – ALMA maleic anhydride production process (14) (17)

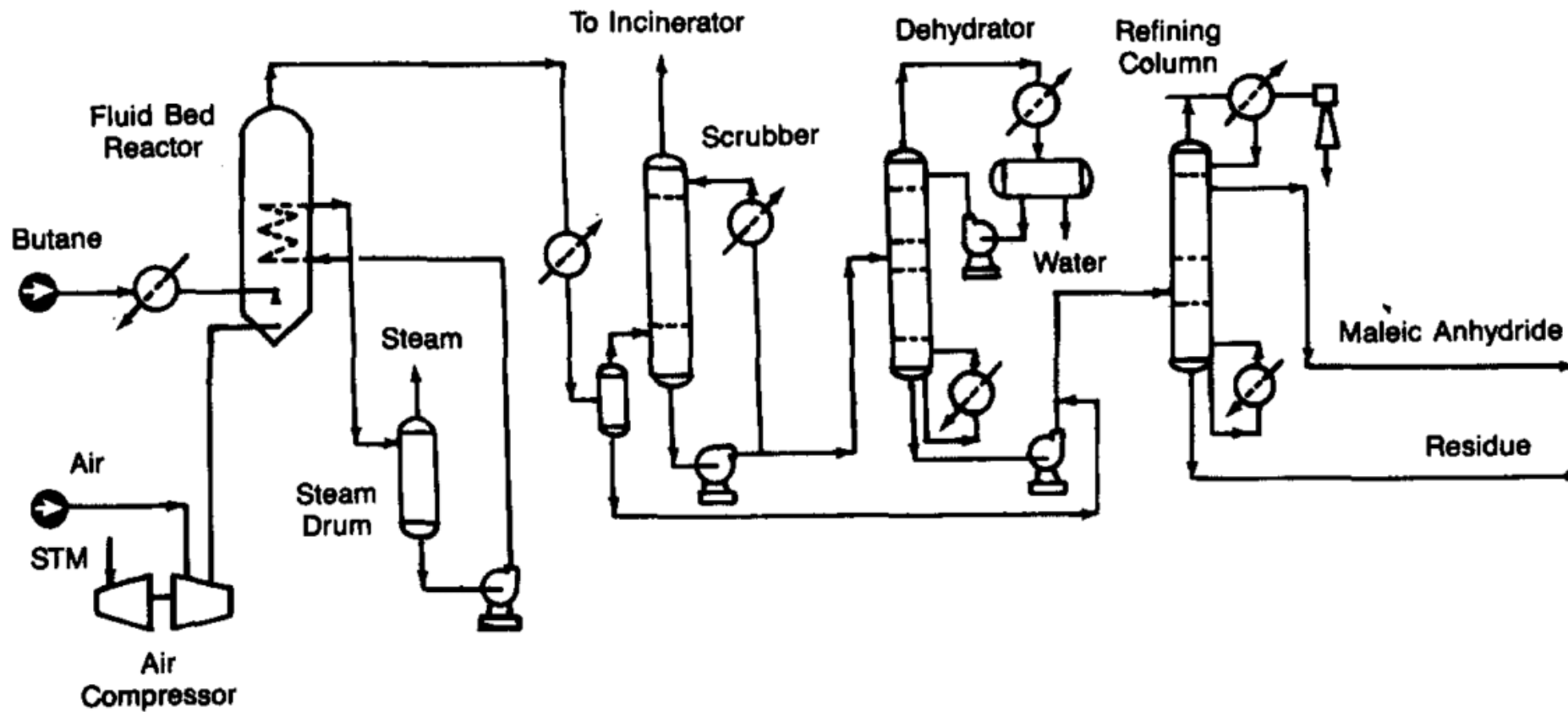


Figure 15 – Badger maleic anhydride process diagram (17)

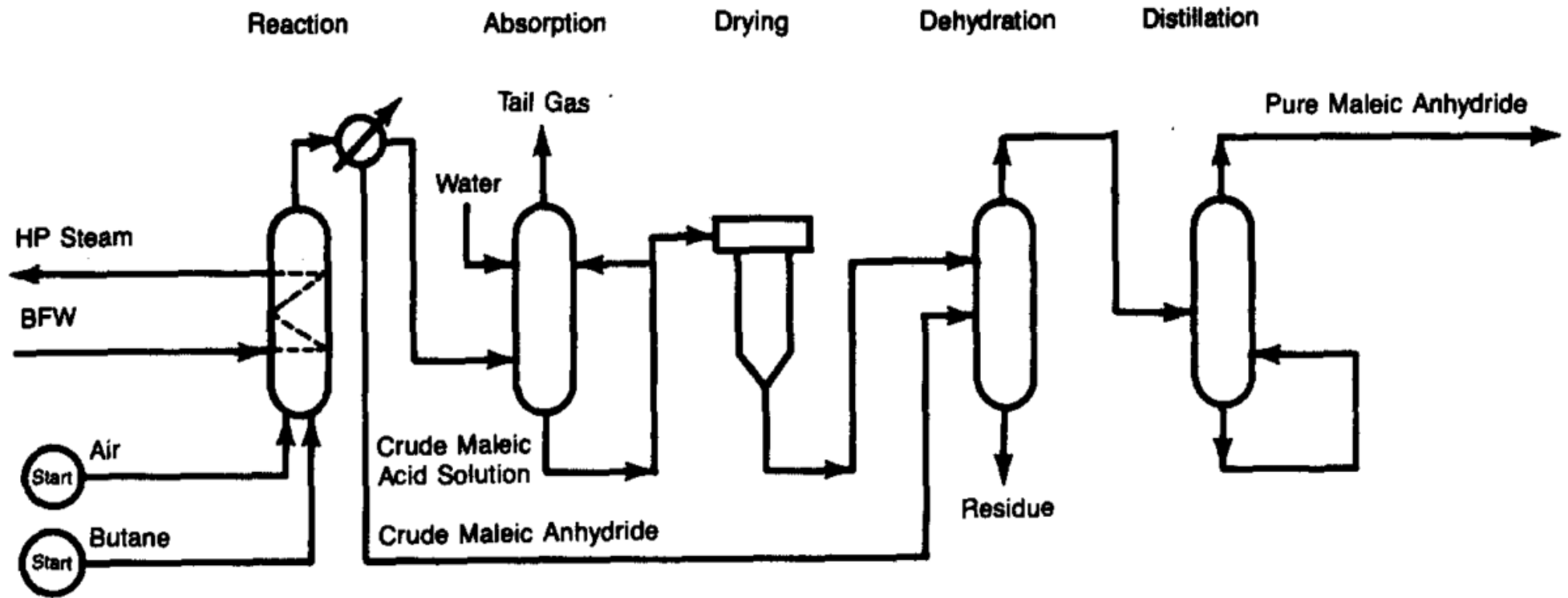


Figure 16 – BP/UCB maleic anhydride diagram flow (17)

2.3.3 Transport bed reactors (CFB)

A new reactor concept for selective oxidation of n-butane to maleic anhydride was created. This innovation reduces or eliminates most of the negatives of fluidized bed reactor mentioned before while maintaining its advantages. Furthermore, additional performance advantages are obtained by separating two steps of the redox process (17).

In these contacting regimes, solids circulate in and out of the bed and must be replaced by using transport bed reactors in continuous operations. Flow models are very sketchy for these flow regimes and research is needed. The surface of the dense bed fades and solids are found increasingly in the lean region above the dense bed (uppermost part). The gas flow in the dense region is somewhere between the bubble fluidized bed, BFB, and plug flow. Unfortunately, no reasonable flow model has been developed for this region being that the parameters for reasonable models are uncertain; hence, the predictions based on these models will likewise be uncertain (20).

Vanadium Phosphorus Oxide, VPO, catalyst is normally used since it has the interesting feature that it uses lattice oxygen atoms for the selective oxidation of n-butane to maleic anhydride. Therefore, no gas phase oxygen is necessary for the desired reaction provided the catalyst is in an oxidation state capable of transferring oxygen atoms to the hydrocarbon. In the reactor's regenerator, the catalyst is then reoxidized with oxygen closing thusly its cycle throughout the CFB (10).

A transport bed reactor can be regarded as a tube in which both, the hydrocarbon and the catalyst are brought into contact entering and exiting the reaction zone in co-current flow. The catalyst is circulated continuously around the loop; between both reactors. n-Butane is oxidized by the catalyst in the lean-phase riser section which has plug flow characteristics. The catalyst is reoxidized in the dense phase fluidized bed regenerator (10)(17).

The most significant feature of this reactor is the separate reduction and oxidation sections allowing much higher n-butane concentrations in the inlet feed as well as higher maleic anhydride selectivity while avoiding the mentioned flammability ranges. The hydrocarbon fraction in the inlet feed may reach up to 50 % n/n. Due to an oxygen-free gas phase, the selectivity of maleic anhydride can be increased by values of about 7 to 10% compared to the conventional use of a hydrocarbon in air gas phase in the other reactor configurations. Together with the attrition resistant catalyst described earlier, it is possible to achieve maleic anhydride yields higher than 70 % and even 90 % selectivity. Temperature operation ranges between 360 – 420 °C and riser top pressure is possible up to 4.1 bar. The rate of reoxidation of the VPO catalyst is slower than the rate of oxidation of butane, and consequently, residence times are longer in the oxidizer than in the transport bed reactor. Therefore, the gas residence time in the riser is about 10 seconds while catalyst residence time ranges from 30 seconds to 5 minutes. Catalyst densities 80 - 60 kg/m³ in the transport bed reactor are substantially lower than the catalyst density in a typical fluidized-bed reactor 480 – 640 kg/m³ (3)(10)(21)(22).

The main general advantages for this reactor configuration are recapped (22):

- Separate catalyst oxidation and reduction zones which lead to independent control of two zones with the catalyst in transient cyclic state. Therefore, separate optimization of each reaction zone is possible (3).
- High selectivity is essentially due to plug flow of gases in the riser, optimized oxidation state of the catalyst, controlled low oxygen concentration in the riser zone and operation at low single pass conversion with recycling of unconverted n-butane.
- Highly concentrated product streams because of high hydrocarbon concentration in the inlet feed and product gas separate from the regenerator off-gas.
- Low catalyst inventory.
- No explosive risks.

However, the major limitation is the intrinsically low oxygen transfer capacity of the vanadyl pyrophosphate VPP catalyst which requires extremely high solid recirculation rates to provide adequate oxygen to the reaction (21).

2.3.3.1 Du Pont's C-4 feedstock

Although maleic anhydride is produced in the reaction section of the process and could be recovered, it is not a direct product of the process. DuPont's technology recovers maleic anhydride as aqueous maleic acid for hydrogenation to tetrahydrofuran. In this configuration, maleic anhydride productivity could be enhanced by using relatively high concentrations of n-butane as main feedstock and effective utilization of catalyst lattice oxygen. However, in practice, due to insufficient catalyst oxygen transfer from the regeneration zone, molecular oxygen has to be fed along with the reduction feed to achieve the designed maleic anhydride production rates and to prevent catalyst over-reduction (10) (17).

DuPont's maleic anhydride technology includes a two-step process as mentioned before. Firstly, normal butane is oxidized to maleic anhydride in a transport bed reactor using an abrasion-resistant catalyst (VPO or VPP). Maleic anhydride is then recovered in an aqueous system where the resulting maleic acid is converted to tetrahydrofuran in a hydrogenation reactor. The oxygen depleted catalyst is then re-oxidized in a separate reactor where the exothermic heat of reaction is removed by steam coils. Therefore, Du Pont has built a production plant comprising a transport bed reactor for the n-butane oxidation and a fluidized bed regenerator for the reoxidation of the VPO-catalyst (3) (10) (13).

The catalyst goes through an oxidation/reduction cycle each time it circulates around the loop. Moreover, the near plug flow of gases in the riser allows the staged addition of reactants to control gas composition in the axial direction for optimal performance. In other words, preventing the negative effect of back mixing on the reaction's selectivity. The reactor concept allows independent control of the process variables for the two steps of the redox operation for defining optimum conditions for each step (3) (22).

The oxidized catalyst is transferred from the regenerator through a standpipe to the bottom section of the reaction vessel (fast bed) which is in turbulent fluidization regime. The solids and gas mixture are then transferred in an upward flow through a riser reactor. Reduced catalyst from the riser top is separated from the reaction products stream by cyclones and is further stripped of products and reactants in a separate stripping vessel. After product separation, the reduced solids were returned to the regenerator through another standpipe for reoxidation. Maleic anhydride in the product stream is removed and converted to a maleic acid solution in a water scrubbing system. The maleic acid is sent to the hydrogenation reactor to produce THF, while the reactor off-gas after scrubbing is sent to the recycle compressor. A small purge stream is sent to incineration (3).

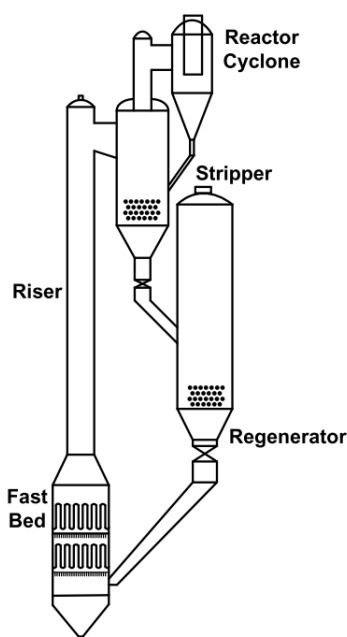


Figure 17 – Transport bed reactor (3)

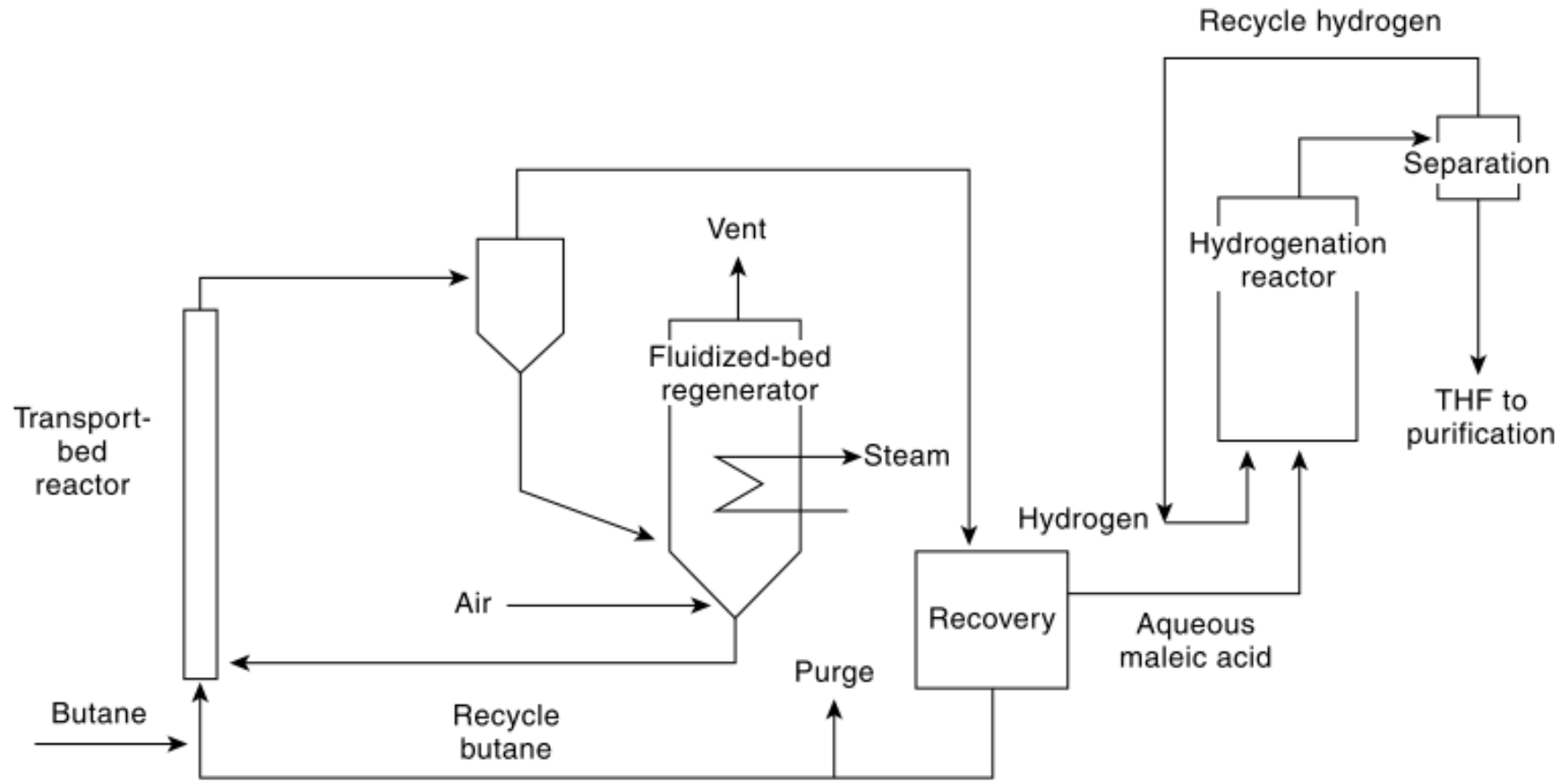


Figure 18 – Du Pont transport-bed process (3)

2.4 Production stages

Every major maleic anhydride production process is equipped with a reactor, gas cooler, separator, scrubber, refiner/condenser and product column collector. Generally, this process consists of five basic stages which are shown in Figure 8. The inlet feed preparation is the beginning of the process covering the delivery of reactants – hydrocarbon and air – to the reactor. This stage includes vaporizing the hydrocarbon inlet feedstock and compressing air as well as perfectly intermixing them together in a controlled manner by using static in-line mixers (13) (6).

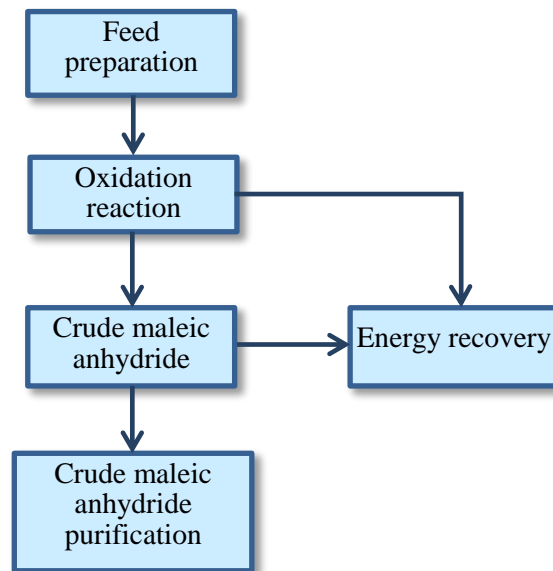


Figure 19 – Basic maleic anhydride plant configuration (13)

Secondly, an oxidation reaction takes place in any one of the specialized reactors discussed before. Highlighting the fact that maleic anhydride production is extremely exothermic, the tremendous heat of reaction must be removed either by internal coils or via circulating molten salt as already explained. When using multitubular fixed bed or fluidized bed reactors, careful control is needed to prevent hydrocarbon-oxygen compositions breaching combustion limits (13).

Once the reaction has taken place, the stream exiting the reaction stage is led to the separation section where more heat is removed from the reaction off-gas and then sent to the recovery system to obtain a crude maleic anhydride stream. The major difference between various commercial processes is observed specifically in the recovery stage, in which maleic anhydride is recovered from the effluent stream of the reactor. The most common methods are the following (13) (14):

- Cooling to recover solid maleic anhydride at melting point 56 °C practiced by Scientific-Design.
- Cooling to recover liquid maleic anhydride executed by Monsanto, as explained earlier.
- Collecting in a solvent such as dibutyl phthalate, dimethyl phthalate or diphenyl pentachloride among others.
- Collecting in water or aqueous maleic anhydride. (Generally, 40 % solution of maleic acid is used in the scrubber. Used to recover MA or may be converted to fumaric acid by thermal isomerization).

The fact that in a C₄ hydrocarbon based process, maleic anhydride is not always recovered directly but as aqueous maleic acid is due to lower feed-air ratio making the product's concentration in exhaust gases uneconomical to recover directly as well as process produces more water than the benzene route both due to the stoichiometry and poorer selectivity (14).

Continuing with the process and if necessary, the stream of crude maleic anhydride is taken to the product purification section. Mainly consisting of removing water through a typical batch or continuous azeotropic

distillation approach involving light ends removal and the separation of a heart cut, usually vacuum assisted. Appropriate care is taken to prevent significant isomerization. Commonly employed solvents for azeotropic removal of water are xylene or o-dichlorobenzene. The fact that solvent methods are also known to accumulate undesirable by-products in the absorbing and stripping loops should be highlighted. In addition, this organic solvent system is able to achieve high MAN recovery, a low energy cost, high thermal stability, low price, and low pollution (23).

After this stage, the obtained maleic anhydride meets all demands generally achieving molar yields within the 50 – 60 % range (13) (14) (6).

A key factor in the economic aspect of producing maleic anhydride is energy recovery. Reactor off- gases, post maleic anhydride recovery, non-condensables from vacuum systems, tank vent gases, and unreacted hydrocarbons are all incinerated to recover energy as super-heated steam. Exploiting this steam by using it to supply energy to integrated units. Only the Du Pont process recycles part of the n-butane, because of its high concentrations in the product stream (10) (13).

3 METHODOLOGY

In this chapter, key aspects of this work will be discussed, mainly including the description of the process, technical specifications, and equipment used. More specifically, this chapter will explain in great detail the process flow diagram obtained through the simulation, as well as its mass and energy balance that are attached in the following chapter.

3.1 Process description

The process studied in this work has been designed to produce about 36,800 m³/year of maleic anhydride at 98% n/n purity by partially oxidizing n-butane and oxygen on a VPO catalyst which is oxidized with a stream of pure oxygen and helium. This capacity is similar to that of a near relatively small scale maleic anhydride production plant (9). The simulation of this work has been carried out with Aspen HYSYS process simulation software.

The technology chosen for this project is the aforementioned Du Pont's circulating bed reactor due to the achievement of high selectivities and no risk of explosions. The energy liberated by the exothermic reaction is used to produce steam. The unreacted n-butane is recycled along with the nitrogen, water and, carbon monoxide and dioxide fractions. This recycle stream is re-used and mixed with the main reactor inlet feed, which mainly consists of nitrogen and n-butane.

The recovery process has been simulated mimicking Monsanto's maleic anhydride recovery technology due to high product recovery and use of thermally stable solvents that do not require multiple stripping stages in order to be separated from maleic anhydride. It starts out by cooling the reactor effluent stream and introducing it into an absorber-stripper loop which is brought into contact with dibutyl phthalate (DBP) organic solvent, preventing the possible production of fumaric acid since there is no production of maleic acid in this absorption process. The gaseous stream exiting the absorber is the aforementioned recycle, which is mixed with the clean n-butane and nitrogen as reactor feed. The bottom stream of the absorber is introduced into a stripper column, as mentioned before, in which maleic anhydride is separated from the organic solvent and traces of the rest of components. The separated organic solvent stream exits the stripper column and is mixed with fresh solvent in order to be recycled into the absorber. Traces of MAN and DBP present in the stripper's gaseous stream are sent to a scrubber unit in order to be extracted by putting into contact with fresh solvent. The bottoms liquid stream is recycled back into the main absorber while the gaseous stream is vented. Thusly, closing all three of the recycles present in this process. The Process Flow Diagram of this work is shown in Figure 20 in which stream numbers, equipment names, recycles (RCY) and SET blocks appear.

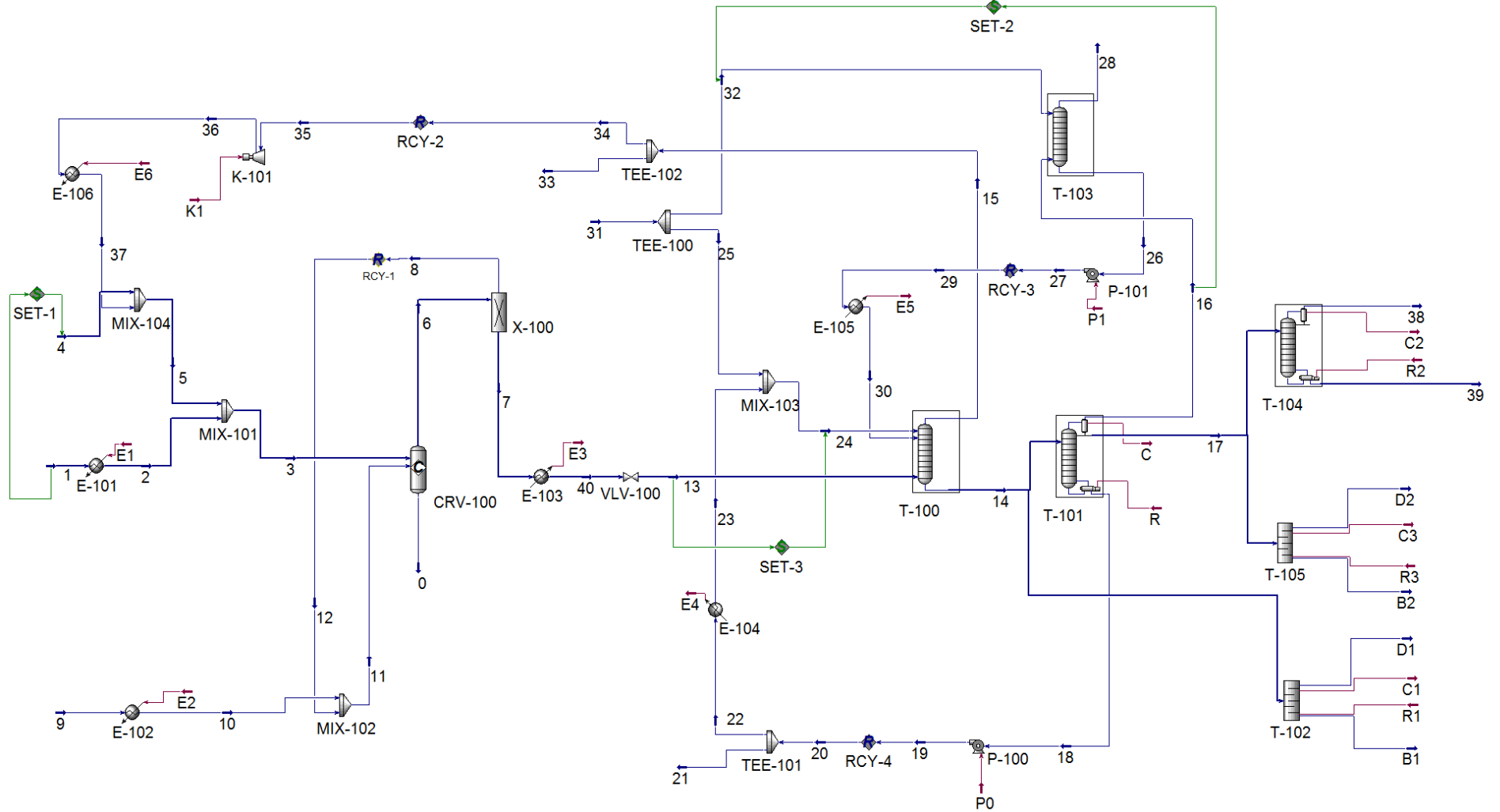


Figure 20 – Maleic anhydride production Process Flow Diagram

3.2 Technical Specifications

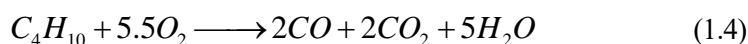
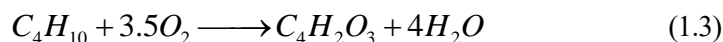
3.2.1 Feed

N-butane is initially stored at 25 °C and approximately 15 kg/cm² in spherical storage tanks at liquid phase which proceeds from a fractionation tower in a hydrocracking process (24). Afterward, it is decompressed to the operating pressure of 150 kPa. Regarding the inlet hydrocarbon feedstock (stream 1) comes from the aforementioned storage tanks (200°C, 150kPa; 100kgmole/h). Since highest selectivities are claimed in absence of gas phase oxygen during the conversion of n-butane to maleic anhydride, the inlet reactor feed (stream 3) is mostly nitrogen and n-butane (25). This stream is a mix of pure oxygen (stream 1), nitrogen (stream 4) and the purged recycle stream coming from the main absorber (stream 37).

3.2.2 Reaction

For the reaction section of the process, this work has been based on the US Patent 4,668,802 by Du Pont. In which four different reactor configurations are offered. The chosen configuration is shown in Figure 17. This patent consists of limiting the amount of oxygen in the feed gas so that it is less than the stoichiometric amount required for the total amount of n-butane converted in the process. That is 3.5 moles of oxygen for each mole of n-butane converted as seen in Equation 1.3. The reduced catalyst resulting from the oxidation is separated from the product stream (stream 6) and reoxidized before contacted again with butane. It must be pointed out that what occurs inside the CFB reactor is out of the scope of this document. Therefore, it has been considered a black box.

Main reactions involved in the reactor are:



For better understanding, Figure 21 shows the streams that interact with reactor CRV-100 and component splitter X-100.

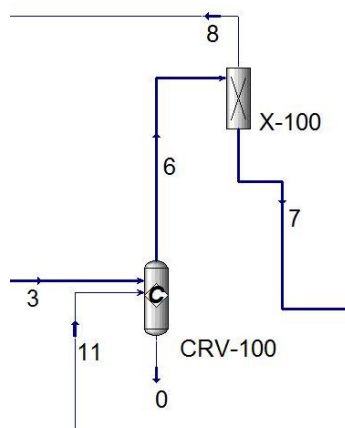


Figure 21 – Reactor configuration (CRV-100) and component splitter (X-100)

The amount of oxygen in the reactor's inlet feed is preferably less than about 30 % of the stoichiometric amount, in other words, less than one mole of oxygen for each mole of n-butane converted for reaction one and 1,5 for reaction two (25). In this case, 26 % of the stoichiometric amount has been used. This means the ratio oxygen/n-butane is equal to 2.34.

$$0.26 * (O_2 \text{kgmole}|_{\text{Reaction1}} + O_2 \text{kgmole}|_{\text{Reaction2}}) = 0.26 * (3.5 + 5.5) = 2.34 O_2 \text{kgmole}$$

$$O_2|_{\text{Stream11}} = C_4 \text{kgmole}|_{\text{Stream3}} * \frac{2.349 O_2 \text{kgmole}}{1 C_4 \text{kgmole}} = \quad (1.5)$$

$$286 C_4 \text{kgmole}|_{\text{Stream3}} * \frac{2.349 O_2 \text{kgmole}}{1 C_4 \text{kgmole}} = 670 O_2 \text{kgmole}$$

The stream which oxidizes the catalyst, stream 11, is made up of 20 % n/n oxygen and 80 % n/n helium (25). Since helium is an inert gas, the helium in the recycle loop (RCY-1) has not been taken into consideration during the process' simulation. In order to simplify and facilitate the convergence of results, stream 11 is only oxygen. However, the total mole flow of helium, considered constant throughout the process, is known due to the aforementioned ratio. This leads to a loop of pure helium of 2,680 kgmole/h obtained through the following equation:

$$O_2|_{\text{Stream11}} = 670 \text{kgmole} \quad (1.6)$$

$$He = O_2|_{\text{Stream11}} * \frac{80\% n / nHe}{20\% n / nO_2} = 2,680 \text{ kgmole}$$

In order to simulate a CFB reactor, this work has used a conversion reactor (CRV-100) followed by a component splitter (X-100) after the reaction has taken place with the objective of completely separating the oxygen in stream 6 which is recycled (stream 8). This way, the oxygen stream intended for the reaction and for the oxidation of the catalyst is represented in one single stream (stream 11). Reactor CRV-100 operates at 150 kPa and 441 °C. These specifications meet the preferred conditions in US Patent 4,668,802, in which the oxidation is carried out at temperatures of 340 °C to about 450 °C and pressures ranging from 0 psig to 50 psig (6.9 kPa to 344.73 kPa). Following *example 7* in the aforementioned US Patent, the inlet reactor feed (stream 3) contains about 97 % n/n nitrogen and 3 % n/n n-butane which leads to 30.2 % conversion and 85.7 % selectivity.

3.2.3 Catalyst VPO

As mentioned before, the catalyst chosen for this process has been Vanadium Phosphorus Oxide. Vanadium oxides represent the most important catalyst class in butane oxidation. The vanadium found in the catalyst toward the production of MAN may exist in two oxidation states (+5, +4). VPO catalyst has a surface area of about 20 m²/g, spherical form and diameter of approximately 200 micras and density of 800 kg/m³. The catalyst's activity could be considered as constant. Therefore, deactivation is approximately inexistent.

The kinetic rate of catalysis is limited by the ability of the reactant gases to internally diffuse into the pore structure of the catalyst body. The catalytic activity could be enhanced by increasing the porosity of the catalyst body (6).

3.2.4 Absorption

The gaseous stream exiting component splitter X-100 – stream 7 – is now free of oxygen and ready to enter the absorber through the bottom after cooling down to 60 °C and compressed to 115 kPa (stream 13). For the simulation of the main absorber, US Patent 4,188,403 developed by Monsanto and shown in Figure 7 has been followed.

Absorber T-100 is a 12 tray column which operates at 113.3 kPa with a pressure drop of 1.7 kPa (26). The liquid inlet feed is pure dibutyl phthalate which is represented by stream 24. This stream enters absorber T-100 at 29 °C and 113.3kPa and is actually a mix of pure and recycled solvent.

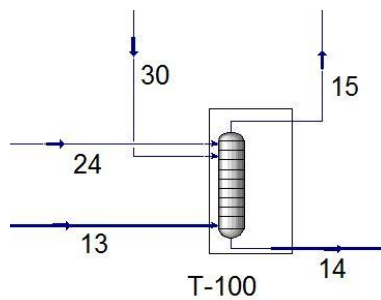


Figure 22 – Absorber T-100 configuration

Also entering the column is stream 30, which comes from the bottom outlet of the second absorber (T-103) that is recycled (RCY-3) into main absorber T-100. This stream contains mostly DBP, water, MAN and unreacted n-butane.

Overhead stream 15 is the process' main recycle (RCY-2) which is a distinguishing specification of Dupont's technology, as mentioned in Chapter 2. Therefore, the composition of this stream is mainly nitrogen and n-butane and in smaller percentages the other oxidation products.

Leaving the absorber through the bottom of the column is stream 14 which is made up of organic solvent and the absorbed maleic anhydride. This stream becomes the inlet liquid feed of the stripper 12-tray column T-101 which operates at vacuum (6.66 kPa and 11.87 kPa) and a reflux of 2.

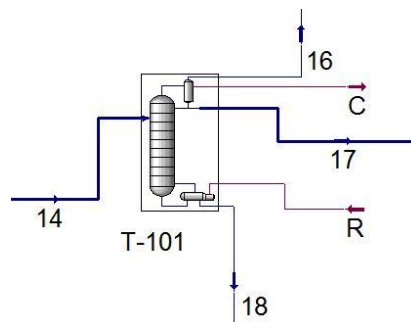


Figure 23 – Stripper T-101 configuration

Since said column operates at vacuum conditions, a reciprocating piston pump has been placed in the exiting liquid organic solvent stream. This pump is a type of positive displacement pump which operates with steam drive directly through gears or belts and is sealed both internally and externally. The operation of this equipment is shown in Figure 24. It mainly works with an initial suction stroke followed by a discharge stroke. The first stroke takes place when the piston pulls out of the cylinder where a low-pressure vacuum is created that causes the suction valve to open and the discharge valve to close. On the return stroke, the suction valve is closed and the fluid is forced out of the discharge. Normally these pumps are placed in parallel in order to reduce flow and pressure fluctuations (27).

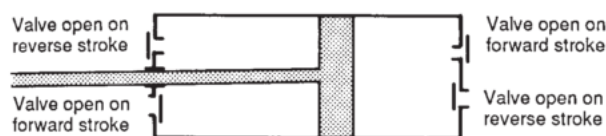


Figure 24 – Reciprocating piston pump operation (27)

From column T-101, there are three streams exiting. Stream 16 is the gaseous product leaving the condenser.

Which is mainly formed by the lower boiling components. Stream 18 is the recuperated organic solvent line which is recycled (RCY-4) back into the main absorber, as mentioned before.

Stream 16 enters scrubber T-103, with the objective of extracting the MAN that may have not been stripped in column T-101. This absorber is a 10-tray column that operates at the same conditions as T-100. From T-103, overhead gaseous stream 28 is vented. Bottoms (stream 26) are recycled (RCY-3) back into T-100 after cooled, as mentioned before. Liquid inlet stream 32 is made up of pure organic solvent.

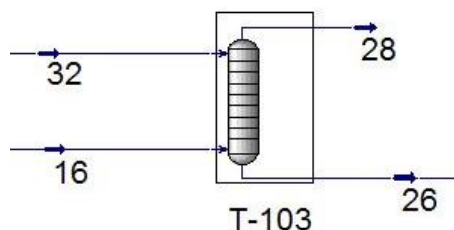


Figure 25 – Scrubber T-103 configuration

3.2.5 Purification

Distillation column T-104 is a 6-tray column condenser operates at 6.66 and reboiler at 11.87 kPa, a reflux of 1 and a MAN molar fraction of 0.98 in stream 39. Stream 17 is the liquid line exiting the condenser which is made up of mostly water and MAN. Since the purity of the end product does not meet the specifications, this stream enters a distillation column where MAN is concentrated to 98 %n/n purity (stream 39). Excess water (stream 38) is recuperated through the column's overhead. Streams C2 and R2 are energy streams that are involved in column T-104 corresponding to the heat removed from the condenser and heat added to the reboiler.

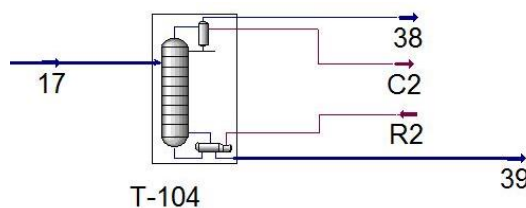


Figure 26 – Distillation column T-104 configuration

3.3 Modeling and process simulation

3.3.1 Components present in simulation

The hydrocarbon used for the simulation is pure n-butane (stream 1) which is inserted into the reactor CRV-100 along with nitrogen (stream 4) in approximately a 3 %n/n / 97 %n/n ratio. Oxygen and helium (streams 8 – 12) are also introduced into the reactor in order to oxidize the VPO catalyst which follows a redox cycle throughout the equipment. The products of the reaction are maleic anhydride, carbon dioxide, carbon monoxide and water. In order to remove the main product from the rest of components, the organic solvent used in the absorbers is dibutyl phthalate.

3.3.2 Thermodynamic aspects

The thermodynamic model chosen for this work has been the Non-Random Two Liquids (NRTL) based on contrasted experimental data obtained from a research paper at three given temperatures: 140.05 °C, 160.05 °C, and 180.05 °C (23). Each figure shows a comparison between the binary P-x(y) graphs for DBP solvent and MAN provided by Aspen HYSYS, located on the left, and the regression obtained by plotting the experimental data, on the right. The fact that the binary interaction data for the NRTL model MAN-DBP pair was inserted manually in HYSYS should be noted since it was not offered by the software.

These figures show the bubble and dew curves for the binary mixture mentioned before. The curves that apply to this case taken from the research paper are the triangle indicators and dotted line. Where the triangle indicators

correspond to the experimental data and the dotted line is the calculated data. Therefore, after comparing both graphs for each temperature and confirming the similarity between each other, it is possible to accept the use of the NRTL thermodynamic model for the liquid phase of this work. In addition, it has also been considered for the vapor phase since the model of ideal gas has been assumed.

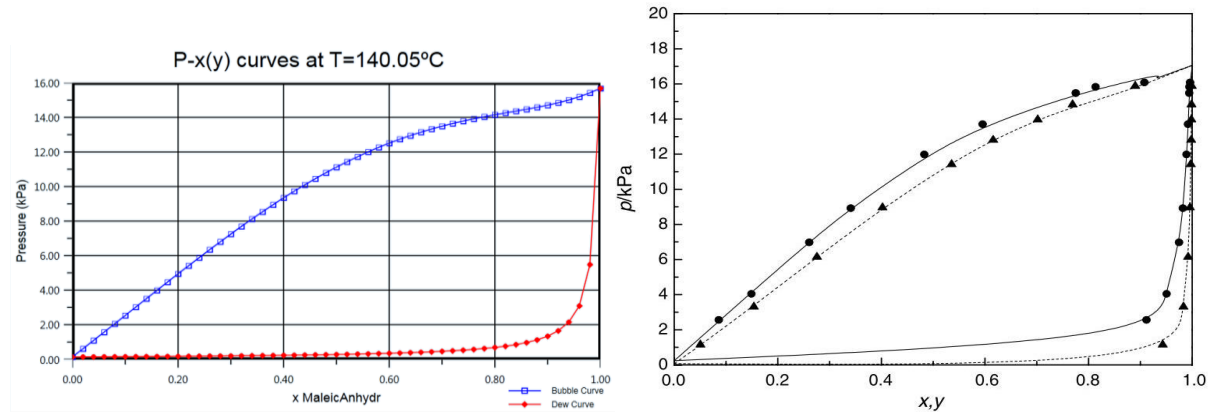


Figure 27 – P-x(y) curves comparison at T=140.05 °C

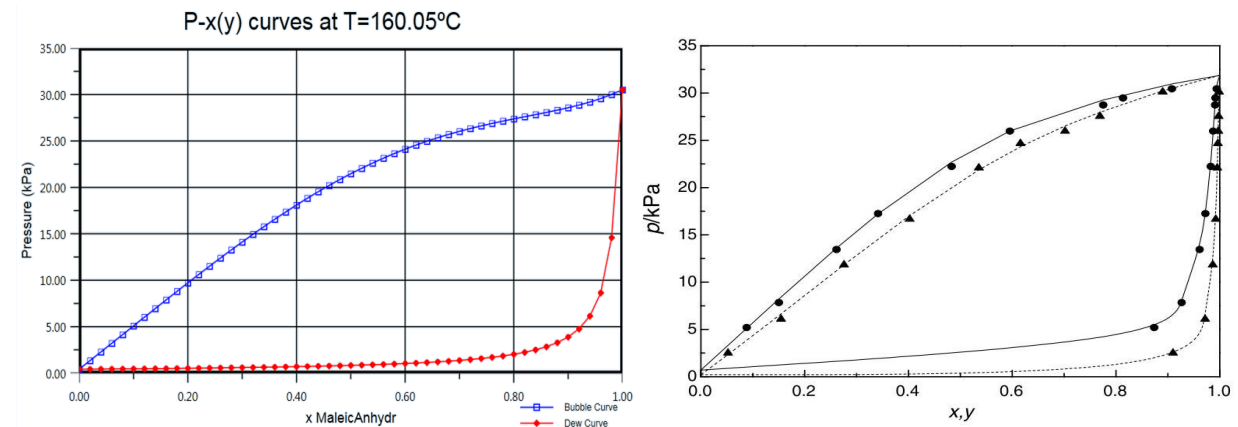


Figure 28 – P-x(y) curves comparison at T=160.05 °C

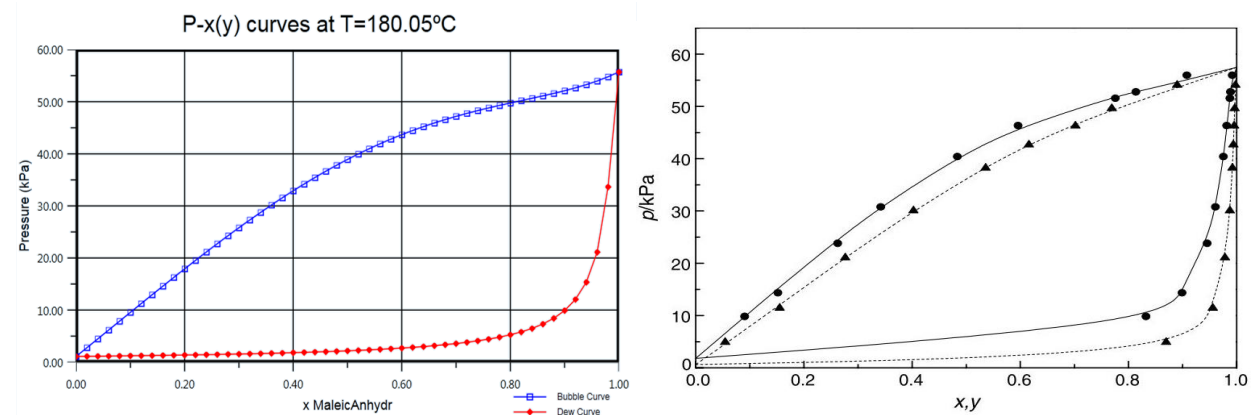


Figure 29 – P-x(y) curves comparison at T=180.05 °C

The five adjustable parameters for the NRTL equation in HYSYS are the a_{ij} (2,204.92 cal/mol), a_{ji} (-278.64 cal/mol), b_{ij} (0.233 cal/mol*K), b_{ji} (-0.898 cal/mol*K), and α_{ij} terms (0.3). Where i is linked to the organic solvent and j is linked to MAN. This is the corresponding data that was inserted manually in HYSYS and obtained from the research paper. Equation 1.7 represents the NRTL equation in HYSYS:

$$\ln \lambda = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \left(\frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \right) \left(\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right)$$

$$G_{ij} = \exp(-\tau_{ij} \alpha_{ij}) \quad (1.7)$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij} T}{RT}$$

Where:

- γ_i = activity coefficient of component i
- x_i = mole fraction of component i
- T = temperature (K)
- n = total number of components
- a_{ij} = non-temperature dependent energy parameter between components i and j (cal/gmol),
- b_{ij} = temperature dependent energy parameter between components i and j (cal/gmol-K),
- α_{ij} = NRTL non-randomness constant for binary interaction note that
- $\alpha_{ij} = \alpha_{ji}$ for all binaries

However, thermodynamic binary interaction data between the solvent DBP and the rest of components in the absorber (water, nitrogen, unreacted butane, carbon monoxide and dioxide) have not been found in reliable sources such as:

- SpringerMaterials which the University of Seville's library does not have access to.
- DECHEMA's DETHERM software demo does not offer Vapor-Liquid Equilibria (VLE) thermodynamic data for the aforementioned binary mixture.
- The DETHERM tab in ASPEN Plus has not been available for this work and the NIST tab did not provide any data for said mixture.
- Journals or Databases such as The Journal of Chemical Engineering Data or Science Direct possibly could have offered certain data through research. However, it would have jeopardized the established deadlines for this work.

Therefore, the thermodynamic binary interaction has been considered ideal mixture.

3.3.3 Equipment

In this subsection, the simulation of each equipment used in this work shall be explained. As seen in the attached PDF (Figure 20), the following equipment have been included in the production process.

3.3.3.1 Reactor CVR-100

The simulation of reactor CVR-100 has been carried out by specifying its inlet streams (streams 3 and 11), the reactions that take place, the desired temperature at which the reaction occurs, conversion and selectivity.

3.3.3.2 Component splitter X-100

This equipment has been used in order to separate the oxygen exiting the reactor in stream 6 since the strict simulation of a CFB reactor has not been carried out in this work where its inlet stream is put into contact with

the oxidized catalyst.

The splits were introduced manually by specifying that all of the oxygen present in stream 6 shall be transferred to stream 8 and the rest of gaseous products, un-reacted n-butane and nitrogen are separated into stream 7. In other words, oxygen's molar fraction in stream 8 is one and in stream 7 is zero.

3.3.3.3 Absorbers

3.3.3.3.1 T-100

Absorber T-100 has been simulated by specifying the inlet streams as well as the stage at which they enter (streams 24, 13 and 30), the number of stages, and the first and last stage pressure.

3.3.3.3.2 T-103

Scrubber T-103 is simulated in the same manner as T-100. The inlet streams 16 and 32 were specified as well as the number of stages and the pressure of the first and last stage.

3.3.3.4 Shortcut column

In order to obtain initial simulation data for the stripper and distillation column, two shortcut columns have been simulated beforehand.

3.3.3.4.1 T-102

Shortcut column T-102 has been simulated to obtain data for the stripper column T-101. As seen in Figure 30, three streams are involved in this equipment. Firstly, stream 14 containing a liquid mixture of mostly organic solvent and maleic anhydride is introduced into the column. Secondly, streams D1 (MAN and water) and B1 (DBP) are the distillate and bottoms exiting the column. Lastly, streams C1 and R1 are the energy streams linked to the column's condenser and reboiler.

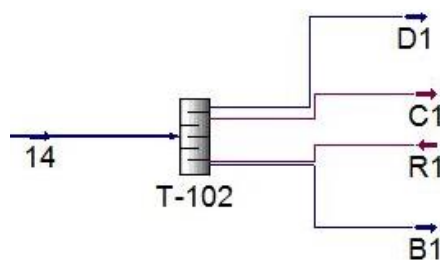


Figure 30 – Shortcut column T-102 configuration

For such column, as seen in Table 1 the following initial parameters were introduced:

Initial parameters	
Light key in Bottoms (MAN) mole fraction	0.0003
Heavy key in Distillate (DBP) mole fraction	0.0003
Condenser pressure (kPa)	6.66
Reboiler Pressure (kPa)	11.87
External Reflux Ratio	1

Table 1– Shortcut Column T-102 initial parameters.

These parameters led to the following simulation data (Table 2) that was later introduced in the stripper column T-101:

Simulation data	
Minimum number of trays	2,553
Condenser temperature (°C)	917.98
Reboiler temperature (°C)	240.5

Table 2 – Shortcut column T-102 simulation data.

3.3.3.4.2 T-105

Shortcut column T-105 has been simulated to obtain data for the distillation column T-104. As seen in Figure 31, three streams are involved in this equipment. Firstly, stream 17 composed of a liquid mixture of water and maleic anhydride is introduced into the column. Secondly, streams D2 (water) and B2 (MAN) are the distillate and bottoms exiting the column. Lastly, streams C2 and R2 are the energy streams linked to the column's condenser and reboiler.

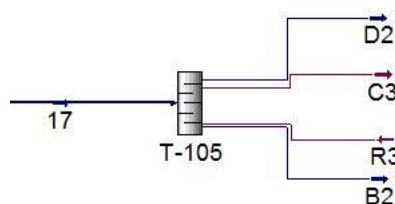


Figure 31 – Shortcut column T-105 configuration

For such column, as seen in Table 3 the following initial parameters were introduced:

Initial parameters	
Light key in Bottoms (MAN) mole fraction	0.0003
Heavy key in Distillate (DBP) mole fraction	0
Condenser pressure (kPa)	6.66
Reboiler Pressure (kPa)	11.87
External Reflux Ratio	1

Table 3 – Shortcut Column T-105 initial parameters.

These parameters led to the following simulation data (Table 4) that was later introduced in the stripper column T-101:

Simulation data	
Minimum number of trays	5.53
Condenser temperature (°C)	38.01
Reboiler temperature (°C)	132.10

Table 4 – Shortcut column T-105 simulation data.

3.3.3.5 Stripper T-101

The simulation of a stripper column is quite a bit more complicated than the absorbers. As mentioned before, first, a shortcut column is simulated. Data such as reflux ratio, reboiler temperature and distillate draw rate is

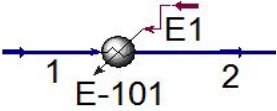
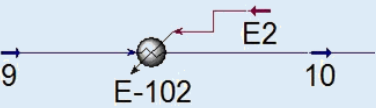
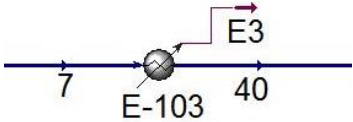
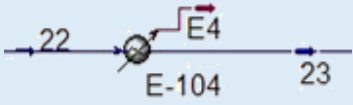
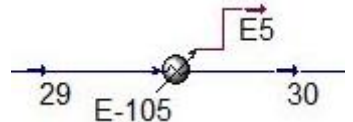
obtained from shortcut column T-102 and introduced into stripper T-101. The inlet stream (stream 14) is specified, as well as, the number of stages, first and last stage pressure and choice of condenser that is a partial condenser.

3.3.3.6 Distillation column T-104

The reflux ratio provided by shortcut column T-105 is introduced into stripper T-101. Since the choice of condenser is a full reflux condenser, there are less degrees of freedom concerning input data compared to stripper T-101. The inlet stream (stream 17) is specified, as well as, the number of stages and first and last stage pressure.

3.3.3.7 Heat exchangers

Throughout the course of this work, six heat exchangers have been used. Table 5 reflects, for each one of these equipment, its name, configuration, streams that are involved, inlet and outlet temperature in degrees Celsius, pressure drop in kilo Pascals and a brief explanation. In the configuration figures (32 through 37), streams *E* preceded by a number correspond to the energy stream involved in that specific heat exchanger. The direction of these energy streams indicates whether heat is added (inwards) or removed (outwards) from the material streams.

Name	Configuration	Material streams involved	Inlet T (°C)	Outlet T (°C)	Delta P (kPa)	Brief explanation
E-101	 <p>Figure 32 – Heat exchanger E-101 configuration</p>	1 and 2	200	370	0	E-101 is used to heat the pure hydrocarbon stream to inlet reactor specifications.
E-102	 <p>Figure 33 – Heat exchanger E-102 configuration</p>	9 and 10	229	370	0	E-102 is used to heat the pure oxygen stream to inlet reactor specifications.
E-103	 <p>Figure 34 – Heat exchanger E-103 configuration</p>	7 and 40	374.5	55	0	E-103 is used to cool the exiting splitter component stream 7 in order to meet absorber T-100 inlet temperature specification.
E-104	 <p>Figure 35 – Heat exchanger E-104 configuration</p>	22 and 23	240	30	0	E-104 is used to cool the recycled organic solvent in order to enter, after being mixed with fresh solvent, absorber T-100 at a specific temperature.
E-105	 <p>Figure 36 – Heat exchanger E-105 configuration</p>	29 and 30	148.6	60	0	E-105 is used to cool the stream exiting scrubber T-103 that is recycled back into main absorber T-100.

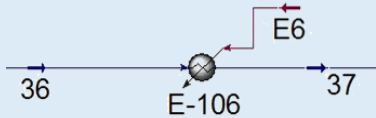
E-106	 <p>Figure 37 – Heat exchanger E-106 configuration</p>	36 and 37	86.89	370	0	E-106 is used to heat the main recycle (RCY-2) stream in order to be mixed with pure nitrogen.
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Table 5 – Heat exchangers used in the simulation

3.3.3.8 Compressors

In this simulation, one compressors has been used. Table 6 provides information including: name, configuration, streams involved, inlet and outlet pressure and a brief explanation. Stream *K* followed by a number is the energy stream that are involved in the equipment operation by supplying the compressor with energy.

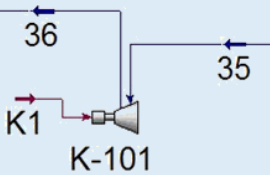
Name	Configuration	Streams involved	Inlet P (kPa)	Outlet P (kPa)	Brief explanation
K-101	 <p>Figure 38 – Compressor K-101 configuration</p>	35 and 36	113	150	K-101 is used to compress recycled gases to process pressure operation.

Table 6 – Compressors used in the simulation

3.3.3.9 Pump

The information provided for the single pump used in this simulation is shown in Table 7. As mentioned in the beginning of this chapter, this pump is a reciprocating piston pump which is used when working at vacuum conditions. Stream P0 is the energy supply for pump P-100.

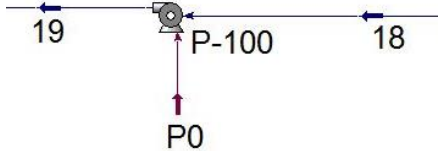
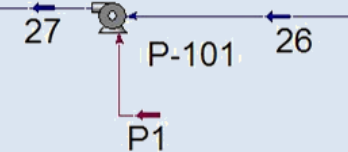
Name	Configuration	Streams involved	Inlet P (kPa)	Outlet P (kPa)	Brief explanation
P-100	 <p>Figure 39 – Pump P-100 configuration</p>	18 and 19	11.87	113.3	P-100 is used to compress organic solvent liquid stream that exits column T-101 in order to be recycled back into column T-100.
P-101	 <p>Figure 40 – Pump P-101 configuration</p>	26 and 27	11.87	113.3	P-101 is used to compress the liquid stream exiting scrubber T-103 in order to recycle stream 27 back into main absorber T-100

Table 7 – Pump used in the simulation

3.3.3.10 Valve

Table 8 shows information on the valve used in the simulation covering aspects such as name, configuration, streams involved, inlet and outlet pressure and a brief explanation.

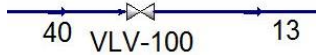
Name	Configuration	Streams involved	Inlet P (kPa)	Outlet P (kPa)	Brief explanation
VLV-100	 <p>Figure 41 – Valve VLV-100 configuration</p>	40 and 13	150	115	VLV-100 is used to release stream 40's pressure down to absorber T-101 appropriate inlet pressure.

Table 8 – Valve used in the simulation

3.3.3.11 Mixers

Throughout the simulation of this process, four mixers were used. The corresponding information to each one of them is shown in the following table.

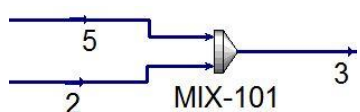
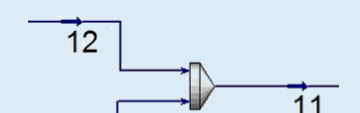
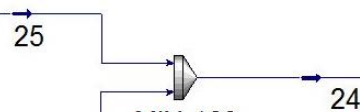
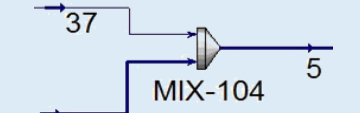
Name	Configuration	Streams involved	Brief explanation
MIX-101	 <p>Figure 42 – Mixer MIX-101 configuration</p>	2, 5 and 3	Following the specifications in the US patent for the simulation of reactor CRV-100, fresh n-butane (stream 2) is mixed with stream 5 which contains nitrogen and the recycle stream giving stream 3.
MIX-102	 <p>Figure 43 – Mixer MIX-102 configuration</p>	10,12 and 11	Pure oxygen stream 10 is mixed with oxygen recycle stream in order to give stream 11 which is fed to reactor CRV-100.
MIX-103	 <p>Figure 44 – Mixer MIX-103 configuration</p>	23, 25 and 24	Due to the fact that the organic solvent DBP is thermally stable, stream 25 being the fresh solvent line, is about 3% of the recycle stream 23.
MIX-104	 <p>Figure 45 – Mixer MIX-104 configuration</p>	4, 37 and 5	Fresh nitrogen (stream 4) is mixed with the main system's recycle stream 37.

Table 9 – Mixers used in the simulation

3.3.3.12 Tees

Table 10 offers information of each one of the tees (3) used in the simulation providing names, configurations, streams involved and brief explanations of their use.

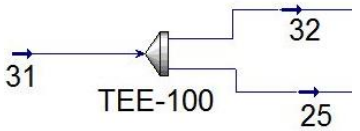
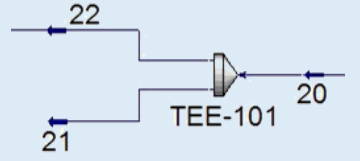
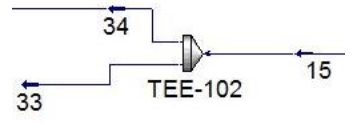
Name	Configuration	Streams involved	Brief explanation
TEE-100	 <p>Figure 46 – TEE-100 configuration</p>	31, 32 and 25	Fresh solvent line is divided into two streams which are each led as an inlet of either absorber T-100 (stream 25) or scrubber T-103 (stream 32).
TEE-101	 <p>Figure 47 – TEE-101 configuration</p>	20, 21 and 22	Through reliable sources, it has been found that between 6% and 10% n/n of dibutyl phthalate is lost due to its thermal decomposition and volatilization (26)(28). This minimal purge is represented by stream 21.
TEE-102	 <p>Figure 48 – TEE-102 configuration</p>	15, 33 and 34	Main recycle line (stream 15) is divided into stream 34 which continues the recycle and stream 33 which is vented.

Table 10 – Tees used in the simulatio

3.3.4 Imposed specifications

Throughout the simulation of this process there have been a few fixed ratios between certain pair of streams. In order to manipulate the value of only one of the streams and thusly having the remaining stream changed according to the established ratio, Aspen HYSYS offers SET blocks. In total, three SET blocks were imposed in this work and shall be explained individually in the following subsections.

Bear in mind that this block does not allow the manipulation of compositions of a certain compound within a stream. This said, the stream must be either a pure component or the specific compound to be manipulated must be present in a way that the stream may be assumed as mainly said compound since it is present in much greater percentage than the rest of components in the stream.

3.3.4.1 Butane-nitrogen feed ratio (SET-2)

The control of the fresh nitrogen/n-butane ratio has also been carried out by including a *Set* block in the simulation (SET-2). The ratio calculation is obtained as indicated below:

$$\frac{N_2}{C_4} = \frac{97\%n/n}{3\%n/n} = 32.33 \quad (1.8)$$

$$N_2|_{Stream4} = 1,500C_4kgmole * \frac{97\%n/nN_2}{3\%n/nC_4} = 48,850N_2kgmole$$

Data input for block SET-1 is shown in Table 11 and Table 12 where the target value is the molar flow of stream 4 and the source is the molar flow of stream 1.

	Object	Variable
Target Variable	4	Molar flow
Source	1	

Table 11 – Data input in block SET-2 (Connections)

The ratio between nitrogen and n-butane is obtained through the equation of a straight line as seen in equation 1.9.

Parameters	
Multiplier	32.33
Off-set (kgmole/h)	0

Table 12 – Data input in block SET-2 (Parameters)

$$\begin{aligned}
 Y &= 32.33X + 0 \\
 Y &= Stream4 \\
 X &= Stream1
 \end{aligned} \quad (1.9)$$

3.3.4.2 Solvent/gaseous stream ratio inlet scrubber T-103 (SET-2)

The amount of fresh solvent entering scrubber T-103 has been calculated taking into account the mass flow of stream 16. Data input for block SET-2 is shown in Table 13 and Table 14 where the target value is the mass flow of stream 32 and the source is the mass flow of stream 16.

	Object	Variable
Target Variable	32	Molar flow
Source	16	

Table 13 – Data input in block SET-4 (Connections)

The ratio between the organic solvent mass flow and gaseous mixture stream 13 is obtained through the equation of a straight line as seen in equation 1.10.

Parameters	
Multiplier	0.25
Off-set (kgmole/h)	0

Table 14 – Data input in block SET-4 (Parameters)

$$Y = 0.25X + 0$$

$$Y = \text{Stream32} \quad (1.10)$$

$$X = \text{Stream26}$$

3.3.4.3 Solvent/gaseous stream ratio inlet absorber T-100 (SET-3)

In order to calculate the required organic solvent flow entering column T-100, a set block has been used. Data input for block SET-3 is shown in Table 15 and Table 16 where the target value is the mass flow of stream 24 and the source is the mass flow of stream 13.

	Object	Variable
Target Variable	24	Mass Flow
Source	13	

Table 15 – Data input in block SET-3 (Connections)

The ratio between the organic solvent mass flow and gaseous mixture stream 13 is obtained through the equation of a straight line as seen in equation 1.11.

Parameters	
Multiplier	6.11E-02
Off-set (kgmole/h)	0

Table 16 – Data input in block SET-3 (Parameters)

$$Y = 6.11 \cdot 10^{-2} X + 0$$

$$Y = \text{Stream24} \quad (1.11)$$

$$X = \text{Stream13}$$

4 RESULTS

This chapter gathers the results obtained through the simulation of the maleic anhydride production plant proposed, Table 26. The attached results include mass balance of each active stream in the simulation as well as each component's molar flow, temperature and pressure among other specifications. Besides the results table attached, the following subsections process' basic calculations.

4.1 Process efficiency

Process efficiency is defined as the ratio between the MAN obtained in the product stream (stream 39) and the MAN if all of the inlet n-butane produced MAN (stream 1). By applying equation 1.12, the process efficiency for this work is 73.01 %.

$$\text{ProcessEfficiency} = \frac{\text{Stream39}}{\text{Stream1}} * 100 \quad (1.12)$$

Stream	kgmole/h
39	73.01
1	100
Process efficiency (%)	73.01

Table 17 – Process efficiency

4.2 Reactive losses

N-butane losses mainly occur in streams 28 and 33 and is calculated through equation 1.13. In this case, reactive losses are 20.14 %.

$$\text{ReactiveLosses} = \text{InletC4} - \text{OutletC4} = \text{Stream1} - (\text{Stream28} + \text{Stream33}) \quad (1.13)$$

Stream	kg/h n-butane
28	8.37
33	1,162.48
1	5,812.40
Total reactive losses (kg/h)	1,170.85
Total reactive losses (%)	20.14%

Table 18 – Reactive losses

4.3 Product recuperation

The percentage of recuperated MAN is defined as the MAN obtained in the product stream that exits column T-104 (stream 39) divided by the MAN produced in the reactor (stream 6) multiplied by 100. In this case, Table 21 shows a recuperation of 99.01 %.

$$\text{ProductRecuperation}(\%) = \frac{\text{MAN ExitDistillationColumn}}{\text{MAN Exit Reactor}} * 100 = \frac{\text{Stream 39}}{\text{Stream 6}} * 100 \quad (1.14)$$

Stream	kgmole/h MAN
6	73.74
39	73.01
Total product recuperation (%)	99.01

Table 19 – Product recuperation

4.4 Energy consumption

The energy required per kilogram of product is shown in Table 22 in which heaters, compressors and pump are included. The information provided is obtained directly from HYSYS after the simulation has been completed. The total kilograms of maleic anhydride are represented through stream 39.

	Name	Power kW
Heater	E-101	753.15
	E-102	834.55
	E-106	69,759.70
Pump	P-100	3.06
	P-101	0.43
Compressor	K-101	9,086.41
Total power		80,437.31
Energy consumption per MAN kg (kW/MAN kg)		11.23

Table 20 – Total energy consumption per kilogram of maleic anhydride

4.5 Product recuperation in absorber T-100

As seen in Table 23, the MAN recuperation in column T-100 is 99.10 %. The recuperation rate is defined as the ratio between MAN in product stream 14 and the total MAN entering the column (stream 13,24 and 30) times 100.

$$\begin{aligned} \text{ProductRecuperation}(\%) &= \frac{\text{MAN ExitMainAbsorber}}{\text{MAN InMainAbsorber}} * 100 \\ &= \frac{\text{Stream 14}}{\text{Stream 13} + \text{Stream 24} + \text{Stream 30}} * 100 \end{aligned} \quad (1.15)$$

Stream	kg/h MAN
13	7,231.50
24	7.10
30	708.88
14	7,876.56
15	70.93
Total MAN mass flow entering T-100 (kg/h)	7,947.48
MAN recuperation (%)	99.10

Table 21 – T-100 MAN recuperation

4.6 Product recuperation in scrubber T-103

Table 24 offers information related to the streams involved in the scrubber MAN recuperation. The recuperation rate is defined as the ratio between MAN in product stream 26 and the total MAN entering the column (stream 16 and 32) times 100, resulting in 100 % in column T-103.

$$\begin{aligned} \text{ProductRecuperation}(\%) &= \frac{\text{MAN ExitScrubber}}{\text{MAN InScrubber}} * 100 \\ &= \frac{\text{Stream 26}}{\text{Stream 16} + \text{Stream 32}} * 100 \end{aligned} \quad (1.16)$$

Stream	kg/h MAN
32	0.00
26	708.87
16	708.87
28	0
Total MAN mass flow entering T-100 (kgmole/h)	708.87
MAN recuperation (%)	100.00

Table 22 – T-103 MAN recuperation

As for the organic solvent recuperation, the streams involved in the scrubber concerning DBP recuperation are shown in Table 25. The solvent recuperation rate is defined the same as MAN rate, resulting in this case a percentage of 99.97 in column T-103.

$$\begin{aligned} \text{ProductRecuperation}(\%) &= \frac{\text{DBP ExitScrubber}}{\text{DBP InScrubber}} * 100 \\ &= \frac{\text{Stream 26}}{\text{Stream 16} + \text{Stream 32}} * 100 \end{aligned} \quad (1.17)$$

Stream	kg/h DBP
32	10,500.25
26	10,497.74
16	0
0	2.51
Total DBP mass flow entering T-100	10,500.25
DBP recuperation (%)	99.97

Table 23 – T-103 DBP recuperation

	<i>Unit</i>	1	2	3	4	5
Vapour Fraction		1	1	1	1	1
Temperature	<i>C</i>	200.00	370.00	363.57	300.00	363.46
Pressure	<i>kPa</i>	150.00	150.00	150.00	150.00	150.00
Molar Flow	<i>kgmole/h</i>	100.00	100.00	33,190.54	3,233.00	33,090.54
Mass Flow	<i>kg/h</i>	5,812.40	5,812.40	923,283.47	90,566.03	917,471.07
Comp Mole Flow (H2O)		0	0	1,835.36	0	1,835.36
Comp Mole Flow (MaleicAnhydr)		0	0	0	0	0
Comp Mole Flow (DiiBPhthlate)		0	0	0	0	0
Comp Mole Flow (Nitrogen)		0	0	30,670.73	3,233.00	30,670.73
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		0	0	198.75	0	198.75
Comp Mole Flow (CO)		0	0	198.83	0	198.83
Comp Mole Flow (n-Butane)		100.00	100.00	286.13	0	186.13
	<i>Unit</i>	6	7	8	9	10
Vapour Fraction		1	1	1	1	1
Temperature	<i>C</i>	441.55	469.50	300.00	229.00	370.00
Pressure	<i>kPa</i>	150.00	150.00	150.00	150.00	150.00
Molar Flow	<i>kgmole/h</i>	40,368.93	33,586.00	6,782.93	670.00	670.00
Mass Flow	<i>kg/h</i>	1,150,791.28	933,737.38	217,053.90	21,440.00	21,440.00
Comp Mole Flow (H2O)		2,192.19	2,192.19	0	0	0
Comp Mole Flow (MaleicAnhydr)		73.75	73.75	0	0	0
Comp Mole Flow (DiiBPhthlate)		0	0	0	0	0
Comp Mole Flow (Nitrogen)		30,670.73	30,670.73	0	0	0
Comp Mole Flow (Oxygen)		6,782.93	0	6,782.93	670.00	670.00
Comp Mole Flow (CO2)		224.50	224.50	0	0	0
Comp Mole Flow (CO)		224.58	224.58	0	0	0
Comp Mole Flow (n-Butane)		200.15	200.15	0	0	0

	Unit	11	12	13	14	15
Vapour Fraction		1	1	1	0	1
Temperature	<i>C</i>	306.65	300.00	58.26	62.21	65.75
Pressure	<i>kPa</i>	150.00	150.00	115.00	115.00	113.32
Molar Flow	<i>kgmole/h</i>	7,109.62	6,439.62	33,586.00	499.13	33,349.12
Mass Flow	<i>kg/h</i>	227,507.81	206,067.81	933,737.38	78,597.90	923,619.32
Comp Mole Flow (H2O)		0	0	2,192.19	175.73	2,028.76
Comp Mole Flow (MaleicAnhydr)		0	0	73.75	80.33	0.72
Comp Mole Flow (DiiBPhthlate)		0	0	0	242.64	0.12
Comp Mole Flow (Nitrogen)		0	0	30,670.73	0	30,670.47
Comp Mole Flow (Oxygen)		7,109.62	6,439.62	0	0	0
Comp Mole Flow (CO2)		0	0	224.50	0	224.48
Comp Mole Flow (CO)		0	0	224.58	0	224.58
Comp Mole Flow (n-Butane)		0	0	200.15	0	200.00
	Unit	16	17	18	19	20
Vapour Fraction		1	0.00	0	0	0
Temperature	<i>C</i>	60.63	60.63	240.80	240.87	240.87
Pressure	<i>kPa</i>	6.66	6.66	11.87	113.30	113.30
Molar Flow	<i>kgmole/h</i>	150.90	105.51	242.72	242.72	243.62
Mass Flow	<i>kg/h</i>	3,305.99	7,745.49	67,546.42	67,546.42	67,796.04
Comp Mole Flow (H2O)		143.23	32.49	0	0	0
Comp Mole Flow (MaleicAnhydr)		7.23	73.02	0	0	0
Comp Mole Flow (DiiBPhthlate)		0	0	242.64	242.64	243.54
Comp Mole Flow (Nitrogen)		0	0	0	0	0
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		0	0	0	0	0
Comp Mole Flow (CO)		0	0	0	0	0
Comp Mole Flow (n-Butane)		0	0	0	0	0

	Unit	21	22	23	24	25
Vapour Fraction		0	0	0	0	0
Temperature	<i>C</i>	240.87	240.87	30.00	29.46	35.00
Pressure	<i>kPa</i>	113.30	113.30	113.30	113.30	113.30
Molar Flow	<i>kgmole/h</i>	16.44	227.17	227.17	205.01	22.16
Mass Flow	<i>kg/h</i>	4,576.23	63,219.81	63,219.81	57,051.35	6,168.45
Comp Mole Flow (H2O)		0	0	0	0	0
Comp Mole Flow (MaleicAnhydr)		0	0	0	0	0
Comp Mole Flow (DiiBPhthlate)		16.44	227.10	227.10	204.94	22.16
Comp Mole Flow (Nitrogen)		0	0	0	0	0
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		0	0	0	0	0
Comp Mole Flow (CO)		0	0	0	0	0
Comp Mole Flow (n-Butane)		0	0	0	0	0
	Unit	26	27	28	29	30
Vapour Fraction		0	0	1	0	0
Temperature	<i>C</i>	84.60	84.68	66.58	84.67	60.00
Pressure	<i>kPa</i>	11.87	113.30	6.66	113.30	113.30
Molar Flow	<i>kgmole/h</i>	57.24	57.24	131.38	57.24	57.24
Mass Flow	<i>kg/h</i>	11,428.15	11,428.15	2,378.10	11,428.48	11,428.48
Comp Mole Flow (H2O)		12.30	12.30	130.94	12.30	12.30
Comp Mole Flow (MaleicAnhydr)		7.23	7.23	0	7.23	7.23
Comp Mole Flow (DiiBPhthlate)		37.71	37.71	0	37.72	37.72
Comp Mole Flow (Nitrogen)		0	0	0	0	0
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		0	0	0	0	0
Comp Mole Flow (CO)		0	0	0	0	0
Comp Mole Flow (n-Butane)		0	0	0	0	0

	Unit	31	32	33	34	35
Vapour Fraction		0	0	1	1	1
Temperature	<i>C</i>	35.00	35.00	65.75	65.75	65.82
Pressure	<i>kPa</i>	113.30	113.30	113.32	113.32	113.32
Molar Flow	<i>kgmole/h</i>	15.56	37.72	3,334.91	30,014.21	29,857.54
Mass Flow	<i>kg/h</i>	4,331.81	10,500.26	92,361.93	831,257.38	826,905.04
Comp Mole Flow (H2O)		0	0	202.88	1,825.88	1,835.36
Comp Mole Flow (MaleicAnhydr)		0	0	0	0	0
Comp Mole Flow (DiiBPhthlate)		15.56	37.72	0	0	0
Comp Mole Flow (Nitrogen)		0	0	3,067.05	27,603.42	27,437.73
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		0	0	22.45	202.03	198.75
Comp Mole Flow (CO)		0	0	22.46	202.12	198.83
Comp Mole Flow (n-Butane)		0	0	20.00	180.00	186.13
	Unit	36	37	38	39	40
Vapour Fraction		1	1	1	0	1
Temperature	<i>C</i>	101.98	370.00	38.08	121.40	60.00
Pressure	<i>kPa</i>	150.00	150.00	6.66	11.87	150.00
Molar Flow	<i>kgmole/h</i>	29,857.54	29,857.54	31.00	74.51	33,586.00
Mass Flow	<i>kg/h</i>	826,905.04	826,905.04	558.55	7,186.93	933,737.38
Comp Mole Flow (H2O)		1,835.36	1,835.36	31.00	1.49	2,192.19
Comp Mole Flow (MaleicAnhydr)		0	0	0	73.02	73.75
Comp Mole Flow (DiiBPhthlate)		0	0	0	0	0
Comp Mole Flow (Nitrogen)		27,437.73	27,437.73	0	0	30,670.73
Comp Mole Flow (Oxygen)		0	0	0	0	0
Comp Mole Flow (CO2)		198.75	198.75	0	0	224.50
Comp Mole Flow (CO)		198.83	198.83	0	0	224.58
Comp Mole Flow (n-Butane)		186.13	186.13	0	0	200.15

	Unit	B1	B2	D1	D2
Vapour Fraction		0	0	1	0
Temperature	<i>C</i>	240.53	132.09	97.98	38.01
Pressure	<i>kPa</i>	11.87	11.87	6.66	6.66
Molar Flow	<i>kgmole/h</i>	242.64	73.04	256.49	32.47
Mass Flow	<i>kg/h</i>	67,510.29	7,160.47	11,087.61	585.01
Comp Mole Flow (H2O)		0	0.02	175.73	32.47
Comp Mole Flow (MaleicAnhydr)		0	73.02	80.18	0
Comp Mole Flow (DiiBPhthlate)		242.49	0	0	0
Comp Mole Flow (Nitrogen)		0	0	0	0
Comp Mole Flow (Oxygen)		0	0	0	0
Comp Mole Flow (CO2)		0	0	0	0
Comp Mole Flow (CO)		0	0	0	0
Comp Mole Flow (n-Butane)		0	0	0	0

Table 24 – Maleic anhydride production workbook.

5 CONCLUSIONS

The motivation of this present work was the documentation of several maleic anhydride production technologies. This dissertation's goal was to select a specific technology that produced MA via n-butane partial oxidation and simulate it with Aspen HYSYS software.

The simulation's objective was successfully achieved by obtaining a plant capable of producing 36,800 cubic meters per year of maleic anhydride at a purity of 98 % n/n. and a global product recuperation of up to 99.10 %. Un-reacted n-butane has been recycled limiting the losses to about 20 %. Furthermore, values higher than 99 % product recovery from the absorber and scrubber have been obtained for both MAN and DBP recuperations.

This work has not taken into consideration the fact that maleic anhydride reacts readily with water to produce its acid and fumaric acid as well. For future works, is an interesting point to introduce these reactions in the absorption and purification sections of the process plant. Since this process has such an exothermic reaction, it does require precise temperature control. Thusly aspects concerning process control would also be very interesting to perform. Lastly, matters that this work has not considered such as rigorous equipment modelling, energy integration and economic studies are other aspects to be taken into account for future works.

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