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Tetraacetylethylenediamine (TAED): Development of a process and design of the basic engineering for its manufacture

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Voldria agrair al meu tutor, el Dr. José María Gutiérrez, per la seva paciència, consells i temps dedicat al llarg d’aquest projecte, com també durant els últims anys del grau.

També donar les gràcies als amics que he conegut i que m’han acompanyat durant aquesta etapa.

Agrair a la meva família per ajudar-me i animar-me durant tots aquests anys. I a la meva parella, per estar sempre al meu costat.

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SUMMARY

Tetraacetylethylenediamine (TAED) is an organic compound that is generally used as a bleach activator in household detergents. The reaction of TAED with hydrogen peroxide is known as perhydrolysis, which results in the formation of peroxyacids that allow washing at very low temperatures.

The purpose of this project is to develop a continuous plant for the production process of TAED, as well as to perform its basic engineering. Generally, TAED is produced in two reactions: acetylation of ethylenediamine (EDA) generates diacetylethylenediamine (DAED), which in reaction with acetic anhydride, produces TAED as the final product.

The manufacturing process design has been carried out for an annual production of 15 000 tons of TAED. This amount has been chosen taking into account the worldwide production volume of such substance. Different patents have been studied in order to find a basic recipe that could be scaled to industrial level. A production process based on the recipe has been synthesized, including also all the equipment involved. After that, all this information has been uploaded to Aspen Plus software, simulating the plant and determining the operating conditions and basic dimensions of the main equipment. To conclude, the project includes a selection of suitable equipment, extracted from the catalogues of different existing suppliers, that would be required in order to bring the proposed production process to a real industrial situation.

Keywords: Tetraacetylethylenediamine, production process, equipment selection, equipment sizing, patent recipe.

RESUM

La tetraacetiletilendiamina (TAED) és un compost orgànic que s'utilitza generalment com activador del blanquejador en detergents domèstics. La reacció del TAED amb el peròxid d'hidrogen es coneix com a perhidròlisi, que dona com a resultat la formació de peroxiàcids que permeten el rentat a temperatures molt baixes.

L'objectiu d'aquest treball és desenvolupar una planta contínua pel procés de producció del TAED, així com realitzar la seva enginyeria bàsica. Generalment, el TAED es produeix en dues reaccions: l'acetilació de l'etilendiamina (EDA) genera diacetiletilendiamina (DAED), que per reacció amb l'anhídrid acètic, produeix com a producte final el TAED.

El disseny del procés de fabricació s'ha realitzat per a una producció anual de 15.000 tones de TAED, seleccionades tenint en compte el seu volum de producció global. S'han estudiat diferents patents de la seva producció, per trobar una recepta base que es pogués escalar a nivell industrial. Amb la recepta, s'ha sintetitzat un procés de producció on s'han seleccionat tots els equips involucrats i a partir d'aquí, s'han introduït al programa Aspen Plus per a poder simular la planta, de tal manera que es poguessin conèixer les condicions d'operació i les dimensions bàsiques dels equips principals. Per concloure el treball, s'ha fet un anàlisis dels catàlegs de diferents proveïdors, seleccionant equips concrets que podrien portar la producció a un entorn industrial real.

Paraules clau: Tetraacetiletilendiamina, procés de producció, selecció d'equips, dimensionament d'equips, recepta de patent.

1. INTRODUCTION

N,N,N’,N’-tetraacetylethylenediamine (TAED) is the most extended bleach activator used in laundry products (Schneemann, 2005). It is an ecologic and efficient activator, and part of detergents composition. It is used for washing away the stain and the dirt agents, even at low temperatures, simultaneously having disinfectant properties, without affecting colours, cloth or attacking the skin (Stepan et al., 2008).

To make the performance of household detergents better, manufacturers use sodium perborate as a bleaching agent simultaneously with a bleaching activator, whose function is to allow the bleaching to happen at lower temperature. Between such bleaching activators, TAED is one of the most commonly used (Ryczkowski, 2005). While many others bleach activators have been used in the bleaching of cotton, TAED continues to be of high interest because of its commercial use in the textile industry (Xu et al., 2013).

As stated, TAED is used as bleaching activator in household detergents but a small quantity of TAED is also used in bleaching of paper, textiles and for the generation of peracetic acid in disinfectants.

2. TAED.

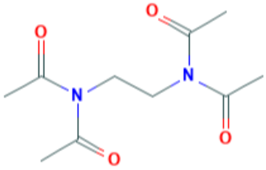
1. Detergent powders.

TAED is available both in powder and granular form. TAED is used in granular form in detergent and washing powders and in powder form in other applications like biocides, fabric bleaching etc. TAED is not used in liquid detergents and liquid dish washers. (Venkataraman., 2015).

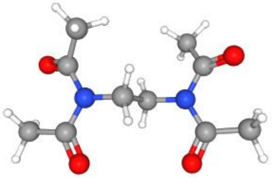
Regarding environmental aspects, TAED and DAED dissolve well in aqueous alkaline solutions and the elimination at sewage treatment plants is very high. The ecotoxicity of TAED and DAED is low and there are not adverse ecological effects from the use of TAED in laundry products (Clariant (Lead & Report) et al., 2002).

1.1. **PROPERTIES**

TAED is a white crystalline amide having the structural formula (Hutzinger, 1992):



4. 2D structure.



3. 3D conformer.

Empirical formula	$C_{10}H_{16}N_2O_4$
Molecular weight	228.25 g/mol
CAS Number	10543-57-4
Melting point	149-154ºC
Boiling point	140ºC
Density	900 kg/m^3

TAED is characterized by a high degree of purity and a high melting point, that ensure appropriate processing properties (Stepan et al., 2008).

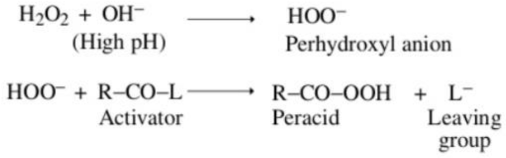
The TAED molecule is electrically neutral, but has a polar character as a result of its two amide structures (Clariant, 1999).

The product has a small particle size and, therefore, a large surface area. This reduces its stability on contact with detergent ingredients. As a result, the product is further granulated to reduce its contact with incompatible formulation ingredients. Granulation has not only an effect on storage stability but also reduces TAED dissolution rate, which prevents undesired hydrolysis of the amide bond in the wash liquid. The granulation ingredients used include carboxymethylcellulose and surfactants (Zoller, 2008).

1.2. **BLEACH ACTIVATOR**

The last years, wash temperature has lowered because of factors that include governmental energy-saving campaigns and more. This has led to decreaded bleaching efficiency of persalts (Zoller, 2008).

This was made up for by the introduction of activators in detergent formulations. Activators are organic compounds that are able to perhydrolyzed in the wash with the formation of a percarboxylic acid, which is a more efficient bleaching agent than persalts at lower washing temperatures. An activator has at least one acyl group (RCO-) and a leaving group (L). It reacts with the perhydroxyl anion formed from persalts in the wash as follow (Zoller, 2008):



$$H_2O_2 + \underset{\text{(High pH)}}{OH^-} \longrightarrow \underset{\text{Perhydroxyl anion}}{HOO^-}$$

$$HOO^- + \underset{\text{Activator}}{R\text{–}CO\text{–}L} \longrightarrow \underset{\text{Peracid}}{R\text{–}CO\text{–}OOH} + \underset{\text{Leaving group}}{L^-}$$

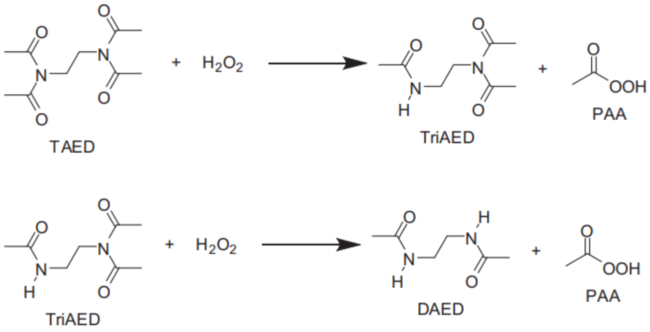
5. Perhydrolysis of bleach activator (Zoller, 2008).

Four hydrophilic activators were developed in Europe. They all produced peracetic acid (PAA) in the wash. These are tetraacetylglycoliril (TAGU), diacetyldioxohexahydrotriazine

(DADHT), glucose pentaacetate and tetraacetylethylenediamine (TAED). Today, the principal activator is TAED. The bleaching performance, chemical stability, low cost and biodegrability were the principal reasons for the prosperity of TAED in Europe (Zoller, 2008).

TAED has two active groups, from which two molecules of oxidizing and disinfecting peracetic acid are released in the presence of H_2O_2 (Ryczkowski, 2005).

In the wash, TAED reacts with H_2O_2 (nucleophilic attack) to form triacetylethylenediamine (TriAED) and diacetylethylenediamine (DAED) with the release of two molecules of peracetic acid (PAA). The remaining acetyl groups of DAED cannot be displaced by peroxide in the wash bath. The name of this reaction is perhydrolysis. PAA is more kinetically active specie than H_2O_2 and enables bleaching at low temperatures (Long et al., 2013).



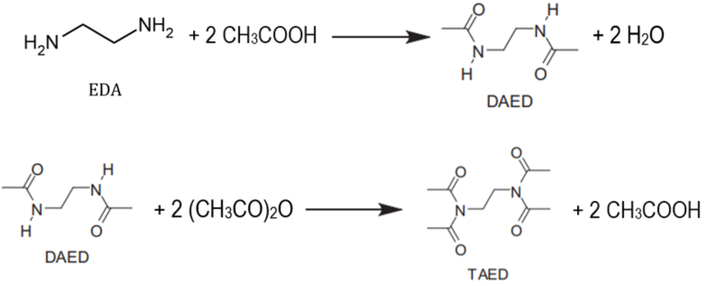
6. Perhydrolysis of TAED.

In most previous investigations of TAED for low-temperature bleaching, TAED was used with an excess of H_2O_2 under alkaline conditions, because it was expected that this excess produce more effect on bleaching performance. Actually, it has been demonstrated in a recent study that TAED is more effective under near neutral pH conditions instead of alkaline conditions and the use of an excess of H_2O_2 has no effect on bleaching performance under neutral pH conditions, but reduces bleaching performance under alkaline conditions (Long et al., 2013).

In a study, it has been demonstrated that the optimal situation comprises a treatment of the fabric with an aqueous formulation consisting of alkaline pectinase enzyme (2 g/L), TAED (15 g/L), H_2O_2 (5 g/L), non-ionic wetting agent (0.5 g/L) and sodium silicate (2 g/L). The treatment is carried out at 60 ºC for 60min, with pH 8 (Hebeish et al., 2009).

1.3. **MANUFACTURING ROUTE**

The system from TAED was described for the first time in 1959. TAED is generally produced at a large industrial scale in a two-stage reaction: firstly ethylenediamine (EDA) reacts with acetic acid to form diacetylethylenediamine (DAED); then DAED is converted into TAED by reaction with acetic anhydride (Ryczkowski, 2005).

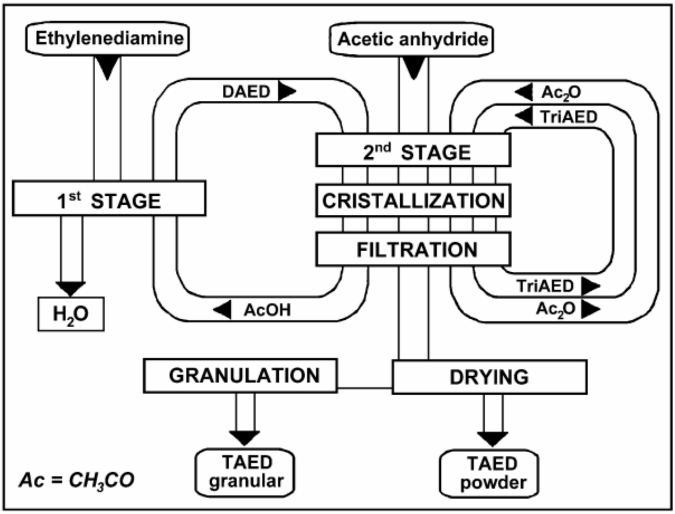


7. TAED manufacturing route.

TAED is crystallized, filtered, washed, dried and if necessary granulated. This gives colorless crystals of TAED.

A continuous reaction method makes sure a product purity of more than 99%. Almost all the raw materials used are produced in the product and the water, which is the only by-product, can be placed of without problems in a biological clarification plant (Ryczkowski, 2005).

Below is a scheme from TAED production process:



8. Scheme of TAED production (Ryczkowski, 2005)

2. OBJECTIVES

The main objective of this work is the development of the process and basic engineering of a TAED manufacturing plant.

The completion of this work includes the following tasks:

- Selection of the production scale through bibliographic search for market analysis.

A research of market share websites will be carried out to choose the TAED production.

- Selection of the manufacturing recipe.

To achieve this task, a bibliographic search will be applied to obtain different patents. Several patents will be compared and the most appropriate one will be chosen, explaining the reason of the selection.

- Synthesis of the process by scaling the selected recipe and selecting the necessary equipment.

The laboratory recipe will be scaled to an industrial level and the new equipment will be selected.

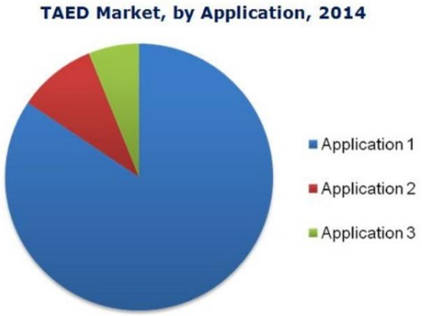
- Sizing of necessary equipment.

AspenPlus software will be used to size the equipment to execute the production.

3. PRODUCTION SCALE

3.1. APPLICATIONS AND REGIONS

TAED has few applications, being detergents (1) the main among them. Apart from this, TAED is used in bleaching agents (2) and cleaning agents (3). TAED's main application is to be bleaching activator in the household detergents. In the following study, the three key applications of TAED are considered (TAED Market, 2014).



9. TAED Applications (TAED Market, 2014).

The global market for TAED is principally concentrated in Europe region with more than 50% of the global share. This is caused by many considerations like availability of raw materials, usage of advanced technology to produce the product and create consciousness among consumer related to the advantages and applications of TAED. Latin America and North America possess the second largest market share and simultaneously is the fastest growing market for TAED. It is followed by the increasing market in the Asia Pacific region which is growing in the urbanization and high disposable earnings of consumers (TAED Market, n.d.)

3.2. **GLOBAL PRODUCTION VOLUME AND PRODUCERS**

TAED production information has been found at different-dated sources, in both Europe and in worldwide. All production volumes are cited below to observe the growth of TAED over the years. For this work, the latest production information is used.

- 1999. 48 000 t/year of TAED were employed in European detergents (Jacobi, 2001).
- 2002. 61 000 t/year of TAED were employed in household detergents in Europe (Clariant (Lead & Report) et al., 2002).
- 2010. 85 000 t/year of TAED were employed in Europe. 100 000 t/y of Global TAED were employed (The Chinese market research, 2011).
- 2015. 100 000 t/year of Global TAED were employed (Venkataraman, N.S., 2015).

The major global producers of TAED in the world include the following (The Chinese market research, 2011):

- Warwick Chemicals (United Kingdom). Their market share was 45% in 2010, which corresponds to 50 000 t/year.
- Clariant (Germany). Their market share was 30 000 t/year in 2010 and is the second largest company.
- Jinke Chemicals Co. Ldt. (China).
- Dubag (Germany).

3.3. **DETERMINATION OF PRODUCTION**

As previously stated, the two main producers of TAED produce a total of 50 000 t / year (Warwick) and 30 000 t / year (Clariant) compared to total 100 000 t / year. Since in this work is considered that it is not necessary study so much quantity, this big production of these two main producers is not used.

20 000 t / year is the production that corresponds to other companies of not so large scale. It is decided that this work is intended to work as such companies. Therefore, as there are at least two other companies (Jinke and Dubag), the 20 000 t / year are not taken. Since the exact production value of those companies is not known, a lower and feasible value would be 15 000 t / year, which corresponds to half of the production of Clariant company.

This production is considered adequate to carry out this work. Therefore, a **total production of 15 000 t / year** is going to be studied, which corresponds to 15% of Global TAED production (latest data obtained).

Despite corresponding to the production of the smallest companies, it is a large production and as a result, a continuous process will be used. As stated in the 'introduction' section, a continuous reaction method ensures a product purity of more than 99%.

4. RECIPE SELECTION

Given the route explained in the introduction, the process must take advantage as much as possible of acetic anhydride. The main reason for this is it being a relatively expensive reagent. If acetic anhydride was used for the whole acetylation, the process would become too expensive. Consequently, if it is used only in the second stage and the cheaper reactant, acetic acid, is used for the preliminary acetylation of EDA to DAED, the process is cheaper.

4.1. BIBLIOGRAPHIC SEARCH

The patent research was carried out at the following portals: Espace.net and Google Patent. In its search engine, these key words were wrote down: “TAED”, “Tetraacetylethylenediamine”, “TAED production” and “TAED process”. A large number of patents were obtained.

One criteria for patent selection was the language. Some of them were in Chinese or German. Only patents in English were downloaded.

Another criteria was that several of them did not explain the production process, but rather explained the purification of TAED, so they were discarded too.

Finally, the research ended up with 14 patents. Some of them were the same patent but published by different countries and others used acetic anhydride in both reactions, which, as explained before, is very expensive and the acetic acid by-product has to be recycled as acetic anhydride. These patents were not selected.

With all of this, the research ends up with 6 patents that are the ones that best fit what is needed in this work. These 6 patents explain the production of TAED.

4.2. **MANDATORY REQUISITES**

For the final selection of the patents some characteristics will be evaluated. The required conditions that the process must meet are explained below. The final patent will be the one that best matches these conditions.

If the process cannot be adjusted to the requisites that will be seen below, it is automatically discarded.

Manufacturing route: the selected manufacturing route has two reactions, EDA with acetic acid to form DAED and reacting DAED with acetic anhydride to form TAED. The purpose of this selection is to make the work more complete. For this reason, the selected patent has to be comprised of these two reactions. If this option had not been chosen, production could start, for example, with DAED, eliminating the first reaction.

- High Purity: As stated in the 'introduction' section, it is easy to obtain a purity of 99% if it works as a continuous process, therefore it cannot be lower.
- Use of anhydride acetic only in the second reaction: As explained before, acetic acid will be used for the first reaction. In this way, only acetic anhydride will be used in the second reaction, thus making the process cheaper.

4.3. **PATENT PRESELECTION**

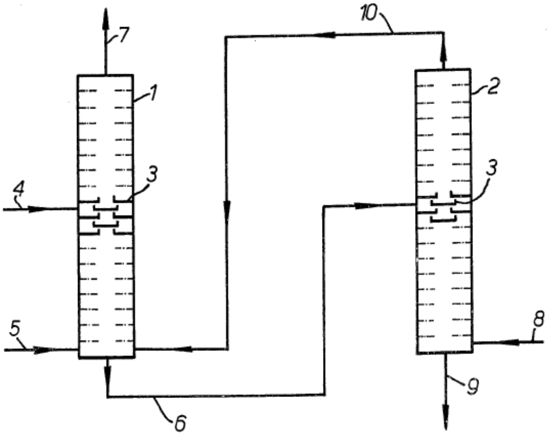
The 6 preselected patents have to meet with the three above requisites. Firstly, they will be cited and explained.

- **GB2143522(A)**

This invention is a batch producer which comprises reactors and distillation columns and it is executed as a multi-cyclic process for making TAED, in which each cycle includes reacting EDA with acetic acid to form DAED and reacting all the DAED with acetic anhydride recovered from another cycle and by that means forming reaction mixture containing TAED and acetic acid and anhydride. TAED crystallizes cooling the last mixture.

- **GB2096133(A)**

According to the invention, a continuous process for making TAED is provided, which comprises a first and a second columnar reactor. EDA is supplied to the middle region of the first column (4) and a first flash evaporator supplies acetic acid vapor to the column (5). Distillate water is removed from the top (7) and produced DAED is passed from the lower region of this column to the middle region of the second column (6). A second flash evaporator supplies acetic anhydride vapor to the lower region of the second column (8). Distillate acetic acid is remove from the top (10) and TAED (produced in this column) is removed from the lower region (9).



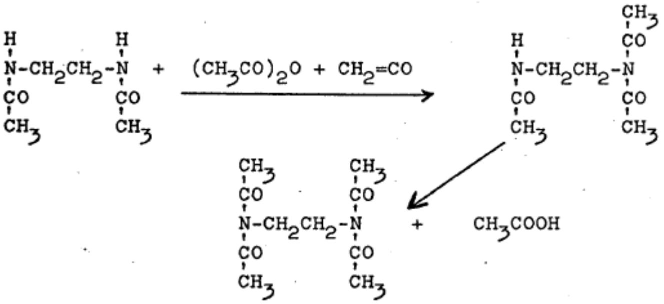
10. Two columnar reactors.

- **GB1335204(A)**

This invention is carried out in a reaction vessel, provided with a stirrer, thermometer, dropping funnel, a reflux cooler and receiver. It contains EDA and through the dropping funnel acetic acid is added continuously for a time. DAED is dissolved with acetic anhydride in other reaction vessel provided with the same instruments and also a vigreux column. After the distillation is finished the reaction is cooled and TAED crystals are formed.

- **CA974256(A)**

The invention relates to a process for the production of TAED by reaction of DAED with acetic anhydride and ketene (C_2H_2O). The apparatus used is a bubble column. DAED is dissolved in acetic anhydride and the mixture is brought to the reaction temperature. The ascending vapor is condensed in a reflux condenser and flows back into the reaction mixture. Ketene is introduced in to the column during three hours. After, all is cooled so TAED crystallizes out.



11. TAED manufacturing route with Ketene.

- **GB1378308(A)**

A mixture of DAED and acetic anhydride is passed per hour into a cascade consisting of two reaction vessels, both provided with a packed column. A total of a mix of 37% of acetic anhydride and 63% of acetic acid is distilled off per hour from both reaction vessels. The mixture that comes out from the cascade is cooled and it precipitates TAED.

- **US4240980(A)**

DAED is refluxed with acetic anhydride at 140ºC. After that, the batch is cooled to 100ºC and a quantity of Tonsil (bleaching earth) are added. The batch is then filtered hot. Because of the treatment with Tonsil, the initially brown reaction mixture becomes light yellow. The purified reaction mixture is cooled to 0ºC and precipitated colorless crystals of TAED are filtered.

4.4. **PATENT COMPARISON**

After this summary of what patents contain, a comparison will be carried out.

In order to do this, the most relevant characteristics have been selected: models, involved reactions, main necessary equipment and TAED yield. There are also individual characteristics.

Next, the characteristics of each patent are summarized, and the advantages and disadvantages offered by each of them are written below.

- **GB2143522 (A)** patent is a batch process and the reactions are EDA with acetic acid to form DAED and reacting DAED with acetic anhydride to form TAED and acetic acid. The necessary equipment comprises reactors and distillation columns. The yield is 86% (including crystallization). It is a 3 cycles process.

Advantages: high yield and anhydride acid is only used in second reaction.

Disadvantages: batch (only small quantities can be produced).

- **GB2096133 (A)** patent explains well the process. It is a continuous process and the reactions are EDA with acetic acid to form DAED and reacting DAED with acetic anhydride to form TAED and acetic acid and anhydride. The necessary equipment comprises a first and a second columnar reactor. The yield is 32% because it does not include crystallization. It has not recipes.

Advantages: continuous (long quantities can be produced) and anhydride acid is only used in second reaction.

Disadvantages: low yield and with no recipes.

- **GB1335204 (A)** patent is a batch process and the reactions are EDA with acetic acid to form DAED and reacting DAED with acetic anhydride to form TAED and acetic acid. The necessary equipment comprises two reaction vessels. The yield is 91% (including crystallization). It only uses 2/5 of formed DAED.

Advantages: high yield and anhydride acid is only used in second reaction.

Disadvantages: batch (only short quantities can be produced) and use 2/5 of DAED.

- **CA974256 (A)** patent is a batch process and the reaction is DAED with acetic anhydride and ketene to form TAED. The necessary equipment comprises a bubble column. The yield is 95.5% (including crystallization).

Advantages: high yield and anhydride acid is only used in second reaction.

Disadvantages: batch (only small quantities can be produced), starts with DAED (only one reaction takes place) and Ketene involves high expenditure for equipment.

- **GB1378308 (A)** patent is a continuous process and the reaction is DAED with acetic anhydride to form TAED. The necessary equipment comprises two reaction vessels provided with a packed column. The yield is 85.7% (including crystallization).

Advantages: high yield, continuous (long quantities can be produced) and anhydride acid is only used in second reaction.

Disadvantages: starts with DAED (only one reaction takes place).

- **US4240980 (A)** patent is a batch process and the reaction is DAED with acetic anhydride and Tonsil (bleaching earth) to form TAED. The necessary equipment comprises one reaction vessel. The yield is 97% (including crystallization). The molar ratio DAED:Acetic anhydride has to be 1:1 to 1:10.

Advantages: high yield and anhydride acid is only used in second reaction.

Disadvantages: batch (only small quantities can be produced), starts with DAED (only one reaction takes place) and Tonsil is not necessary to carry out TAED production.

To make the comparison easier, a table is shown below containing: patent name, reactants that participate in the reaction, main necessary equipment, models, TAED yield and an observations section.

PATENTS	REACTANTS	EQUIPMENT	MODELS	YIELD	OBSERVATIONS
GB2143522(A)	EDA Acetic acid Acetic anhydride	Reactor and distillation column	Batch	86%	3 cycles process
GB2096133(A)	EDA Acetic acid Acetic anhydride	Two columnar reactor	Continuous	32%	It doesn't have recipes and the yield is without crystallization
GB1335204(A)	EDA Acetic acid Acetic anhydride	Two reaction vessels	Batch	91%	It only uses 2/5 of DAED
CA974256(A)	DAED Acetic anhydride Ketene	Bubble column	Batch	95.5%	It starts with DAED and uses Ketene
GB1378308(A)	DAED Acetic anhydride	Two reaction vessels with a packed column	Continuous	85.7%	It starts with DAED
US4240980(A)	DAED Acetic anhydride Tonsil (bleaching earth)	Reaction vessel	Batch	97%	It starts with DAED and uses Tonsil Molar ratio DAED:Acetic anhydride = 1:1 to 1:10

4.5. **PATENT SELECTION**

This section details the patent selection process.

The first step is the advantage / disadvantage analysis

The advantage that is shared by almost all is the high yield. The only one that does not comply with this is patent **GB2096133 (A)**. Since TAED quantity should be maximized, a patent with a low yield will not be regarded as acceptable. For this reason patent **GB2096133 (A) is discarded.**

Now, disadvantages are analyzed:

Three of them share the same disadvantage. Patents **CA974256 (A), GB1378308 (A)** and **US4240980 (A)** start with DAED. This is a problem because the manufacturing route has to include two reactions (as it is one of the mandatory requisites explained before). Therefore, in this project, a patent that includes all the reactions of the manufacturing route is required. For this reason, patents **CA974256 (A), GB1378308 (A) and US4240980 (A) are discarded.**

Only two patents remain; **GB2143522 (A)** and **GB1335204 (A).** The last one has another disadvantage; it only uses 2/5 of formed DAED. This is not a good option, because 3/5 of DAED is wasted and it is not used in another place. For this reason, patent **GB1335204 (A) is discarded.**

The only patent left is **GB2143522 (A)**. Before selecting this patent, it must be verified that it meets all the requirements, and consequently, it could be used in the project:

It has the recipe with all the reactions involved (EDA with acetic acid and DAED with acetic anhydride) and, in this way, only acetic anhydride is used in the second reaction, making the process cheaper. Also, TAED yield is high.

This process is satisfactory, but has the disadvantage that it is a batch producer, and as stated in the 'production scale' section, in this project is wanted to work continuously (15 000 t / year). Nevertheless, this is not a problem, because continuous operation can be adapted using recycle streams and purge streams. This is explained and executed in the next section 'synthesis of the process'.

Since this patent meets most of the requisites and the only disadvantage can be adapted to the project needs, the **selected patent is GB2143522 (A)**.

4.6. **GB2143522 (A) RECIPE SUMMARY**

The summary of the patent recipe to be used to scale is written below.

In the first cycle, EDA and acetic acid are mixed at 110ºC and heated to distillation. Water is distilled off and then the last traces of acetic acid are stripped by vacuum.

Acetic anhydride is added and the mixture brought to reflux at 140ºC. A slow distillation at atmospheric pressure is carried out after 30 minutes refluxing. This is to remove the acetic acid formed in the reaction.

Cooling is then applied and the solid formed is filtered off, washed with acetic anhydride and dried. The yield of TAED is 56% based on EDA. The mother liquors separated by filtration are used in the second cycle.

In the second cycle new EDA reacts with new acetic acid and the mix is distilled as before. Then, the mother liquors from the first cycle are added. The mix is refluxed, distilled and filtered to give solid and other mother liquors. The solid is treated as before.

In the third cycle the process described in the second cycle is repeated except that the amount of EDA used is different.

The TAED total yield at the end of the process is 86% overall of EDA.

5. SYNTHESIS OF THE PROCESS

5.1. OPERATING HOURS FOR CONTINUOUS PLANT

In the chemical industry, the maximum production hours per year are 8,760. In discontinuous plants, where the process is in batches and operate during weekend is not common, they operate for 2,000 hours / year or 5,800 hours / year, which is equivalent to 8 hours / day or 24 hours / day respectively. In continuous plants, since there are not practically shutdowns (only for maintenance and occasionally due to problems) and they operate 24 hours a day and also in weekend, the operation annual hours are longer (Skogestad, 2009).

The operating time for a continuous plant is frequently presupposed to be 8000 hours per year, which is the same to an uptime (availability) of 91% or 330 days (Skogestad, 2009). They typically have a 15-30 days annual shutdown for maintenance, which usually concur with holidays.

Therefore, with this information, taking into account that the operating hours for a continuous plant, such as the study case of this work, are 8,000 hours / year and knowing that 1 ton is equivalent to 1,000 kilograms, the production of 15 000 tons / year is the same as **1,875 kg / hour of TAED.**

5.2. SCALE OF THE SELECTED RECIPE

Since this process is continuous (despite the recipe being discontinuous), the ratio between the recipe reactants are used to scale it up to the desired production amount of TAED (1,875 kg / hour). As previously stated, the patent has 3 cycles, which is therefore adapted to a continuous operation using recirculate and purge streams, in order to have an equivalent process.

The data is collected from the first cycle assuming that, by recirculating the mother liquor the yield would be greater than 86%.

In the first cycle of the recipe, 60g (1M) of EDA and 120g (2.66M) of acetic acid are mixed and heated to distillation. Then, 720g (7.05M) of acetic anhydride is added and the mixture brought to reflux.

With this information, the reactants ratio can be calculated:

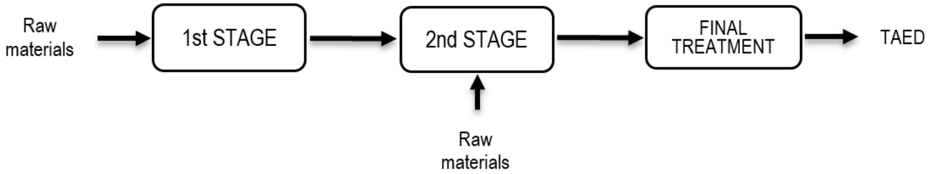
-60g of EDA is used versus 120g of acetic acid, therefore the **EDA:acetic acid ratio is 1:2.**

-If the amount of acetic anhydride used, 720 g, is compared to the amount of acetic acid, 120 g, the **acetic acid:acetic anhydride ratio** is obtained and **is 1:6**.

In the simulation that is carried out in the next section, "sizing of the necessary equipment", the reactant flow rates are uploaded following these ratios, in order to obtain the desired TAED production of 1875 kg / hour.

5.3. **EQUIPMENT SELECTION**

Through the carried out study, the necessary steps to produce TAED at a laboratory level have been learned. To scale the recipe to an industrial process, other appropriate equipment will be selected. The general obtention process of TAED can be divided in three parts, shown in the following scheme:



12. General diagram of TAED's process.

Below, each part is explained:

At the 1st stage, the first reaction is carried out: EDA + 2Acetic Acid => DAED + 2Water.

Therefore two raw materials are introduced by input streams: EDA and acetic acid.

To carry out the reaction a reactor (1) is needed, but it also has to have a distillation column (1) on top to separate the evaporated water and acetic acid. This is because the reaction has to take place at the same time as the distillation to displace the reaction and be able to achieve a high conversion. The column is an enriching column, since the water and acetic acid saturated vapor are fed from the bottom and rise throughout the column. This mixture is condensed and in part is returned to the column as reflux. This reflux is enriched in acetic acid so part of this reactant is returned to the column, while the water is extracted from the top of the column. At the same time, the DAED obtained and the excess of acetic acid that has not condensed are removed.

To finish removing the acetic acid, the mixture has to be taken to another distillation (2). As the difference between the boiling points of DAED and acetic acid is very high, this distillation is practically an evaporation, which is done under vacuum.

In this way remains a mixture with practically only DAED and this mixture is sent to the second stage.

At the 2nd stage, the second reaction is carried out: DAED + 2Acetic Anhydride => TAED + 2Acetic Acid.

Therefore, there is a new input stream of acetic anhydride.

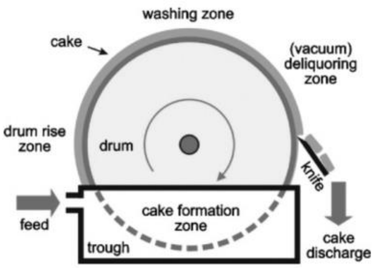
As in the first stage, a reactor (2) is needed where the first stage DAED stream and the new anhydride acid stream are mixed. Another enriching column (3) is needed on top. The reasons are the same, to displace the reaction and a high conversion. Only acetic acid is condensed, so it can be recirculated to the first reactor, supplying much of what is needed to carry out the reaction. At the same time that acetic acid is being extracted on the upper part of the reactor through the column, the TAED formed and the excess of acetic anhydride that has not reacted are removed.

Adding another distillation column was considered in order to eliminate the excess of acetic anhydride, but the boiling points between both products are practically the same. A small amount of anhydride would be removed and there would still be a lot left. Therefore, what comes out of the reactor is separated during the final treatment.

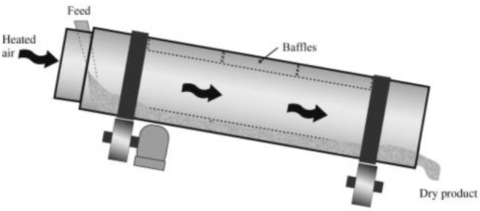
At the final treatment, in order to separate TAED from the mixture, a crystallization of the second reactor product is carried out by cooling it. The stream leaving the crystallizer contains TAED crystals that remain in suspension in the liquid mixture and they form 95% of the liquid TAED that has entered in the crystallizer.

Then, the crystals are filtered in a vacuum drum filter, where the liquid and the solid are aspirated by vacuum. The liquid reaches to the central part of the drum and the solid adheres to the exterior part. The filtrate (liquid), mostly acetic anhydride, is recirculated to the second reactor as mother liquor, along with new acetic anhydride which is used to wash the crystallized TAED, supplying much of the acetic anhydride that is needed in the reactor.

Finally, the solid TAED is dried inside a rotary drum dryer, which is an inclined rotating cylindrical tube, so that the transport of the solid is by gravity.



14. Vacuum drum filter (Sparks, 2016).



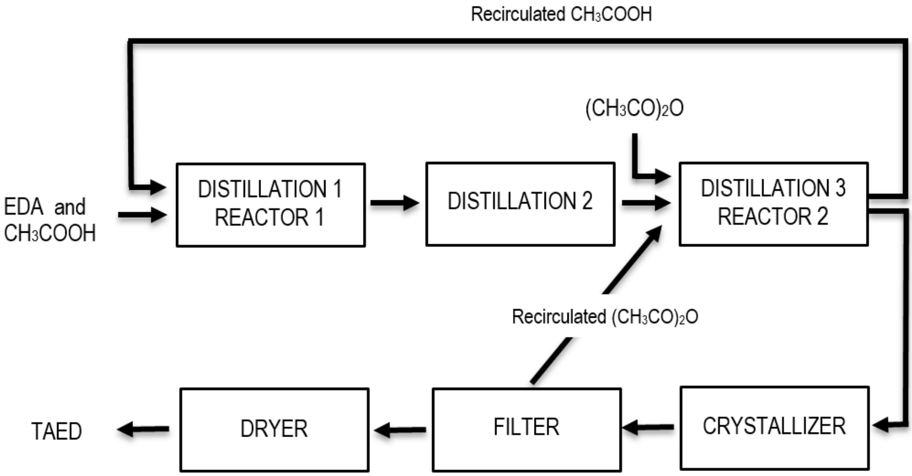
13. Rotary drum dryer (William, 2019).

During the last recirculation, 90% of the filtrate stream is recirculated to avoid the accumulation of impurities, since it not only contains acetic anhydride, but there are residues of DAED, acetic acid and the 5% of TAED that is not possible to crystallize. In order to accomplish this, a purge stream is needed, which extracts 10% of the mix.

However, at the acetic acid recirculation from enriching column 3 to reactor 1, 100% can be recirculated since it comes from the top of the column and it only contains acetic acid.

In this study the steps that belong to the TAED production process are exposed.

The whole process explained before is represented in the next diagram, which contains all the necessary equipment to produce TAED.



15. Equipment diagram of TAED's process.

As a result, the TAED production process needs 8 equipment.

As decided, only some equipment are studied deeply in this work, so sizing all of the equipment is not necessary. The two reactors and the three distillation columns are considered as main equipment and therefore, they will be sized. Crystallization, filtering and drying are outside the scope of this work, therefore they will not be sized.

Below, the details and characteristics of the main equipment are shown.

5.4. **MAIN EQUIPMENT**

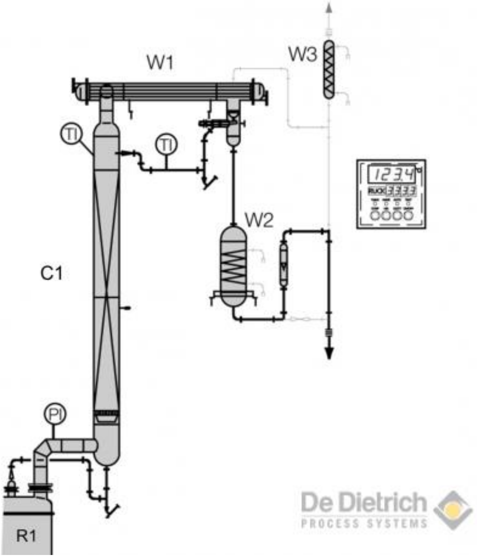
- REACTORS:

In practice, the reaction and distillation processes are executed consecutively in the same equipment, so that the starting materials are subjected to a reaction process and generate the desired products and these products are then separated in a process of distillation.

The equipment is used at atmospheric pressure or under vacuum, usually in batch but also continuously.

There are several design examples for different applications: reflux boiling and distillation with coil exchanger, reflux boiling and distillation with shell and tube exchanger, distillation with phase separation, vacuum distillation and rectification.

This project requires a rectifying column. By using a column with a reflux between the condenser and the reactor it is possible to separate volatile substances with closer boiling points by a mutual rectification process. The height and type of internal column devices are determined according to the specific separation problem and the available height. The reflux is fed to the column above the bed pack. The extracted distillate is cooled and finally is collected by receivers. The ratio between the reflux and the distillate extraction required for the rectification is adjusted using a magnetically controlled reflux divider along with an electronic timer or a process control system (Distillation Equipment for Reactors, n.d.).



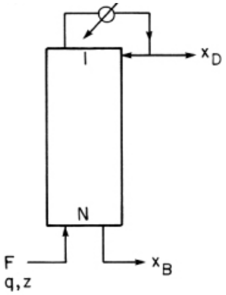
16. Reactor with rectification column (Distillation Equipment for Reactors, n.d.)

- DISTILLATION COLUMNS:

At the distillation stage, vapor from a boiling mixture is richer in the components that have the lowest boiling temperatures. Therefore, when the mixture is condensed, the distillate contains the most volatile components. Also, the main mix contains the less volatile components (Distillation, 1997).

In this work there are two types of columns, which are exposed below:

- Enriching column: At the rectifying or enriching column, the feed is a superheated vapor or a saturated vapor, and the distillate could be extremely pure but the bottoms would not, so they are used when pure bottoms are not needed (Wankat, 2011). These are the case, as mentioned before, of columns 1 and 3.



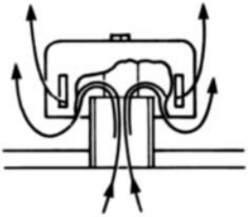
17. Enriching column (Wankat, 2011).

- Vacuum column: Vacuum distillation is a method that is performed at low pressure, below atmospheric pressure. This option is used when the boiling point of the compound is difficult to achieve or there is a possibility of decomposition. If the pressure is lower, the boiling point is also lower.

Distillation columns have several components: a vertical shell, column internals such as trays and packings, a reboiler, a condenser and a reflux drum.

One of the parts that has to be chosen when the column is sized are the trays. For this reason the different tray types are studied to finally choose the most suitable for this work. There are different types designs (Distillation, 1997):

-Bubble cap trays: a bubble cap tray has riser implemented over each perforation and a cover that protect the riser. The cover is set for there to be a space between riser and cover to let the movement of vapor. Vapor ascents through the riser and is sent down by the cover, emitting through apertures in the cover, and finally bubbling through the liquid on the tray.



18. Bubble cap trays (Alireza, 2014).

- Valves trays: in valve trays, holes are closed by liftable covers. Vapor flows raise the covers, forming a flow area for the movement of vapor. The liftable cover sends the vapor to flow horizontally into the liquid, supplying better mixing.
- Sieve trays: are metal plates with perforations in them. Vapor goes directly up through the liquid on the plate. The configuration, number and size of the perforations are design parameters.

The first ones, the bubble cap trays, are the most widely used, and therefore, they are going to be applied in the sizing of the distillation columns.

5.5. **FLOW DIAGRAM**

The following section, 'Sizing of the necessary equipment', details how Aspen Plus software is used to design and size the equipment. As previously stated, it is only used to size the main equipment. For this reason, the flow diagram introduced in the Aspen Plus simulation is not the exact one, as some equipment is missing (crystallizer, filter and dryer). Consequently, it has not been included in this work.

Instead of that, in order to show all the required equipment for the TAED production process, an AutoCAD flow diagram has been used. AutoCAD is a software recognized for its extensive editing capabilities, which makes the digital drawing of all equipment possible and therefore, allows the drawing of all the complete flow diagram.

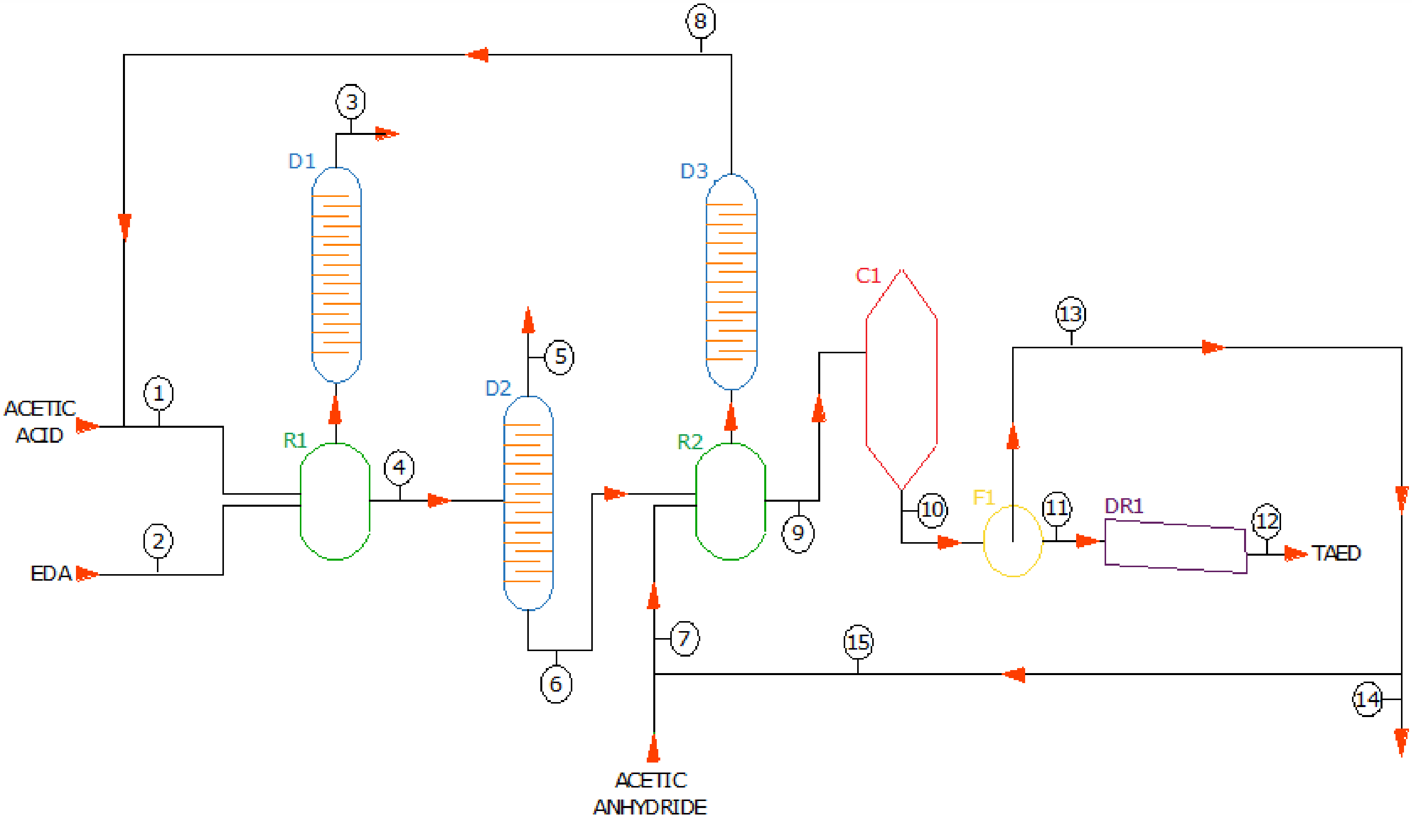
Below, the flow diagram and a table with the mass flow values of each stream, as well as their temperature and pressure, are shown. These mass flows have been obtained from the simulation of Aspen Plus. In order to understand the flow diagram, this table is located on the next page, even though Aspen Plus results are explained in the next section.

The crystallizer and filter mass flows have been calculated knowing that 95% of the incoming TAED is crystallized, and that everything else is recirculated. The temperature of 30 ºC has been taken from the patent. For drying, the amount of TAED does not change.

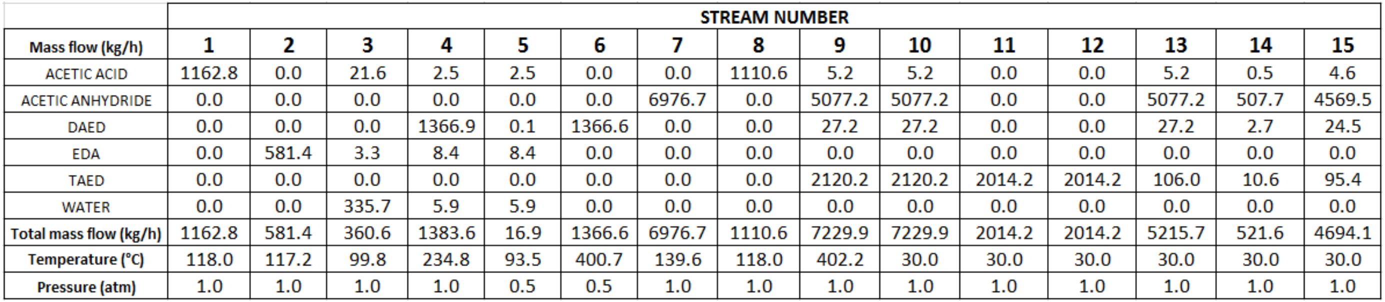
Stream 13, which is the one that is recirculated, is divided in two streams: stream 14 contains 10% of the filtrate mix and thus, stream 15 contains a 90%. In this way, impurities accumulations are reduced.

There are several abbreviations in the flow diagram:

- R1 and R2: reactors.
- D1, D2 and D3: distillation columns.
- C1: crystalizer.
- F1: filter.
- DR1: dryer.



19. *TAED's flow diagram, made with AutoCad.*



	STREAM NUMBER														
Mass flow (kg/h)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
ACETIC ACID	1162.8	0.0	21.6	2.5	2.5	0.0	0.0	1110.6	5.2	5.2	0.0	0.0	5.2	0.5	4.6
ACETIC ANHYDRIDE	0.0	0.0	0.0	0.0	0.0	0.0	6976.7	0.0	5077.2	5077.2	0.0	0.0	5077.2	507.7	4569.5
DAED	0.0	0.0	0.0	1366.9	0.1	1366.6	0.0	0.0	27.2	27.2	0.0	0.0	27.2	2.7	24.5
EDA	0.0	581.4	3.3	8.4	8.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TAED	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2120.2	2120.2	2014.2	2014.2	106.0	10.6	95.4
WATER	0.0	0.0	335.7	5.9	5.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total mass flow (kg/h)	1162.8	581.4	360.6	1383.6	16.9	1366.6	6976.7	1110.6	7229.9	7229.9	2014.2	2014.2	5215.7	521.6	4694.1
Temperature (°C)	118.0	117.2	99.8	234.8	93.5	400.7	139.6	118.0	402.2	30.0	30.0	30.0	30.0	30.0	30.0
Pressure (atm)	1.0	1.0	1.0	1.0	0.5	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

20. Mass flow table.

6. SIZING OF THE MAIN EQUIPMENT

6.1. ASPEN PLUS

As previously stated, one of the work main aims is sizing the necessary equipment. To accomplish it, Aspen Plus software (Advanced System for Process Engineering) is used, which allows simulating the desired process. It is a tool used to analyze and evaluate the process flow diagram, obtaining the properties of the output streams given the input streams, the basic parameters and the operating conditions of the equipment involved.

A summary of the steps that have been followed to implement the simulation of this work is exposed below.

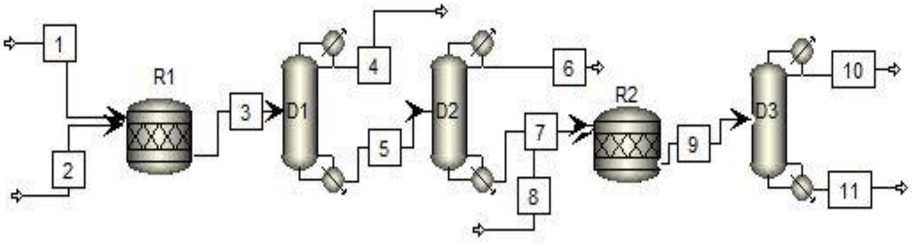
Firstly, all the reaction compounds are uploaded. The program server contains most of them, but if some of them are not found, as TAED and DAED, their known properties have to be uploaded and their molecular structure have to be drawn.

Then, the flow diagram is represented. As stated before, the flow diagram introduced in Aspen Plus software is not the exact one. In the simulation only 5 equipment are entered: the two reactors and the three columns. Crystallization, filtration and drying are not part of the scope of this work. Moreover, they cannot be simulated in Aspen Plus. However, this is not a problem. The software can calculate the streams, properties and operating conditions of the main equipment, since, those equipment that cannot be simulated, are at the end of the process and they do not interfere with the main equipment.

Furthermore, two considerations must be taken into account:

As shown in the next picture, the stream numbers entered in Aspen do not correspond to the numbers in the AutoCAD flow diagram.

The enriching columns (1 and 3) are not positioned on top of each reactor, since this is not possible in the simulation. Despite this, they can be considered equivalent, since they are also fed from the bottom. This is shown in the next point, where the results of each equipment are presented.



21. Aspen flow diagram.

The next step is entering all the feed data. As explained in the previous section, the reactants ratios taken from the patent are used to calculate the necessary feed to obtain 15 000 t / year of TAED. The calculation is made and, as seen in the table of the previous section, the necessary acetic acid is 1162.8 kg / h, the amount of EDA is 581.4 kg / h and the acetic anhydride needed is 6976.7 kg / h. These values follow the ratios of the patent and in this way, the required TAED is obtained.

Finally, the last step is the configuration and optimization of each equipment. In the next point, where the results are exposed, the necessary data that the program needs to calculate the operating conditions and the sizing of each equipment is explained. As well as the steps followed to optimize each of them.

6.2. **EQUIPMENT RESULTS**

- REACTOR (R1)

The reactor 1 objective is to operate at the right temperature and pressure conditions so that the first reaction of TAED production process takes place inside it:

$$\text{EDA} + 2\ \text{Acetic Acid} \rightarrow \text{DAED} + 2\ \text{Water}$$

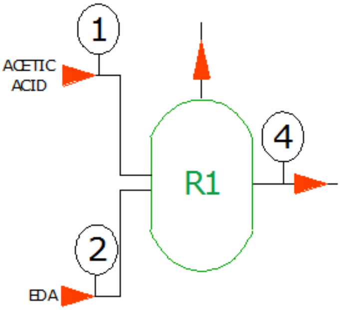
These operating conditions are obtained from the selected patent GB2143522 (A) and are entered in the Aspen Plus simulation to configure the reactor: the temperature is 110 ºC and the reaction takes place at atmospheric pressure.

Two phases are considered in phase equilibrium calculation: vapor and liquid. The reactants enter at liquid phase, and as the reaction is carried out at these operating conditions, a saturated vapor mainly with water and acetic acid is formed, which rises through the enrichment column above the reactor.

About the reactor type, a stoichiometric reactor has been chosen, based on known fractional conversions or extents of reaction. The reason for this choice is that knowing all the kinetic properties of the reaction is not possible and therefore, neither calculating the reactor volume with Aspen Plus simulation is possible. However, the stoichiometric reactor can be simulated only with the definition of the reaction and conversion, without kinetics information.

As in this work the enriching column is on top of the reactor and, because of this, the reaction and distillation take place at the same time, achieving a high conversion is possible. For these reason, it is decided that the products are generated with a 98% fractional conversion of the EDA component.

Once the reaction, the operating conditions and desired conversion have been entered, the reactor can be simulated. As the feed stream data (stream 1 and 2) has already been filed in the previous step, the following reactor results are obtained considering that the reaction takes place at the same time as distillation.



22. Reactor R1 representation, made with autocad.

	STREAM NUMBER		
	1	**2**	**4**
Total mass flow (kg/h)	1162.8	581.4	1383.6
Temperature (°C)	118.0	117.2	234.8
Pressure (atm)	1.0	1.0	1.0

As explained before, the volume of the reactor cannot be calculated with the simulation, since obtaining the kinetic data of the reaction is not possible. For this reason, since the objective is to size the reactor, i.e. knowing its volume, it is calculated approximately with the residence time of the reaction.

This residence time has been searched in different patents and it has been found in patent US4219500 (A), which describes the production of DAED only. In its example number 2, it is stated that there is an EDA addition period of 30 minutes, and it takes 3 hours to carry out the distillation.

As in this work the distillation column is located above the reactor, assuming that the reaction is displaced accordingly as the water is extracted, this distillation time is considered equivalent to the residence time of the reactor, being a total of 3.5 hours.

It must be taken into account that in the patent a mixture of water and excess acetic acid (40%) is extracted in the distillation. However, in this work, only water is extracted since, as it is a rectification, the acetic acid is returned to the reactor. For this reason, the residence time in reactor R1 is somewhat shorter, considering it to be 3 hours.

With this **residence time of 3 hours** and knowing that the sum of the input volumetric flows of stream 1 and 2 (acetic acid and EDA) is 1.9 m^3 / h, an approximate **volume of 5.8 m^3** for reactor R1 is obtained.

- ENRICHING COLUMN (D1)

The objective of the first enriching column is to operate under specific conditions to be able to separate the components of the mixture arriving from reactor R1.

Given the boiling temperatures of this mixture components, 100ºC for water, 118ºC for acetic acid and 439ºC for DAED, as a result of distillation, a distillate stream is obtained practically of water (with a small amount of acetic acid), and a bottom stream of mostly DAED, with the remainder acetic acid that has not been distilled. The temperatures between water and DAED are widely separated from each other, so separating water by distillation is a proper option.

To carry out the simulation in Aspen Plus, the condenser and reboiler type have to be indicated. In this case a total condenser and a kettle reboiler are selected.

Another important feature is the distillate ratio. As all the water is intended to be extracted, a distillate ratio of 0.66 is introduced. This value is equivalent to the molar fraction of water obtained at the end of the reaction. In this way, the extraction of practically all the water is guaranteed.

To size the enriching column, 5 variables are needed: the number of trays, the feed tray, the reflux ratio, the food input and work pressure. The food input is directly obtained from reactor 1 and the column works at 1 atmosphere. The remaining variables are not known, but they are obtained by optimizing the simulation.

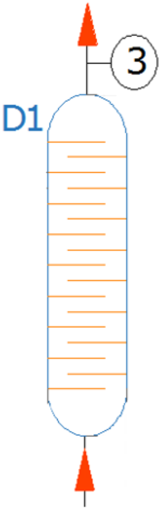
Since it is an enriching column, as it is located just above the reactor so that the reaction and distillation take place at the same time, the feed tray is located in the lower part of the column.

Therefore, this variable does not have to be optimized, since the value entered is equivalent to the number of trays.

Thereby, only the number of trays and the reflux ratio have to be optimized. The optimization has been carried out manually, changing both values until the desired results are obtained: a distillate of practically all the water and a bottom stream of DAED that returns to the reactor. Keeping the number of trays as small as possible has been taken into consideration, so that the costs are lower.

With all these data entered, the diameter of the column can be obtained with the simulation. The only additional indications are the tray type which, as stated before, bubble cap trays are chosen, and the tray spacing. Aspen Plus has the standard value of a separation of 0.6096 meters.

Knowing the number of trays and the distance between them, the height of the column is obtained (considering that there is 1 meter at the bottom of the column below the last tray by flow rate retained).

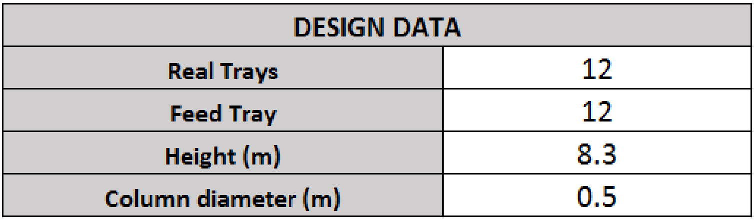


23. Enriching column D1 representation, made with autocad.

It must be taken into account that the number of trays obtained in the simulation is theoretical, since the vapor-liquid equilibrium is not fully achieved in them. To know the real number of trays, an efficiency of 70% is taken, which is the most common value.

With all these information, the following results for the first enriching column are obtained.

Condenser Heat duty (kJ/h)	2 318 765.4
Reboiler Heat duty (kJ/h)	2 672 184.9
OPERATION DATA	
	STREAM 3
Total mass flow (kg/h)	360.6
Temperature (°C)	99.8
Pressure (atm)	1.0
Reflux ratio	2.0
Distillate ratio	0.7



DESIGN DATA	
Real Trays	12
Feed Tray	12
Height (m)	8.3
Column diameter (m)	0.5

DISTILLATION COLUMN (D2)

The objective of the distillation column D2 is to operate under specific conditions to be able to separate the components that could not be extracted in the enriching column (D1). This is because a bottom stream with only DAED component is needed, to send it to the second reactor.

The feed stream to the column is stream number 4. As it can be seen in this stream, which comes from reactor R1, there are remains of acetic acid, EDA and water. Therefore, they have to be extracted in their entirety in this column to separate them from DAED.

As the difference between the boiling points of DAED and the other components is very high, this distillation is practically an evaporation, and it is done under vacuum.

As opposed to the first column, this is not an enriching one, since there is no need to have a reaction and distillation at the same time. For this reason, the feed tray is not located in the lower part of the column, but will be in the central part instead.

Despite this difference, the data required to simulate the distillation column D2 is very similar:

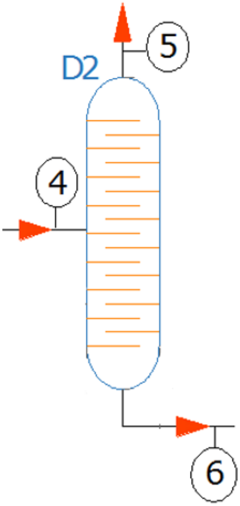
This column also has a total condenser and a kettle reboiler.

The distillate ratio value is 0.05, which is equivalent to the total molar fraction of EDA, acetic acid and water entering the column. This ensures their total extraction.

As mentioned before, the food input is stream 4, which comes from the first reactor. And the column works under vacuum at a pressure of 0.5 atmospheres.

Since it is not an enriching column, the feed tray is not known. Therefore, in this distillation 3 variables are optimized: the number of trays, the feed tray and the reflux ratio. As in the previous case, the optimization is done manually until the desired results are obtained: a bottom stream of DAED and a distillate with all the other components. The optimization is made with the objective of having the least number of trays.

This column also uses bubble cap tray type and the tray spacing is 0.6096 meters. As stated before, with this additional information the simulation can calculate the column diameter. With the distance between trays and using the same efficiency of 70%, the column height is known.



24. Distillation column D2 representation, made with autocad.

With all these data entered, the following results for the distillation column D2 are obtained.

Condenser Heat duty (kJ/h)	74 508.2		
Reboiler Heat duty (kJ/h)	626 266.1		
OPERATION DATA			
	STREAM 4	**STREAM 5**	**STREAM 6**
Total mass flow (kg/h)	1383.6	16.9	1366.6
Temperature (°C)	234.8	93.5	400.7
Pressure (atm)	1.0	0.5	0.5
Reflux ratio	2.0		
Distillate ratio	0.1		
DESIGN DATA			
Real Trays	9		
Feed Tray	5		
Height (m)	6.5		
Column diameter (m)	0.4		

- REACTOR (R2)

The reactor R2 objective is to operate at the right conditions so that the second reaction of the TAED production process takes place inside of it:

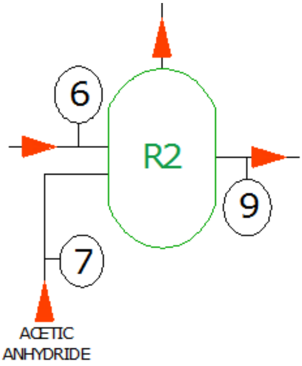
$$DAED + 2\ Acetic\ Anhydride \rightarrow TAED + 2\ Acetic\ Acid$$

As reactor R1, these operating conditions are earned from the selected patent GB2143522 (A): the reaction takes place at 140 ºC and at atmospheric pressure.

Also, two phases, liquid and vapor, are considered. The stream 6 coming from the previous equipment (distillation column D2) and the new acetic anhydride feed stream (stream 7) are in liquid phase, while the acetic acid product is got as saturated vapor that rises through the enrichment column of this reactor.

As in the previous case, it is a stoichiometric reactor, which can be simulated with the definition of the reaction and conversion only, and since this reaction also takes place at the same time as the distillation, high conversions of 98% can be achieved.

With all this information entered, the results are as follows.



25. Reactor R2 representation, made with autocad.

	STREAM NUMBER		
	6	**7**	**9**
Total mass flow (kg/h)	1366.6	6976.7	7229.9
Temperature (°C)	400.7	139.6	402.2
Pressure (atm)	0.5	1.0	1.0

As reactor R1, the rector R2 volume is calculated approximately with the residence time of the reaction, since it cannot be calculated in the simulation as no kinetic data of the reaction is known.

This residence time has been searched in different patents and it has been found in patent GB1335204 (A). In this patent, in Example II it is stated that it takes 4 hours to extract the acetic acid. As it is considered that the reaction is displaced according as the acetic acid is extracted, this distillation time is considered equivalent to the residence time of the reactor R2, being 4 hours.

With this **residence time of 4 hours** and knowing that the sum of the input volumetric flows of stream 6 and 7 is 9.4 m^3 / h, an approximate **volume of 37.6m^3** for reactor R2 is obtained.

• ENRICHING COLUMN (D3)

The last equipment to size is the enriching column D3. The objective of the second enriching column D3 is to operate under specific conditions to separate the components of the mixture that arrives from reactor R2.

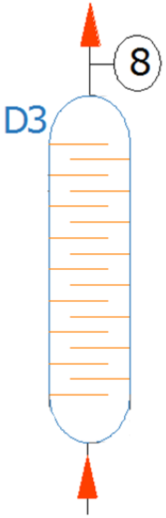
Since TAED is intended to be obtained as a final product, this distillation aims to separate the maximum possible components that are generated in the reaction.

The main components of the mixture that rise through this column are the products acetic acid and TAED and the reactant acetic anhydride excess, whose boiling temperatures are respectively 118ºC, 140ºC and 139ºC. As can be seen, the boiling points between acetic anhydride and TAED are similar so therefore, acetic anhydride is difficult to separate in the distillation and will come out almost entirely by the bottom stream together with TAED. As only TAED is wanted as a product, the acetic anhydride will be separated later by a cooling crystallization equipment and its subsequent filtration, and it may be recirculated to the reactor R2.

Accordingly, in this distillation only acetic acid is removed. Being the only distilled component, it has the advantage of being able to be recirculated to the first reactor as a reactant, supplying much of what is needed to carry out the first reaction. This means that in the entire TAED production process, only water is a by-product.

To perform the simulation, the required data is the same as the first enriching column. The only different value is the distillate ratio, which is 0.24, being equivalent to the molar fraction of acetic acid that there is at the end of the reaction.

Having followed the same steps and optimizing the number of trays and the reflux ratio (the feed stream is not optimized since it corresponds to the last tray), the enriching column D3 is simulated and the following results are obtained.



26. Enriching column D3 representation, made with autocad.

Condenser Heat duty (kJ/h)	1 774 633.8
Reboiler Heat duty (kJ/h)	8 249 937.0
OPERATION DATA	
	STREAM 8
Total mass flow (kg/h)	1110.6
Temperature (°C)	118.0
Pressure (atm)	1.0
Reflux ratio	3.0
Distillate ratio	0.2
DESIGN DATA	
Real Trays	17
Feed Tray	17
Height (m)	11.4
Column diameter (m)	0.8

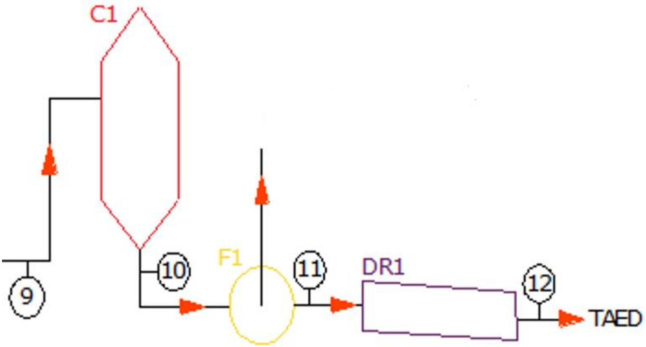
6.3. **FINAL TAED PRODUCTION**

As explained before, TAED is formed as a product of the second reaction in reactor R2, and leaves it by stream 9. As in the last distillation only acetic acid can be separated, in this stream there is not only TAED, but there are other components. The main remaining component is acetic anhydride which, due to its similar boiling temperature with TAED, cannot be separated by distillation. Exactly, through stream 9 comes out 5,077 kg / hour of acetic anhydride, small remains of other components and 2,120 kg / hour of TAED.

In order to separate TAED from the acetic anhydride, a crystallization by cooling at 30ºC is used. In this equipment, 95% of the TAED that comes from stream 9 crystallizes, and the rest of the components remain in liquid phase. The stream 10 leaving the crystallizer contains 2,014 kg / hour of TAED crystals that remain in suspension in the liquid mixture.

This stream 10 goes to a rotary vacuum drum filter, where the solid TAED is separated from the liquid mixture, which is recirculated towards the reactor R2 since it can contribute a large amount of acetic anhydride. Finally, the TAED crystals go, by stream 11, through a rotary drum dryer to remove the remaining moisture.

Therefore, 2,120 kg / hour of TAED are produced in the reactor, and when passing through the crystallizer they are reduced by 5%, to 2,014 kg / hour. This is the quantity that is extracted by stream 12 as final product.



27. TAED final treatment, made with autocad.

In the 'Production Scale' section, it was decided, for this work, to produce a quantity of TAED of 15 000 tons / year, which being a continuous process, are equivalent to 1,875 kg / hour of TAED. As can be seen, once the simulation of the entire production process of TAED has been carried out, a similar amount is obtained, but slightly higher. **In this simulation, 2,014 kg / hour are produced which is equivalent to 16 000 tons / year of TAED**. These 1,000 tons / year more are considered as overdesign.

6.4. **SELECTION OF SPECIFIC EQUIPMENT UNITS**

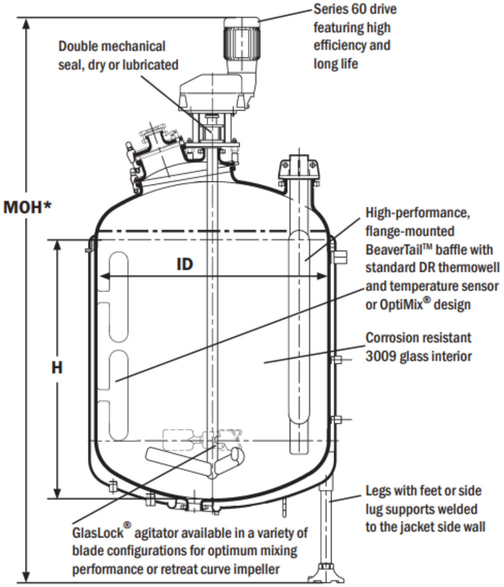
Once the equipment have been decided by simulation, they must be selected from suppliers. In this last section, the equipment involved in the TAED production process are searched in different catalogues of several companies, in order to select the ones that best suit in this work. Analyzing the suppliers' catalogs, those equipment that meet the characteristics stated in the simulation are selected, so concrete equipment can be specified. The companies selected to supply each equipment and the specific equipment units are listed below.

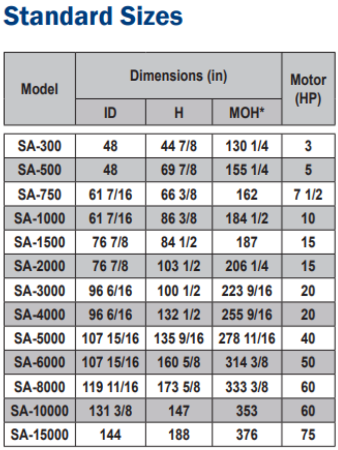
- REACTORS

De Dietrich Process Systems offers glass-lined reactors, which have been the focus of chemical operations for a long time. They have a robust design and are built to withstand very hostile conditions. Vessels are built following the ASME code and they are lined on the inside with patented 3009 Glass, which has benefits such as very good resistance to corrosion, mechanical resistance to blows and abrasions, etc (Glass-Lined Vessels Catalogue).

Within this section of reactors, the most suitable for this project would be SA Reactors. Among the most outstanding features are; robust reactors with large cap that enables installation and removal of one piece agitators, the narrow gap of the annular jacket allows it to heat up and cool down quickly, GlasLock® agitator standard, without plugs, volumes from 1 to 95 m^3, total vacuum pressures up to 7 atm, temperatures from -30 ° C to 260 ° C and different jacket options (Glass-Lined Vessels Catalogue).

Following the standardized size of the SA reactors that the company manufactures, select the **SA-1500** and **SA-10000** reactors is convenient for this project, which have the approximate working volume of R1 and R2 reactors, 5.8 m3 and 37.6 m3 respectively.





Standard Sizes

Model	Dimensions (in)			Motor (HP)
	ID	H	MOH*	
SA-300	48	44 7/8	130 1/4	3
SA-500	48	69 7/8	155 1/4	5
SA-750	61 7/16	66 3/8	162	7 1/2
SA-1000	61 7/16	86 3/8	184 1/2	10
SA-1500	76 7/8	84 1/2	187	15
SA-2000	76 7/8	103 1/2	206 1/4	15
SA-3000	96 6/16	100 1/2	223 9/16	20
SA-4000	96 6/16	132 1/2	255 9/16	20
SA-5000	107 15/16	135 9/16	278 11/16	40
SA-6000	107 15/16	160 5/8	314 3/8	50
SA-8000	119 11/16	173 5/8	333 3/8	60
SA-10000	131 3/8	147	353	60
SA-15000	144	188	376	75

28. Drawing represents a SA-2000 reactor (Glass-Lined Vessels Catalogue).

- COLUMNS

The *Bachiller* company designs and builds custom columns and towers, in accordance with the main mechanical design codes, using the most modern design software and in accordance with the client's particular specifications. They build columns up to a weight of 130 t, with diameters from 200mm to 7,500mm, maximum height of 50 000mm and thicknesses from 3mm to 50mm. In addition, they manufacture the internals (stages, rings ...), the support of the column, inserted tubular bundles, among other characteristics. Their usual applications are: Distillation, Evaporation, Fractionation, Oxidation, Purification, Regeneration, catalytic, Rectification and Separation (Columns and Towers Catalogue).

Therefore, this company is considered suitable to carry out the custom construction of columns D1, D2 and D3. The construction of the following columns, all of them with bubble cap trays, is requested :

-A column (D1), with a diameter of 500mm, a height of 8,300mm, 12 trays and that is fed by tray number 12.

-A column (D2), with a diameter of 400mm, a height of 6,500mm, 9 trays and that is fed by tray number 5.

-A column (D3), with a diameter of 800mm, a height of 11 400mm, 17 trays and that is fed by tray number 17.

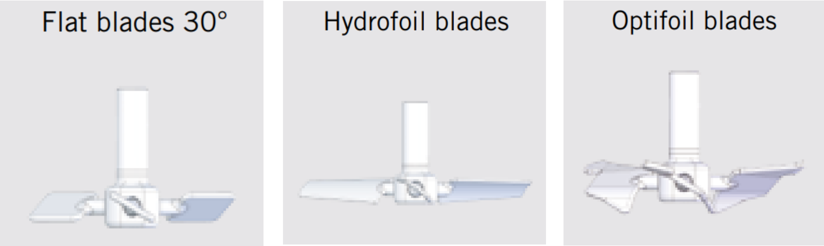
29. Distillation column (Columns and Towers Catalogue).

The remaining three equipment, being the crystallizer, the filter and the dryer, have not been sized as it was decided that they were outside the scope of this project. Despite this, the type of equipment is selected, searching possible suppliers to complete the TAED production process.

- CRYSTALIZER

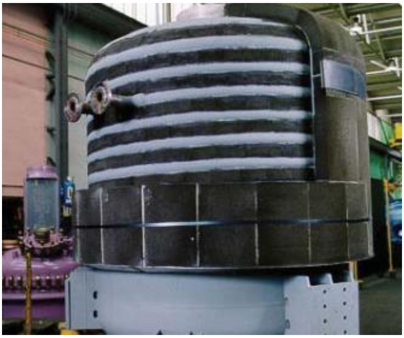
For the crystallization by cooling, it can be done in a similar reactor to those selected in the company *De Dietrich Process Systems*, the SA reactor. Except that the agitator has to be different and the cooling could be done by means of a split jacket that alternates cooling and heating to avoid deposition on the walls.

As in the table found in 'Appendices 3' can be seen, the type of agitator could be: Flat blades 30º, Hydrofoil blades or Optifoil blades. These three are removable agitators with the GlasLock® system (as SA reactor) and are perfectly suitable with fragile particle crystallization (Agitators Catalogue).


Flat blades 30° Hydrofoil blades Optifoil blades

30. Agitators perfectly suitable with crystallization (Agitators Catalogue).

A good option for the jacket could be the HemiCoil® jacketed, that is produced with splitcoil jackets to provide effective heating and cooling of reactor contents. It has the advantage that the film coefficients and heat transfer rates are higher than in common jackets. HemiCoil is available in the selected reactor, being part of the CSA series that uses a standard DDPS Type SA reactor for the vessel (HemiCoil Jacketed Catalogue).



31. HemiCoil® jacketed (HemiCoil Jacketed Catalogue)

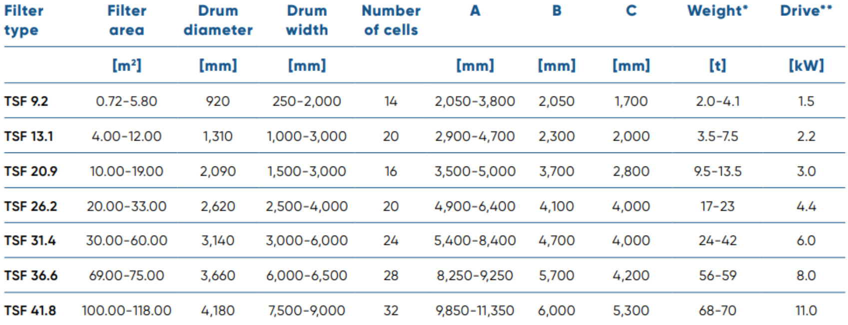
- FILTER

Andritz Engineered Success company manufactures vacuum drum filters, that are the most frequently used in continuous process. The liquid and the solid are aspirated by vacuum and then, the liquid reaches to the central part of the drum and the solid adheres to the exterior part.

The Krauss-Maffei vacuum drum filter TSF is a type of filter of the *Andritz* company that operates continuously, can have a filter area of 0.72 to 118 m^2, a filtration capacity of 100 to 2,000 $l / m^2 h$ and can withstand temperatures of more than 95ºC, between other features. Due to the specially designed pendulum agitator from *Andritz Separation*, sedimentation of the solids is avoided (Separation Catalogue).

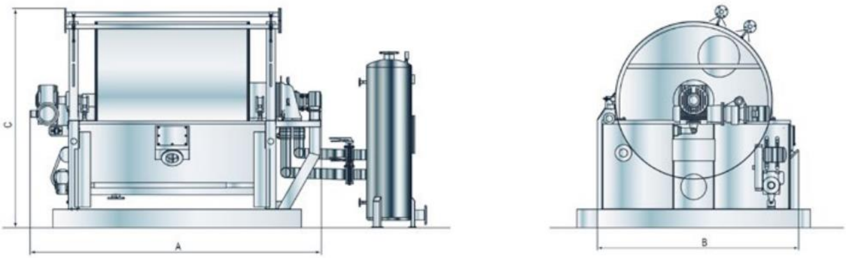
Although the filter has not been dimensioned in this project, one way to select one is with the filter area. If a filtration capacity of 300 kg / h m^2 is assumed and with the solid TAED flow rate of 2,014 kg / hour (stream 11), the necessary filter area of 6.7 m^2 is determined.

With this information and with the table 32 provided by the *Andritz* catalogue, a Krauss-Maffei vacuum drum filter TSF, type **TSF 13.1**, is selected for this project.



Filter type	Filter area	Drum diameter	Drum width	Number of cells	A	B	C	Weight*	Drive**
	[m²]	[mm]	[mm]		[mm]	[mm]	[mm]	[t]	[kW]
TSF 9.2	0.72-5.80	920	250-2,000	14	2,050-3,800	2,050	1,700	2.0-4.1	1.5
TSF 13.1	4.00-12.00	1,310	1,000-3,000	20	2,900-4,700	2,300	2,000	3.5-7.5	2.2
TSF 20.9	10.00-19.00	2,090	1,500-3,000	16	3,500-5,000	3,700	2,800	9.5-13.5	3.0
TSF 26.2	20.00-33.00	2,620	2,500-4,000	20	4,900-6,400	4,100	4,000	17-23	4.4
TSF 31.4	30.00-60.00	3,140	3,000-6,000	24	5,400-8,400	4,700	4,000	24-42	6.0
TSF 36.6	69.00-75.00	3,660	6,000-6,500	28	8,250-9,250	5,700	4,200	56-59	8.0
TSF 41.8	100.00-118.00	4,180	7,500-9,000	32	9,850-11,350	6,000	5,300	68-70	11.0

32. Vaccum drum filters technical data (Separation Catalogue)



33. Krauss-Maffei vaccum drum filter TSF (Separation Catalogue)

- DRYER

By last, the Direct Industry website has been used to search several rotary drum dryers supply companies. This dryer could be selected in companies such as *Andritz*, *General Kinematics, Tianli Energy*, among others.

The rotary drum dryer is a cylinder that is slightly inclined. The material is added from the top end and as the cylinder rotates, the material runs to the bottom end. Dryers can be designed using various drying technologies, including direct drying in counter-current or upstream flow, or indirect drying, using external heat applied to the exterior of the drum casing (Rotary Dryer Equipment Catalogue).

34. Draw from a rotary drum dryer (Rotary Dryer Equipment Catalogue)

With all this information, selecting specific equipment within those that appear in the catalogues of the different companies has been possible, so that the production process of 15000 tons / year of TAED performed in the simulation, can be carried out in a real industrial situation.

7. CONCLUSIONS

In this work, a process for the manufacture of TAED has been developed and its basic engineering has been designed. For this, the following tasks have been performed.

Taking into account the production volume of the global companies that manufacture TAED, an annual production of 15 000 tons / year has been selected, which corresponds to 15% of annual worldwide TAED production. As it is a large production, a continuous process is considered.

Through a patents study, a manufacturing recipe has been selected in which two reactions take place to produce TAED by crystallization. EDA reacts with acetic acid to form DAED and then DAED is converted into TAED by reaction with acetic anhydride.

From the recipe, an industrial production process has been synthesized in which all the necessary equipment to carry out the production of TAED has been selected.

Through simulation by Aspen Plus, the operating conditions and basic dimensions of the main equipment have been determined.

By means of analysis of supplier catalogues, specific equipment has been selected for those dimensioned in the simulation, and the type and different suppliers for the rest of the equipment have been proposed.

As a result, the plant consists of a 5.8m^3 reactor with a 12 tray enriching column, another distillation column that works under vacuum with 9 trays, a second 37.6m^3 reactor with a 17 tray enriching column, a crystallizer by cooling, a vacuum drum filter and a rotary drum dryer.

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Catalogs

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Columns and Towers Catalogue, from *Bachiller.*

Glass-Lined Vessels Catalogue, from *De Dietrich Process Systems.*

HemiCoil Jacketed Catalogue, from *De Dietrich Process Systems.*

Rotary Dryer Equipment Catalogue, from *General Kinematics.*

Separation Catalogue, from *Andritz Engineered Success.*

ACRONYMS

Aspen: Advanced System for Process Engineering

atm: Standard atmosphere

AutoCAD: Computer Aided Design

ºC: Celsius

C1: Crystallizer

CH_3COOH: Acetic acid

$(CH_3CO)_2O$: Acetic anhydride

C_2H_2O: Ketene

$C_2H_8N_2$: Ethylenediamine

$C_6H_{12}N_2O_2$: Diacetylethylenediamine

$C_{10}H_{16}O_4N_2$: Tetraacetylethylenediamine

D1: Enriching column

D2: Distillation column

D3: Enriching column

DR1: Dryer

DADHT: Diacetyldioxohexahydrotriazine

DAED: Diacetylethylenediamine

EDA: Ethylenediamine

F1: Filter

g: Gram

H_2O_2: Hydrogen peroxide

H_2O: Water

h: Hours

kg: Kilogram

kJ: Kilojoule

L: Leaving group

M: Molar

m: Meter

mm: Millimeter

PAA: Peracetic acid

RCO^-: Acyl group

R1: Reactor

R2: Reactor

t: Ton

TAED: Tetraacetylethylenediamine

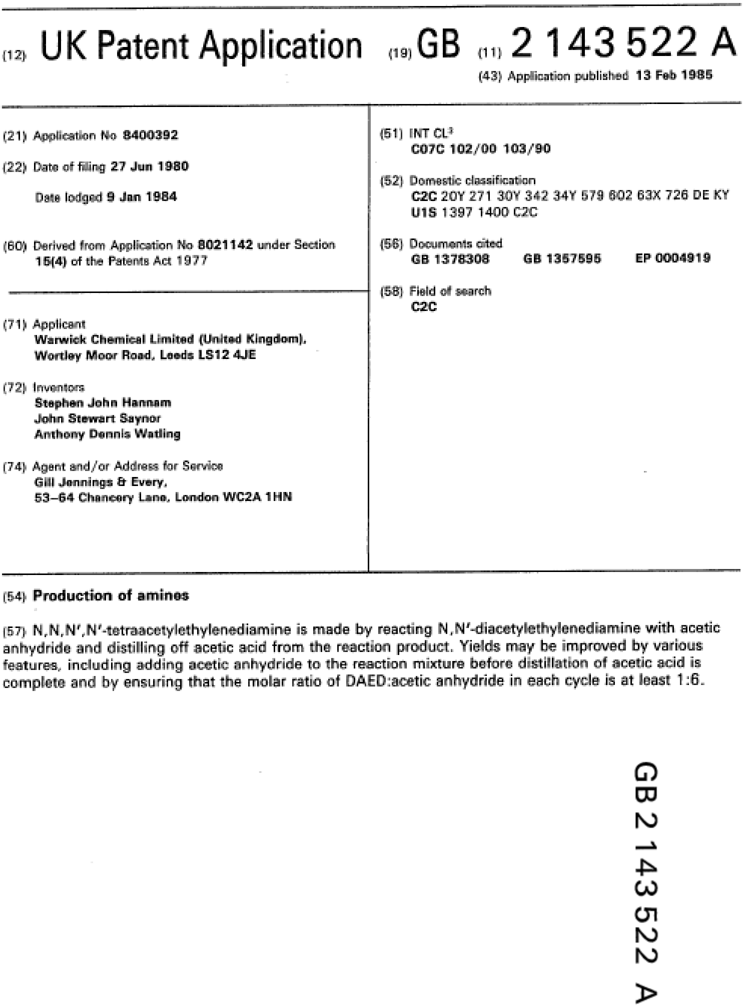
TAGU: Tetraacetylglycoliril

TriAED: Triacetylethylenediamine

y: Year

APPENDICES

APPENDIX 1: SELECTED PATENT GB2143522A



(12) UK Patent Application (19) GB (11) 2 143 522 A

(43) Application published 13 Feb 1985

(21) Application No **8400392**

(22) Date of filing **27 Jun 1980**

Date lodged **9 Jan 1984**

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(51) INT CL^3
C07C 102/00 103/90

(52) Domestic classification
C2C 20Y 271 30Y 342 34Y 579 602 63X 726 DE KY
U1S 1397 1400 C2C

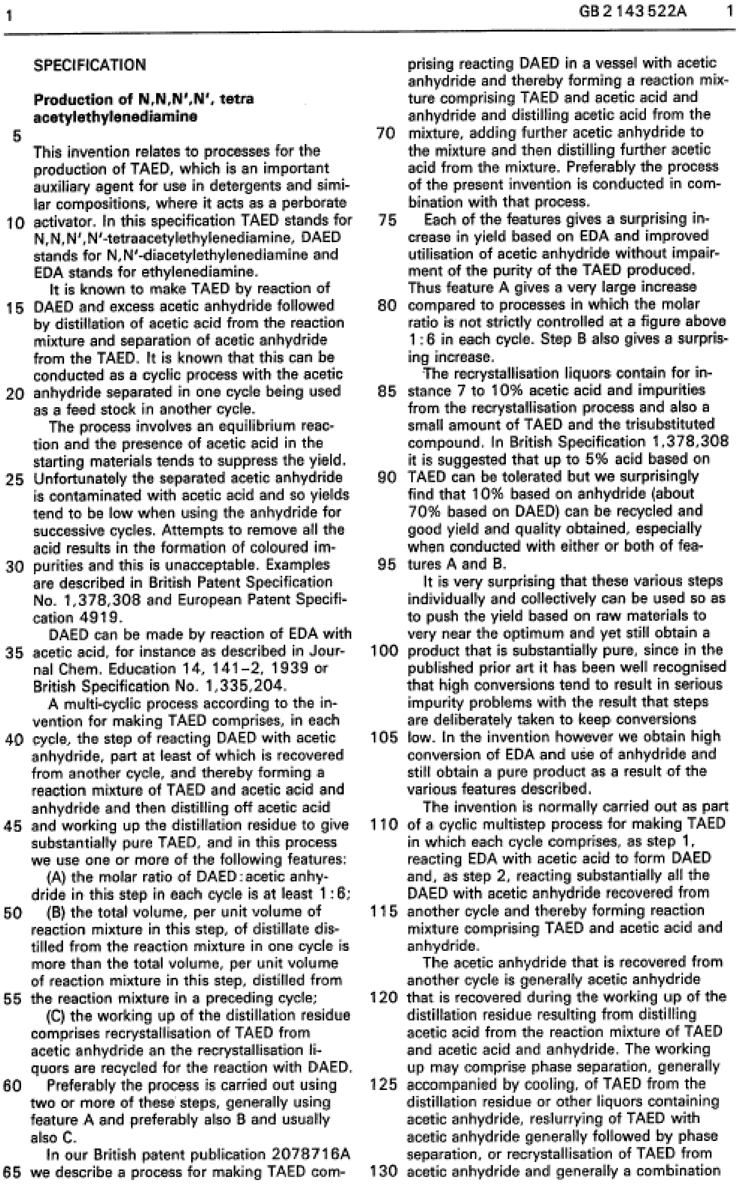
(56) Documents cited
GB 1378308 **GB 1357595** **EP 0004919**

(58) Field of search
C2C

(54) **Production of amines**

(57) N,N,N′,N′-tetraacetylethylenediamine is made by reacting N,N′-diacetylethylenediamine with acetic anhydride and distilling off acetic acid from the reaction product. Yields may be improved by various features, including adding acetic anhydride to the reaction mixture before distillation of acetic acid is complete and by ensuring that the molar ratio of DAED:acetic anhydride in each cycle is at least 1:6.

GB 2 143 522 A



SPECIFICATION

Production of N,N,N',N', tetra acetylethylenediamine

This invention relates to processes for the production of TAED, which is an important auxiliary agent for use in detergents and similar compositions, where it acts as a perborate activator. In this specification TAED stands for N,N,N',N'-tetraacetylethylenediamine, DAED stands for N,N'-diacetylethylenediamine and EDA stands for ethylenediamine.

It is known to make TAED by reaction of DAED and excess acetic anhydride followed by distillation of acetic acid from the reaction mixture and separation of acetic anhydride from the TAED. It is known that this can be conducted as a cyclic process with the acetic anhydride separated in one cycle being used as a feed stock in another cycle.

The process involves an equilibrium reaction and the presence of acetic acid in the starting materials tends to suppress the yield. Unfortunately the separated acetic anhydride is contaminated with acetic acid and so yields tend to be low when using the anhydride for successive cycles. Attempts to remove all the acid results in the formation of coloured impurities and this is unacceptable. Examples are described in British Patent Specification No. 1,378,308 and European Patent Specification 4919.

DAED can be made by reaction of EDA with acetic acid, for instance as described in Journal Chem. Education 14, 141–2, 1939 or British Specification No. 1,335,204.

A multi-cyclic process according to the invention for making TAED comprises, in each cycle, the step of reacting DAED with acetic anhydride, part at least of which is recovered from another cycle, and thereby forming a reaction mixture of TAED and acetic acid and anhydride and then distilling off acetic acid and working up the distillation residue to give substantially pure TAED, and in this process we use one or more of the following features:

(A) the molar ratio of DAED:acetic anhydride in this step in each cycle is at least 1:6;

(B) the total volume, per unit volume of reaction mixture in this step, of distillate distilled from the reaction mixture in one cycle is more than the total volume, per unit volume of reaction mixture in this step, distilled from the reaction mixture in a preceding cycle;

(C) the working up of the distillation residue comprises recrystallisation of TAED from acetic anhydride an the recrystallisation liquors are recycled for the reaction with DAED.

Preferably the process is carried out using two or more of these steps, generally using feature A and preferably also B and usually also C.

In our British patent publication 2078716A we describe a process for making TAED comprising reacting DAED in a vessel with acetic anhydride and thereby forming a reaction mixture comprising TAED and acetic acid and anhydride and distilling acetic acid from the mixture, adding further acetic anhydride to the mixture and then distilling further acetic acid from the mixture. Preferably the process of the present invention is conducted in combination with that process.

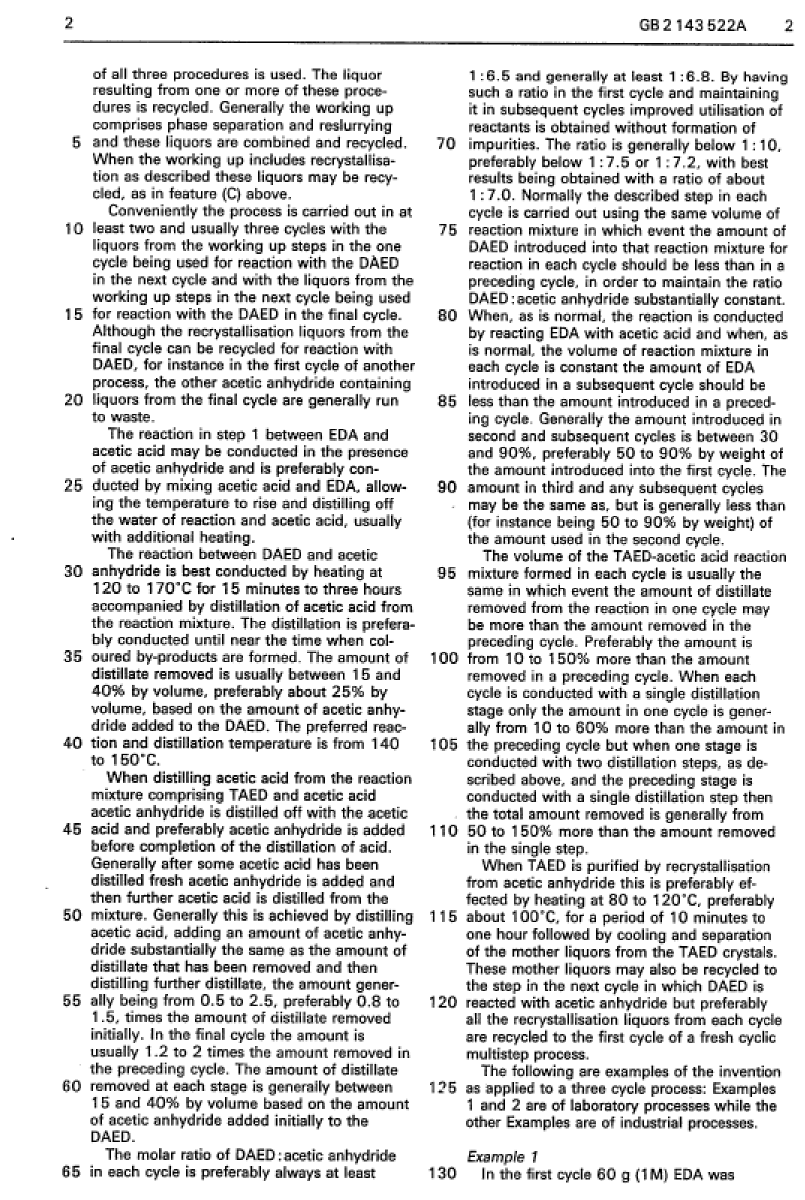
Each of the features gives a surprising increase in yield based on EDA and improved utilisation of acetic anhydride without impairment of the purity of the TAED produced. Thus feature A gives a very large increase compared to processes in which the molar ratio is not strictly controlled at a figure above 1:6 in each cycle. Step B also gives a surprising increase.

The recrystallisation liquors contain for instance 7 to 10% acetic acid and impurities from the recrystallisation process and also a small amount of TAED and the trisubstituted compound. In British Specification 1,378,308 it is suggested that up to 5% acid based on TAED can be tolerated but we surprisingly find that 10% based on anhydride (about 70% based on DAED) can be recycled and good yield and quality obtained, especially when conducted with either or both of features A and B.

It is very surprising that these various steps individually and collectively can be used so as to push the yield based on raw materials to very near the optimum and yet still obtain a product that is substantially pure, since in the published prior art it has been well recognised that high conversions tend to result in serious impurity problems with the result that steps are deliberately taken to keep conversions low. In the invention however we obtain high conversion of EDA and use of anhydride and still obtain a pure product as a result of the various features described.

The invention is normally carried out as part of a cyclic multistep process for making TAED in which each cycle comprises, as step 1, reacting EDA with acetic acid to form DAED and, as step 2, reacting substantially all the DAED with acetic anhydride recovered from another cycle and thereby forming reaction mixture comprising TAED and acetic acid and anhydride.

The acetic anhydride that is recovered from another cycle is generally acetic anhydride that is recovered during the working up of the distillation residue resulting from distilling acetic acid from the reaction mixture of TAED and acetic acid and anhydride. The working up may comprise phase separation, generally accompanied by cooling, of TAED from the distillation residue or other liquors containing acetic anhydride, reslurrying of TAED with acetic anhydride generally followed by phase separation, or recrystallisation of TAED from acetic anhydride and generally a combination



of all three procedures is used. The liquor resulting from one or more of these procedures is recycled. Generally the working up comprises phase separation and reslurrying and these liquors are combined and recycled. When the working up includes recrystallisation as described these liquors may be recycled, as in feature (C) above.

Conveniently the process is carried out in at least two and usually three cycles with the liquors from the working up steps in the one cycle being used for reaction with the DAED in the next cycle and with the liquors from the working up steps in the next cycle being used for reaction with the DAED in the final cycle. Although the recrystallisation liquors from the final cycle can be recycled for reaction with DAED, for instance in the first cycle of another process, the other acetic anhydride containing liquors from the final cycle are generally run to waste.

The reaction in step 1 between EDA and acetic acid may be conducted in the presence of acetic anhydride and is preferably conducted by mixing acetic acid and EDA, allowing the temperature to rise and distilling off the water of reaction and acetic acid, usually with additional heating.

The reaction between DAED and acetic anhydride is best conducted by heating at 120 to 170°C for 15 minutes to three hours accompanied by distillation of acetic acid from the reaction mixture. The distillation is preferably conducted until near the time when coloured by-products are formed. The amount of distillate removed is usually between 15 and 40% by volume, preferably about 25% by volume, based on the amount of acetic anhydride added to the DAED. The preferred reaction and distillation temperature is from 140 to 150°C.

When distilling acetic acid from the reaction mixture comprising TAED and acetic acid acetic anhydride is distilled off with the acetic acid and preferably acetic anhydride is added before completion of the distillation of acid. Generally after some acetic acid has been distilled fresh acetic anhydride is added and then further acetic acid is distilled from the mixture. Generally this is achieved by distilling acetic acid, adding an amount of acetic anhydride substantially the same as the amount of distillate that has been removed and then distilling further distillate, the amount generally being from 0.5 to 2.5, preferably 0.8 to 1.5, times the amount of distillate removed initially. In the final cycle the amount is usually 1.2 to 2 times the amount removed in the preceding cycle. The amount of distillate removed at each stage is generally between 15 and 40% by volume based on the amount of acetic anhydride added initially to the DAED.

The molar ratio of DAED : acetic anhydride in each cycle is preferably always at least 1 : 6.5 and generally at least 1 : 6.8. By having such a ratio in the first cycle and maintaining it in subsequent cycles improved utilisation of reactants is obtained without formation of impurities. The ratio is generally below 1 : 10, preferably below 1 : 7.5 or 1 : 7.2, with best results being obtained with a ratio of about 1 : 7.0. Normally the described step in each cycle is carried out using the same volume of reaction mixture in which event the amount of DAED introduced into that reaction mixture for reaction in each cycle should be less than in a preceding cycle, in order to maintain the ratio DAED : acetic anhydride substantially constant. When, as is normal, the reaction is conducted by reacting EDA with acetic acid and when, as is normal, the volume of reaction mixture in each cycle is constant the amount of EDA introduced in a subsequent cycle should be less than the amount introduced in a preceding cycle. Generally the amount introduced in second and subsequent cycles is between 30 and 90%, preferably 50 to 90% by weight of the amount introduced into the first cycle. The amount in third and any subsequent cycles may be the same as, but is generally less than (for instance being 50 to 90% by weight) of the amount used in the second cycle.

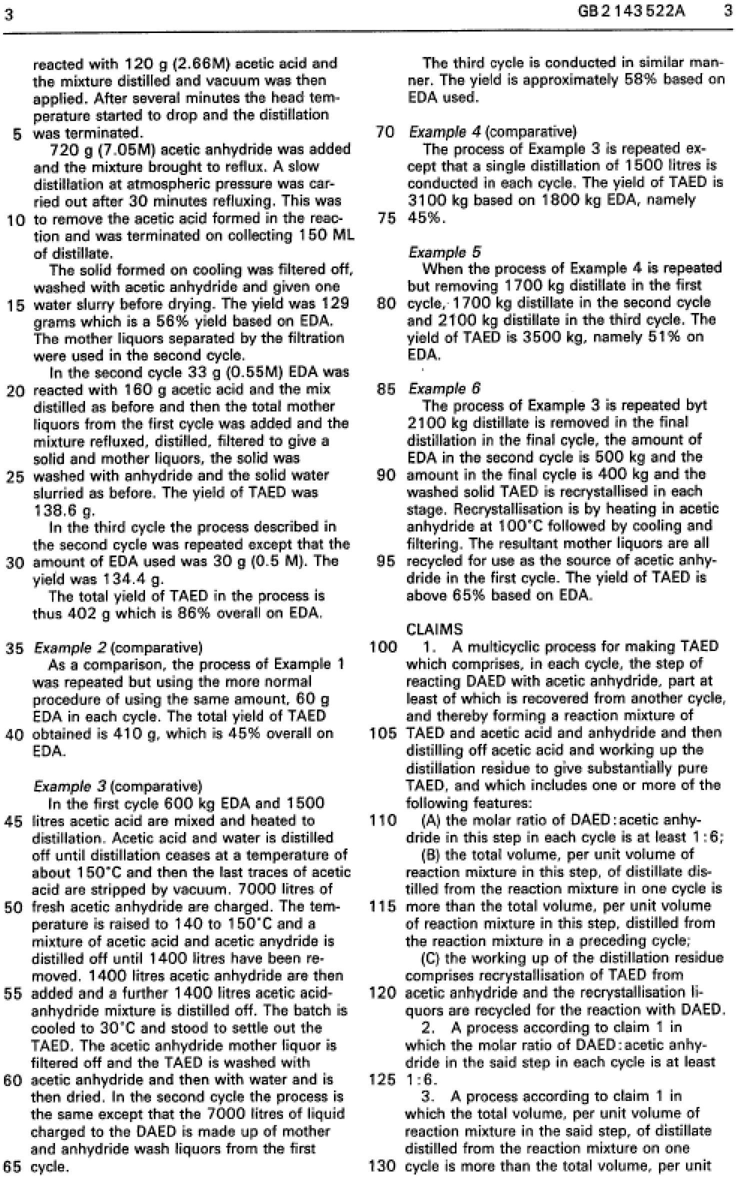
The volume of the TAED-acetic acid reaction mixture formed in each cycle is usually the same in which event the amount of distillate removed from the reaction in one cycle may be more than the amount removed in the preceding cycle. Preferably the amount is from 10 to 150% more than the amount removed in a preceding cycle. When each cycle is conducted with a single distillation stage only the amount in one cycle is generally from 10 to 60% more than the amount in the preceding cycle but when one stage is conducted with two distillation steps, as described above, and the preceding stage is conducted with a single distillation step then the total amount removed is generally from 50 to 150% more than the amount removed in the single step.

When TAED is purified by recrystallisation from acetic anhydride this is preferably effected by heating at 80 to 120°C, preferably about 100°C, for a period of 10 minutes to one hour followed by cooling and separation of the mother liquors from the TAED crystals. These mother liquors may also be recycled to the step in the next cycle in which DAED is reacted with acetic anhydride but preferably all the recrystallisation liquors from each cycle are recycled to the first cycle of a fresh cyclic multistep process.

The following are examples of the invention as applied to a three cycle process: Examples 1 and 2 are of laboratory processes while the other Examples are of industrial processes.

Example 1

In the first cycle 60 g (1M) EDA was



reacted with 120 g (2.66M) acetic acid and the mixture distilled and vacuum was then applied. After several minutes the head temperature started to drop and the distillation was terminated.

720 g (7.05M) acetic anhydride was added and the mixture brought to reflux. A slow distillation at atmospheric pressure was carried out after 30 minutes refluxing. This was to remove the acetic acid formed in the reaction and was terminated on collecting 150 ML of distillate.

The solid formed on cooling was filtered off, washed with acetic anhydride and given one water slurry before drying. The yield was 129 grams which is a 56% yield based on EDA. The mother liquors separated by the filtration were used in the second cycle.

In the second cycle 33 g (0.55M) EDA was reacted with 160 g acetic acid and the mix distilled as before and then the total mother liquors from the first cycle was added and the mixture refluxed, distilled, filtered to give a solid and mother liquors, the solid was washed with anhydride and the solid water slurried as before. The yield of TAED was 138.6 g.

In the third cycle the process described in the second cycle was repeated except that the amount of EDA used was 30 g (0.5 M). The yield was 134.4 g.

The total yield of TAED in the process is thus 402 g which is 86% overall on EDA.

Example 2 (comparative)

As a comparison, the process of Example 1 was repeated but using the more normal procedure of using the same amount, 60 g EDA in each cycle. The total yield of TAED obtained is 410 g, which is 45% overall on EDA.

Example 3 (comparative)

In the first cycle 600 kg EDA and 1500 litres acetic acid are mixed and heated to distillation. Acetic acid and water is distilled off until distillation ceases at a temperature of about 150°C and then the last traces of acetic acid are stripped by vacuum. 7000 litres of fresh acetic anhydride are charged. The temperature is raised to 140 to 150°C and a mixture of acetic acid and acetic anydride is distilled off until 1400 litres have been removed. 1400 litres acetic anhydride are then added and a further 1400 litres acetic acid-anhydride mixture is distilled off. The batch is cooled to 30°C and stood to settle out the TAED. The acetic anhydride mother liquor is filtered off and the TAED is washed with acetic anhydride and then with water and is then dried. In the second cycle the process is the same except that the 7000 litres of liquid charged to the DAED is made up of mother and anhydride wash liquors from the first cycle.

The third cycle is conducted in similar manner. The yield is approximately 58% based on EDA used.

Example 4 (comparative)

The process of Example 3 is repeated except that a single distillation of 1500 litres is conducted in each cycle. The yield of TAED is 3100 kg based on 1800 kg EDA, namely 45%.

Example 5

When the process of Example 4 is repeated but removing 1700 kg distillate in the first cycle, 1700 kg distillate in the second cycle and 2100 kg distillate in the third cycle. The yield of TAED is 3500 kg, namely 51% on EDA.

Example 6

The process of Example 3 is repeated byt 2100 kg distillate is removed in the final distillation in the final cycle, the amount of EDA in the second cycle is 500 kg and the amount in the final cycle is 400 kg and the washed solid TAED is recrystallised in each stage. Recrystallisation is by heating in acetic anhydride at 100°C followed by cooling and filtering. The resultant mother liquors are all recycled for use as the source of acetic anhydride in the first cycle. The yield of TAED is above 65% based on EDA.

CLAIMS

1. A multicyclic process for making TAED which comprises, in each cycle, the step of reacting DAED with acetic anhydride, part at least of which is recovered from another cycle, and thereby forming a reaction mixture of TAED and acetic acid and anhydride and then distilling off acetic acid and working up the distillation residue to give substantially pure TAED, and which includes one or more of the following features:

(A) the molar ratio of DAED: acetic anhydride in this step in each cycle is at least 1:6;

(B) the total volume, per unit volume of reaction mixture in this step, of distillate distilled from the reaction mixture in one cycle is more than the total volume, per unit volume of reaction mixture in this step, distilled from the reaction mixture in a preceding cycle;

(C) the working up of the distillation residue comprises recrystallisation of TAED from acetic anhydride and the recrystallisation liquors are recycled for the reaction with DAED.

2. A process according to claim 1 in which the molar ratio of DAED: acetic anhydride in the said step in each cycle is at least 1:6.

3. A process according to claim 1 in which the total volume, per unit volume of reaction mixture in the said step, of distillate distilled from the reaction mixture on one cycle is more than the total volume, per unit

volume of reaction mixture in the said step, distilled from the reaction mixture in a preceding cycle.

4. A process according to claim 1 in which the working up of the distillation residue comprises recrystallisation of TAED from acetic anhydride and the recrystallisation liquors are recycled for the reaction with DAED.

5. A process according to any preceding claim in which the molar ratio in each cycle of DAED:acetic anhydride is between 1:6.5 and 1:7.5.

6. A process according to claim 5 in which each cycle is carried out using substantially the same volume of reaction mixture and the amount of DAED introduced into that reaction mixture for reaction in each cycle is less than the amount in a preceding cycle and the ratio DAED:acetic anhydride is thereby maintained substantially constant in each cycle.

7. A process according to any preceding claim in which each cycle comprises, as step 1, reacting EDA with acetic acid to form DAED and, as step 2, reacting substantially all the DAED with acetic anhydride recovered from another cycle and thereby forming reaction mixture comprising TAED and acetic acid and anhydride.

8. A process according to claim 7 in which the volume of reaction mixture in each cycle is substantially constant and the amount of EDA introduced in each subsequent cycle is less than the amount introduced in a preceding cycle, the ratio DAED:acetic anhydride in step 2 thereby being maintained substantially constant in each cycle.

9. A process according to claim 8 in which the amount of EDA introduced in second and subsequent cycles is from 50 to 90% by weight of the amount introduced in the first cycle.

10. A process according to any preceding claim in which the total volume, per unit volume of reaction mixture in the said step, of distillate distilled from the reaction mixture on one cycle is from 10 to 150% more than the amount removed in a preceding cycle.

11. A process according to claim 10 in which each cycle is conducted with a single distillation stage and the amount removed in one cycle is from 10 to 60% more than the amount removed in the preceding cycle.

12. A process according to any preceding claim in which liquors from the working up steps in one cycle are used for reaction with DAED in the next cycle and the recrystallisation liquors from the final cycle are recycled for reaction with DAED but the other acetic anhydride containing liquors obtained during the working up in the final cycle are run to waste.

13. A process according to any preceding claim in which the working up of the distillation residue comprises one or more steps selected from phase separation and cooling of the residue, reslurrying TAED with acetic anhydride followed by phase separation, and recrystallisation from acetic anydride.

14. A process according to any preceding claim in which the reaction between DAED and acetic anydride is conducted by heating at 120 to 170°C for 15 minutes to 3 hours accompanied by distillation of acetic acid from the reaction mixture.

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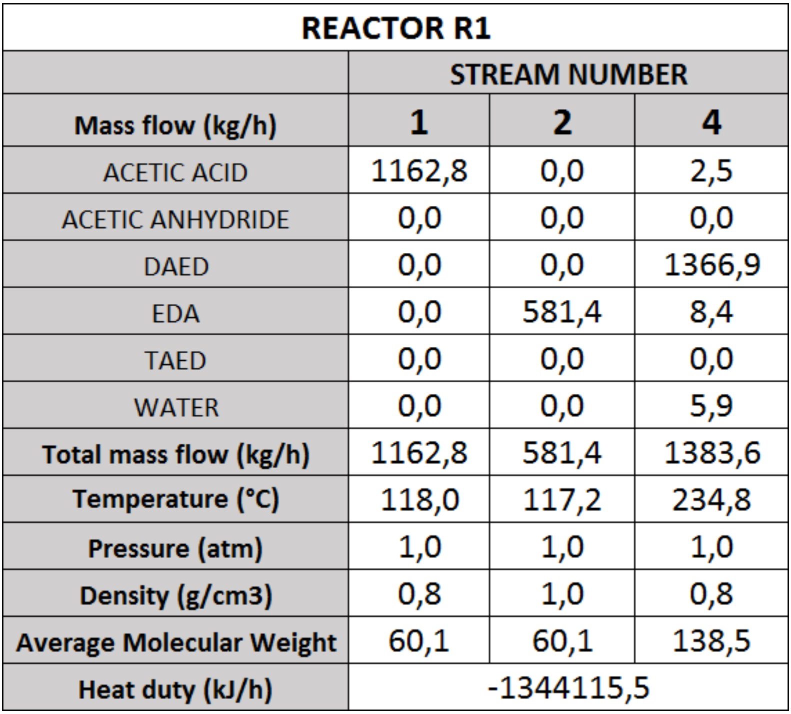
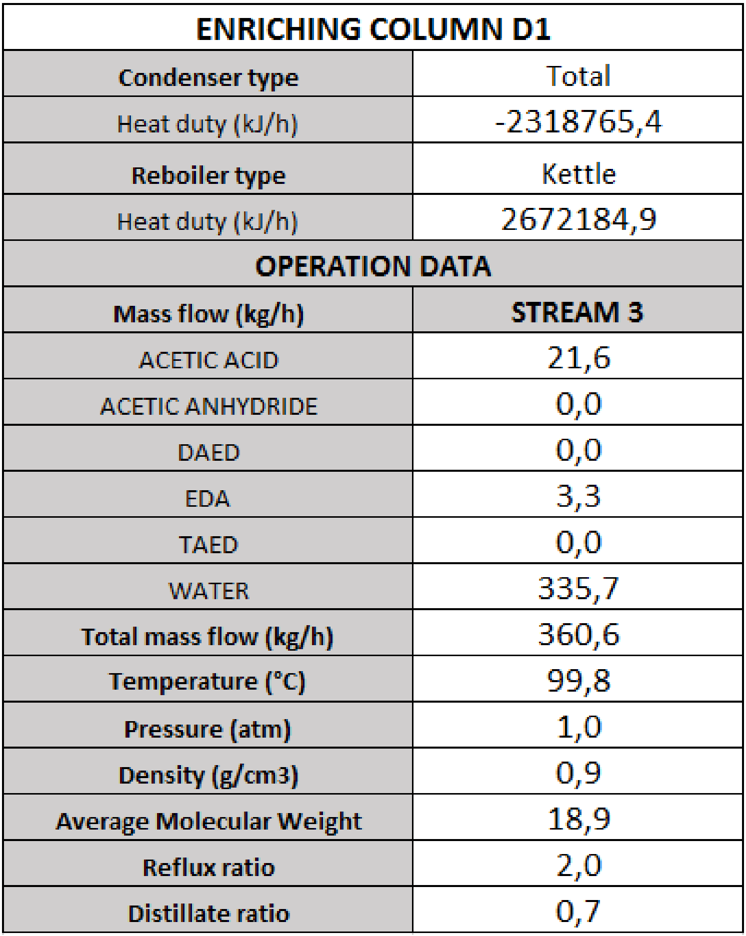
APPENDIX 2: EQUIPMENT RESULTS EXTENSION



REACTOR R1			
	STREAM NUMBER		
Mass flow (kg/h)	**1**	**2**	**4**
ACETIC ACID	1162,8	0,0	2,5
ACETIC ANHYDRIDE	0,0	0,0	0,0
DAED	0,0	0,0	1366,9
EDA	0,0	581,4	8,4
TAED	0,0	0,0	0,0
WATER	0,0	0,0	5,9
Total mass flow (kg/h)	1162,8	581,4	1383,6
Temperature (°C)	118,0	117,2	234,8
Pressure (atm)	1,0	1,0	1,0
Density (g/cm3)	0,8	1,0	0,8
Average Molecular Weight	60,1	60,1	138,5
Heat duty (kJ/h)	-1344115,5		

REACTOR R2			
	STREAM NUMBER		
Mass flow (kg/h)	**6**	**7**	**9**
ACETIC ACID	0,0	0,0	5,2
ACETIC ANHYDRIDE	0,0	6976,7	5077,2
DAED	1366,6	0,0	27,2
EDA	0,0	0,0	0,0
TAED	0,0	0,0	2120,2
WATER	0,0	0,0	0,0
Total mass flow (kg/h)	1366,6	6976,7	7229,9
Temperature (°C)	400,7	139,6	402,2
Pressure (atm)	0,5	1,0	1,0
Density (g/cm3)	0,7	0,9	0,4
Average Molecular Weight	144,2	102,1	121,9
Heat duty (kJ/h)	-3792160,6		

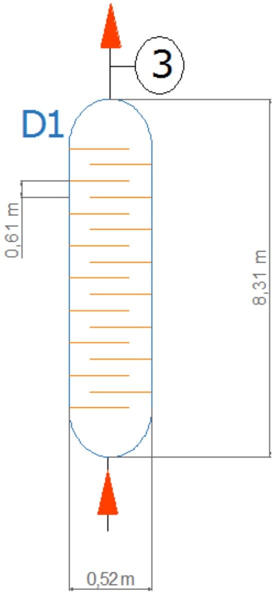


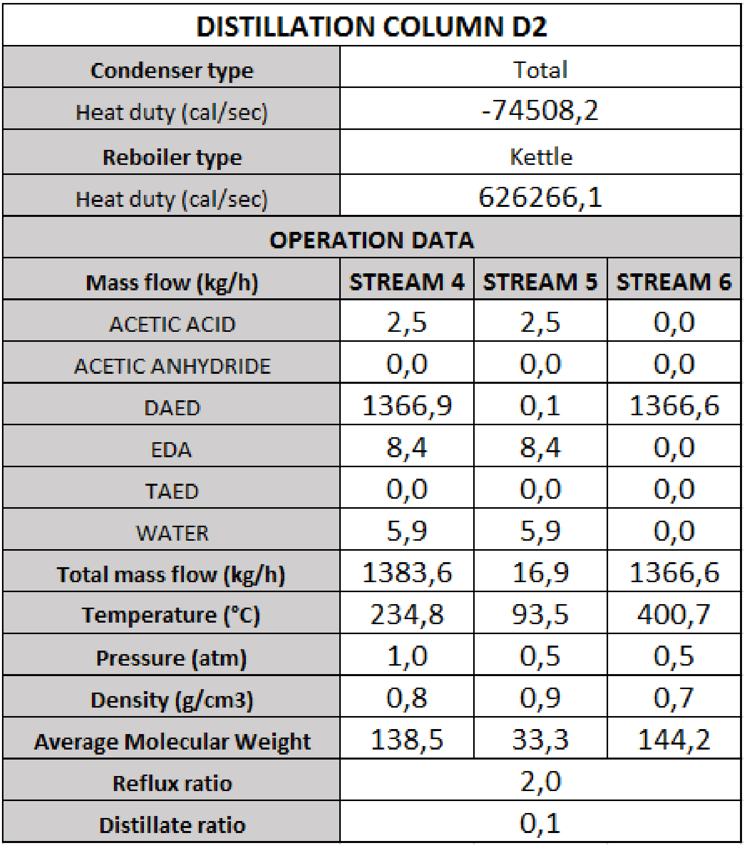
ENRICHING COLUMN D1	
Condenser type	Total
Heat duty (kJ/h)	-2318765,4
Reboiler type	Kettle
Heat duty (kJ/h)	2672184,9
OPERATION DATA	
Mass flow (kg/h)	**STREAM 3**
ACETIC ACID	21,6
ACETIC ANHYDRIDE	0,0
DAED	0,0
EDA	3,3
TAED	0,0
WATER	335,7
Total mass flow (kg/h)	360,6
Temperature (°C)	99,8
Pressure (atm)	1,0
Density (g/cm3)	0,9
Average Molecular Weight	18,9
Reflux ratio	2,0
Distillate ratio	0,7

ENRICHING COLUMN D1

DESIGN DATA	
Theoretical Stages	9
Theoretical Trays	8
Real Trays	12
Feed Tray	12
Height (m)	8,3
Column diameter (m)	0,5
Tray type	Bubble cap
Tray spacing (m)	0,6

DESIGN REPRESENTATION





DISTILLATION COLUMN D2			
Condenser type	Total		
Heat duty (cal/sec)	-74508,2		
Reboiler type	Kettle		
Heat duty (cal/sec)	626266,1		
OPERATION DATA			
Mass flow (kg/h)	**STREAM 4**	**STREAM 5**	**STREAM 6**
ACETIC ACID	2,5	2,5	0,0
ACETIC ANHYDRIDE	0,0	0,0	0,0
DAED	1366,9	0,1	1366,6
EDA	8,4	8,4	0,0
TAED	0,0	0,0	0,0
WATER	5,9	5,9	0,0
Total mass flow (kg/h)	1383,6	16,9	1366,6
Temperature (°C)	234,8	93,5	400,7
Pressure (atm)	1,0	0,5	0,5
Density (g/cm3)	0,8	0,9	0,7
Average Molecular Weight	138,5	33,3	144,2
Reflux ratio	2,0		
Distillate ratio	0,1		

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<tr><td>Real Trays</td><td>9</td></tr>
<tr><td>Feed Tray</td><td>5</td></tr>
<tr><td>Height (m)</td><td>6,5</td></tr>
<tr><td>Column diameter (m)</td><td>0,4</td></tr>
<tr><td>Tray type</td><td>Bubble cap</td></tr>
<tr><td>Tray spacing (m)</td><td>0,6</td></tr>
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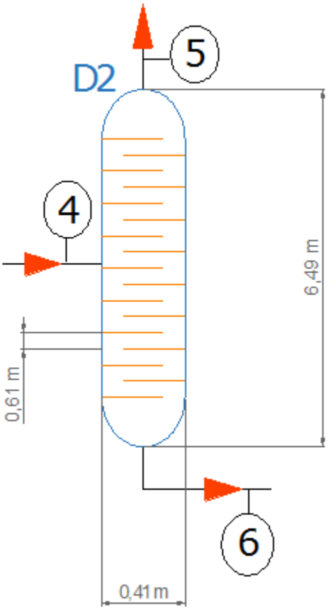
<tr><td colspan="2">
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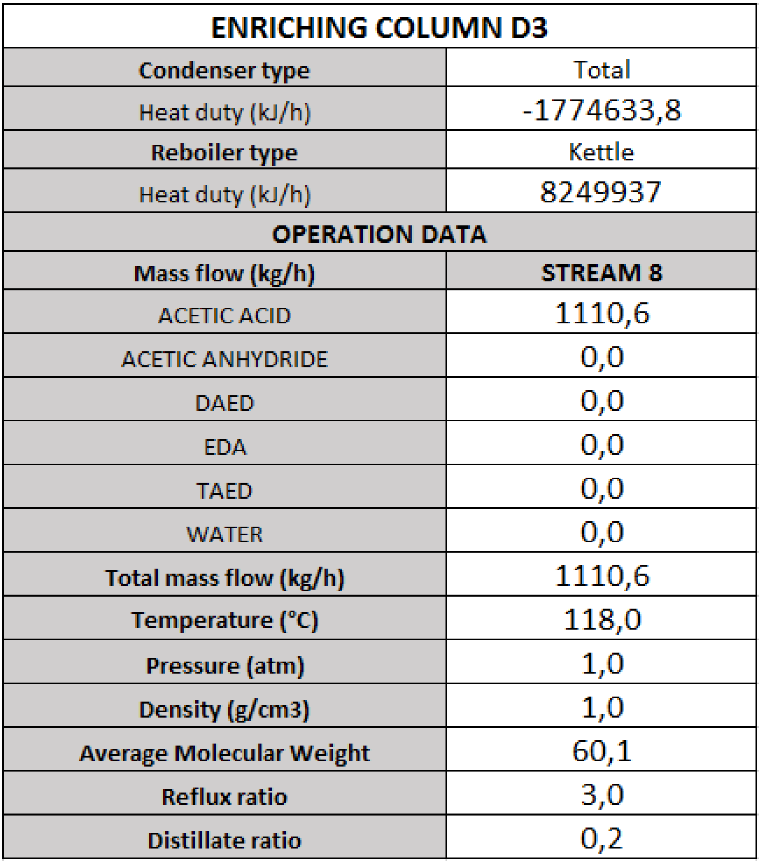
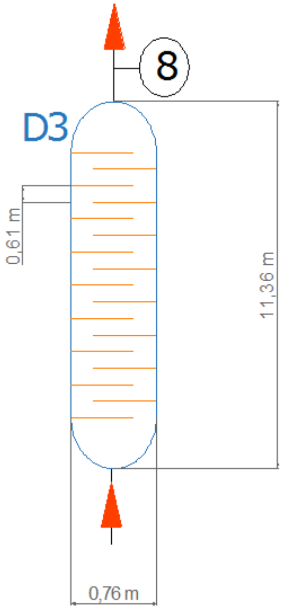


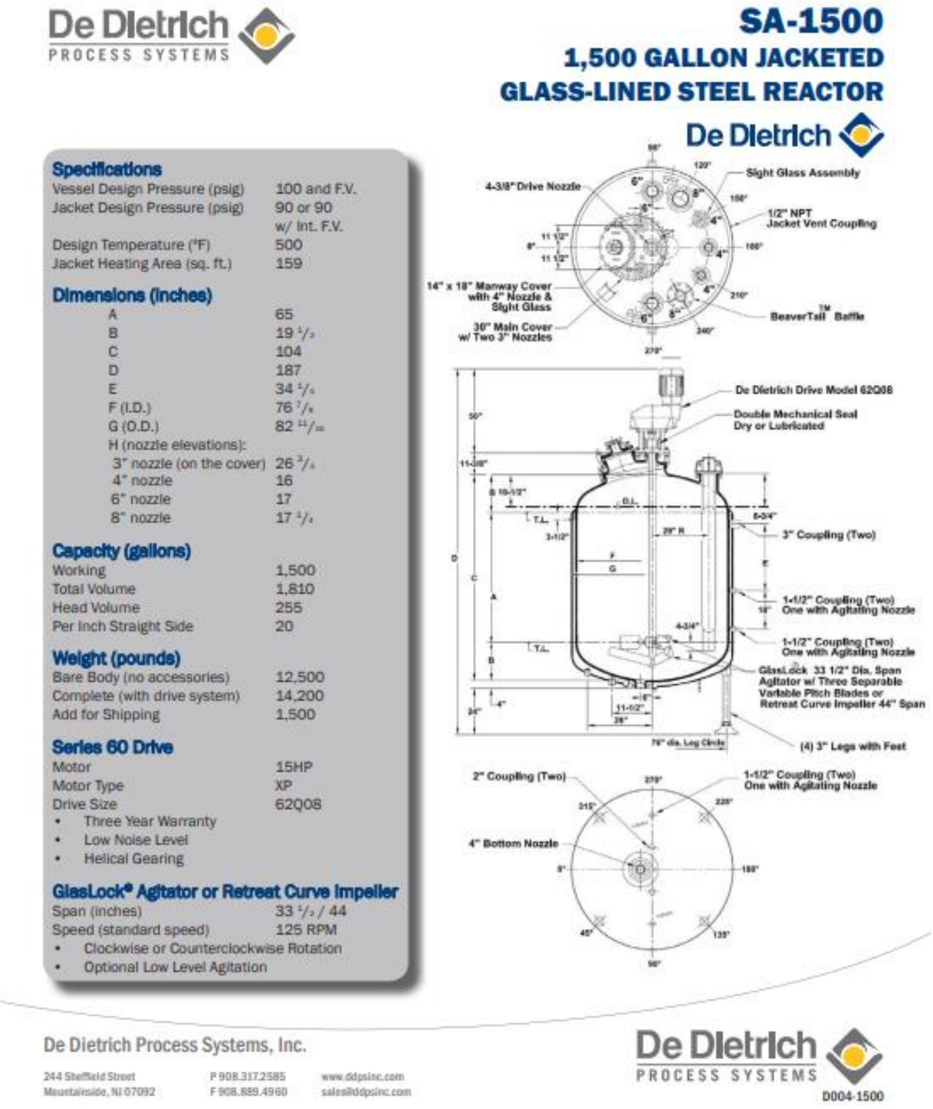
ENRICHING COLUMN D3	
Condenser type	Total
Heat duty (kJ/h)	-1774633,8
Reboiler type	Kettle
Heat duty (kJ/h)	8249937
OPERATION DATA	
Mass flow (kg/h)	**STREAM 8**
ACETIC ACID	1110,6
ACETIC ANHYDRIDE	0,0
DAED	0,0
EDA	0,0
TAED	0,0
WATER	0,0
Total mass flow (kg/h)	1110,6
Temperature (°C)	118,0
Pressure (atm)	1,0
Density (g/cm3)	1,0
Average Molecular Weight	60,1
Reflux ratio	3,0
Distillate ratio	0,2

ENRICHING COLUMN D3	
DESIGN DATA	
Theoretical Stages	13
Theoretical Trays	12
Real Trays	17
Feed Tray	17
Height (m)	11,4
Column diameter (m)	0,8
Tray type	Bubble cap
Tray spacing (m)	0,6

DESIGN REPRESENTATION



APPENDIX 3: CATALOGUES



SA-1500

1,500 GALLON JACKETED GLASS-LINED STEEL REACTOR

Specifications

Vessel Design Pressure (psig)	100 and F.V.
Jacket Design Pressure (psig)	90 or 90 w/ Int. F.V.
Design Temperature (°F)	500
Jacket Heating Area (sq. ft.)	159

Dimensions (inches)

A	65
B	19 1/2
C	104
D	187
E	34 1/4
F (I.D.)	76 7/8
G (O.D.)	82 11/16
H (nozzle elevations):	
3" nozzle (on the cover)	26 3/4
4" nozzle	16
6" nozzle	17
8" nozzle	17 1/4

Capacity (gallons)

Working	1,500
Total Volume	1,810
Head Volume	255
Per Inch Straight Side	20

Weight (pounds)

Bare Body (no accessories)	12,500
Complete (with drive system)	14,200
Add for Shipping	1,500

Series 60 Drive

Motor	15HP
Motor Type	XP
Drive Size	62Q08

- Three Year Warranty
- Low Noise Level
- Helical Gearing

GlasLock® Agitator or Retreat Curve Impeller

Span (inches)	33 1/2 / 44
Speed (standard speed)	125 RPM

- Clockwise or Counterclockwise Rotation
- Optional Low Level Agitation

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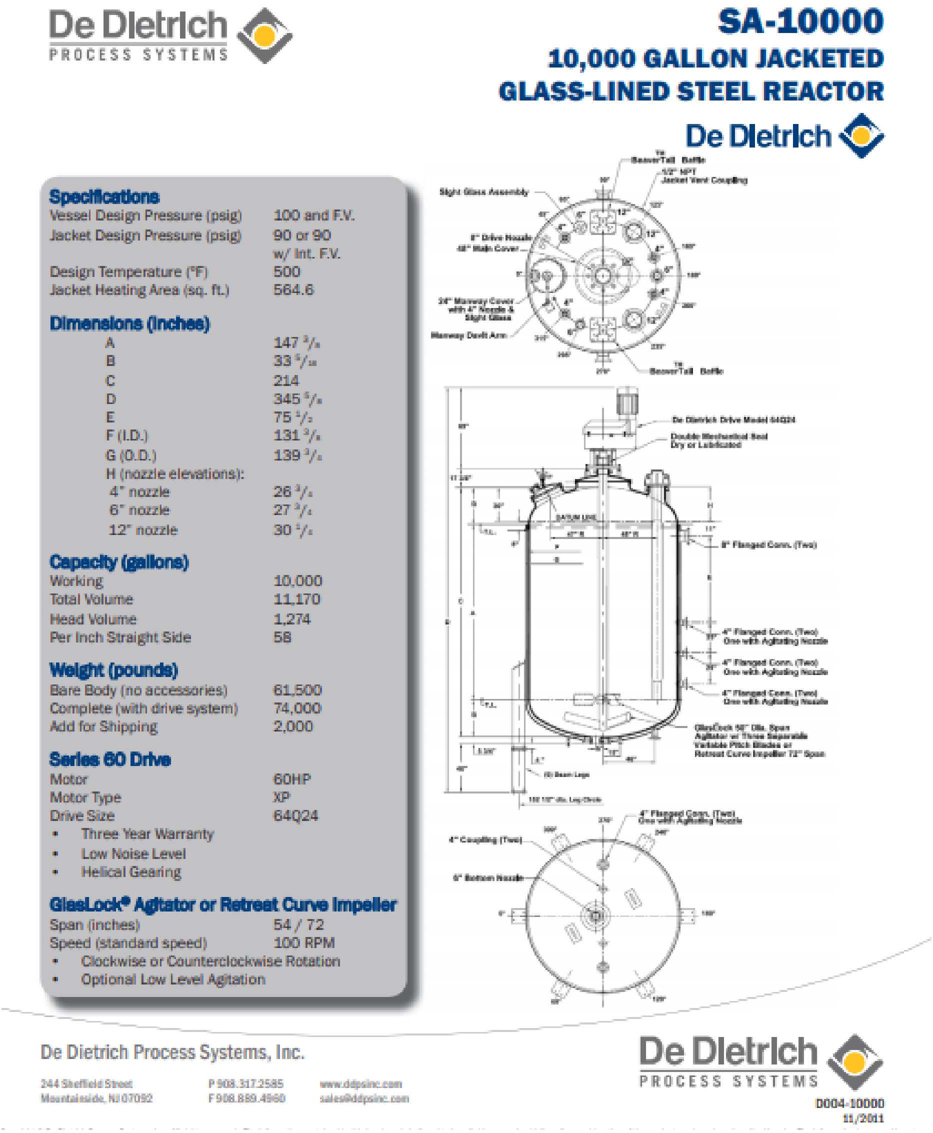

De Dietrich PROCESS SYSTEMS

SA-10000

10,000 GALLON JACKETED GLASS-LINED STEEL REACTOR

De Dietrich

Specifications

Vessel Design Pressure (psig)	100 and F.V.
Jacket Design Pressure (psig)	90 or 90 w/ Int. F.V.
Design Temperature (°F)	500
Jacket Heating Area (sq. ft.)	564.6

Dimensions (inches)

A	147 $^{3}/_{8}$
B	33 $^{5}/_{16}$
C	214
D	345 $^{5}/_{8}$
E	75 $^{1}/_{2}$
F (I.D.)	131 $^{3}/_{8}$
G (O.D.)	139 $^{3}/_{4}$
H (nozzle elevations):	
4" nozzle	26 $^{3}/_{4}$
6" nozzle	27 $^{3}/_{4}$
12" nozzle	30 $^{1}/_{4}$

Capacity (gallons)

Working	10,000
Total Volume	11,170
Head Volume	1,274
Per Inch Straight Side	58

Weight (pounds)

Bare Body (no accessories)	61,500
Complete (with drive system)	74,000
Add for Shipping	2,000

Series 60 Drive

Motor	60HP
Motor Type	XP
Drive Size	64Q24

- Three Year Warranty
- Low Noise Level
- Helical Gearing

GlasLock® Agitator or Retreat Curve Impeller

Span (inches)	54 / 72
Speed (standard speed)	100 RPM

- Clockwise or Counterclockwise Rotation
- Optional Low Level Agitation

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De Dietrich PROCESS SYSTEMS

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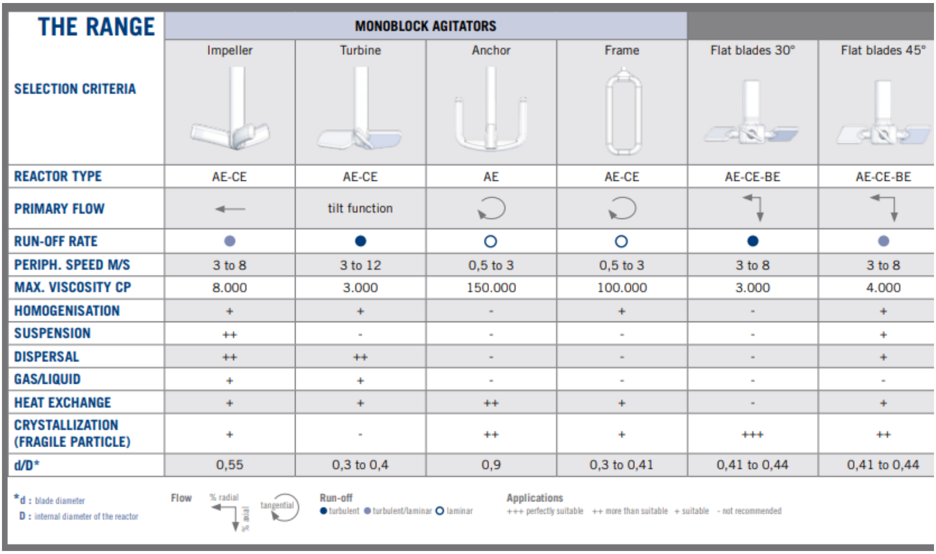
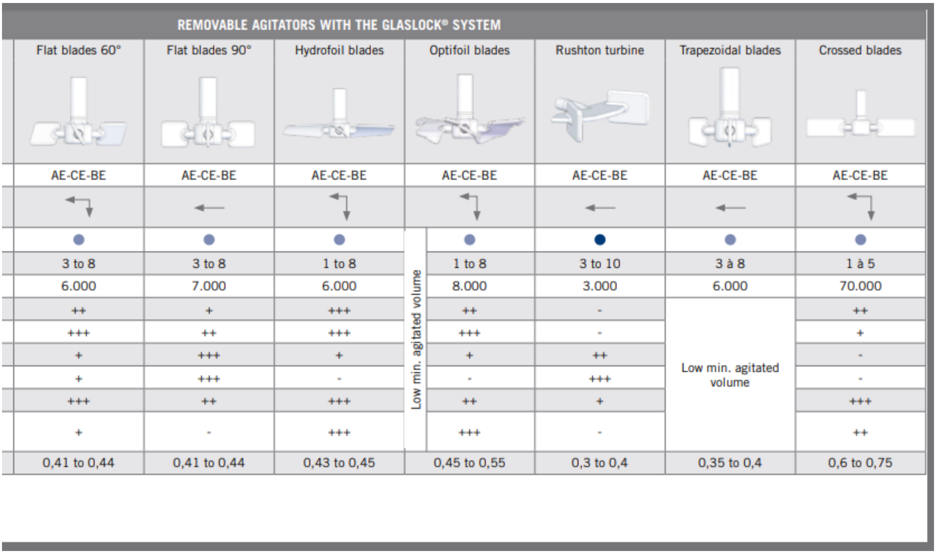
11/2011





THE RANGE	MONOBLOCK AGITATORS						REMOVABLE AGITATORS WITH THE GLASLOCK® SYSTEM							
SELECTION CRITERIA	Impeller	Turbine	Anchor	Frame	Flat blades 30°	Flat blades 45°	Flat blades 60°	Flat blades 90°	Hydrofoil blades		Optifoil blades	Rushton turbine	Trapezoidal blades	Crossed blades
REACTOR TYPE	AE-CE	AE-CE	AE	AE-CE	AE-CE-BE	AE-CE-BE	AE-CE-BE	AE-CE-BE	AE-CE-BE		AE-CE-BE	AE-CE-BE	AE-CE-BE	AE-CE-BE
PRIMARY FLOW	←	tilt function	↺	↺	←↓	←↓	←↓	←	←↓		←↓	←	←	←↓
RUN-OFF RATE	◉	●	○	○	●	◉	◉	◉	◉	Low min. agitated volume	◉	●	◉	◉
PERIPH. SPEED M/S	3 to 8	3 to 12	0,5 to 3	0,5 to 3	3 to 8	3 to 8	3 to 8	3 to 8	1 to 8		1 to 8	3 to 10	3 à 8	1 à 5
MAX. VISCOSITY CP	8.000	3.000	150.000	100.000	3.000	4.000	6.000	7.000	6.000		8.000	3.000	6.000	70.000
HOMOGENISATION	+	+	-	+	-	+	++	+	+++		++	-	Low min. agitated volume	++
SUSPENSION	++	-	-	-	-	+	+++	++	+++		+++	-		+
DISPERSAL	++	++	-	-	-	+	+	+++	+		+	++		-
GAS/LIQUID	+	+	-	-	-	-	+	+++	-		-	+++		-
HEAT EXCHANGE	+	+	++	+	-	+	+++	++	+++		++	+		+++
CRYSTALLIZATION (FRAGILE PARTICLE)	+	-	++	+	+++	++	+	-	+++		+++	-		++
d/D*	0,55	0,3 to 0,4	0,9	0,3 to 0,41	0,41 to 0,44	0,41 to 0,44	0,41 to 0,44	0,41 to 0,44	0,43 to 0,45		0,45 to 0,55	0,3 to 0,4	0,35 to 0,4	0,6 to 0,75

*d : blade diameter
D : internal diameter of the reactor

Flow ← % radial ↓ % axial ↺ tangential

Run-off ● turbulent ◉ turbulent/laminar ○ laminar

Applications +++ perfectly suitable ++ more than suitable + suitable - not recommended