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A Novel Cost-Efficient Tributyl Citrate Production Process

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ABSTRACT

Phthalates are the most widely used plasticizers in the polymers industry; however, their toxicity and environmental impacts have led to their ban in various applications. This has driven the search for more sustainable alternatives, including biobased citrate esters, especially tributyl citrate (TBC) and its acetylated form. TBC is typically produced by refined citric acid (CA) esterification with 1-butanol (BuOH). However, the high energy and materials-intensive downstream purification of fermentation-derived CA involves high production costs, thus limiting the widespread adoption of TBC as a plasticizer. This work presents an innovative approach for TBC production using calcium citrate as feedstock instead of pure CA. The process involves a simultaneous acidification-esterification stage and further hydration of calcium sulfate, thus reducing costs by avoiding multiple CA refining steps. The approach proceeds via a solid-solid-liquid reaction of calcium citrate with sulfuric acid in butanol, releasing CA, which is simultaneously esterified to form TBC. The resultant calcium sulfate aids in water removal to enhance esterification conversion. Based upon experimentally validated models and rigorous simulations, the proposed approach was evaluated, and it exhibited significant reductions in processing times and operating costs, with savings of at least 46% in utilities compared to traditional TBC production. The novel approach was found suitable and promising for industrial deployment.

Keywords: Process integration, Process Intensification, Modelling and Simulations, Calcium citrate, Tributyl Citrate

INTRODUCTION

Polymeric materials and plastic products have significantly contributed to the advancement of modern society. Because of their malleability and flexibility, these materials have been used in many applications. These characteristics are mainly possible by incorporating plasticizers, which decrease molecular interactions among polymer chains, increase elasticity, and reduce the glass transition temperature (Tg)(1). Plasticizers can constitute a significant fraction of some polymers (up to 80% wt.), being the phthalates, the most widely used general-purpose plasticizers. In particular, phthalates are mainly employed in polyvinyl chloride (PVC) products, including flexible films and sheets, hoses, pipes, windows, cable jacketing, flooring, rainwear, shoes, etc. Considering their significant use and that they are not chemical-bonded to the polymers, they can migrate from the material. This has increased concerns regarding environmental pollution and public health due to the potential toxicity of plasticizers (2). In particular, the negative health impacts caused by phthalates has led to restrictions on their use in sensitive applications, prompting the search for alternative molecules that are non-toxic, renewable, and biodegradable. Among these, bio-based plasticizers like citric acid esters have gained attention.

Citric acid esters, particularly tributyl citrate (TBC) and its acetylated form have performed similarly to phthalates in different applications (3). However, citrates have the advantage of being biocompatible, biodegradable, and renewable. TBC is produced via esterification of citric acid (CA) with a large excess of 1-butanol (BuOH) using acid catalysts [4,5]. The process involves long processing times in a semi-batch operation and high-purity anhydrous CA (6). This last requirement is a major challenge because purification of fermentation-derived CA requires highly materials- and energy-intensive processes. As a result, the cost of TBC is highly dependent on that of CA, and it is usually higher than that of phthalates; this limits an extended industrial use of TBC.

Production of bioderived anhydrous CA requires a complex train of physicochemical separation operations. The fermentation broth is filtered to remove biomass and then treated with lime to precipitate CA as a calcium salt. The salt is then separated by filtration, resuspended in water, and finally acidified with sulfuric acid. At this point gypsum is produced and precipitated, releasing CA in the aqueous solution. This aqueous solution is then taken to ion exchange to remove minerals, followed by concentration via multistage evaporation, crystallization, filtration, and drying processes (7). This complex downstream separation train removes nearly 10 kg of water per kg of CA, thus being highly energy intensive. Finally, refined CA is subjected to esterification with BuOH. Anhydrous CA is required as raw material in the esterification process as it produces water, and the reaction conversion is limited by chemical equilibrium. The complete process is depicted in Figure 1.

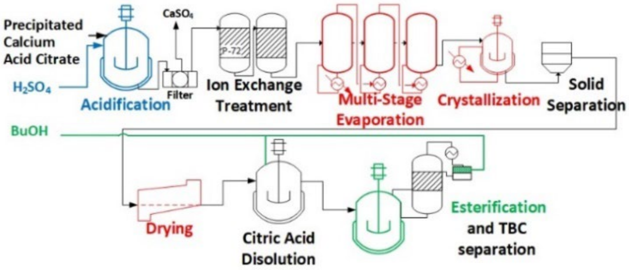

Figure 1: Conventional TBC production process

As an alternative approach, this work proposed and assessed an innovative scheme to overcome most of the steps required to purify CA to produce TBC, by using calcium citrate as raw material. This process is similar to previous reports on the recovery of succinic acid (8) and involves a solid-solid-liquid reaction in which insoluble calcium citrate is suspended in an alcoholic medium (i.e., BuOH), where acidification with sulfuric acid is carried out. As a result, CA is released into the alcoholic medium, where it undergoes simultaneous esterification to TBC catalyzed by the remaining H_2SO_4. The proposed process, described in Figure 2, denoted as simultaneous acidification–esterification (SAE), avoids the conventional purification of CA. Additionally, a reduction in the dissolution times required in the traditional esterification reaction is expected. Furthermore, calcium sulfate is produced as a by-product in an alcoholic phase, reducing salts' solubility and helping to remove water by forming hydrated salts, thus facilitating the separation of esters.

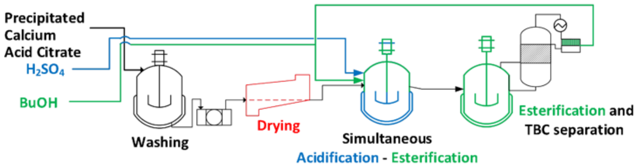

Figure 2: Proposed SAE TBC production process

To assess the proposed SAE process against the conventional one using anhydrous CA, rigorous simulation of both processes was carried out in Aspen Plus® using validated kinetic and thermodynamic models [5,10]. The operating conditions and the configuration of the conventional process were based on data from an existing industrial facility for TBC production.

MODELING AND SIMULATION

Reaction Kinetics: Conventional Process

In the conventional industrial process (Figure 1), the multistep esterification reaction of CA with BuOH (Figure 3b) is catalyzed using methanesulfonic acid (MSA). A validated kinetic model for the multiple sets of parallel-sequential reactions was previously reported (4) and used for simulations here.

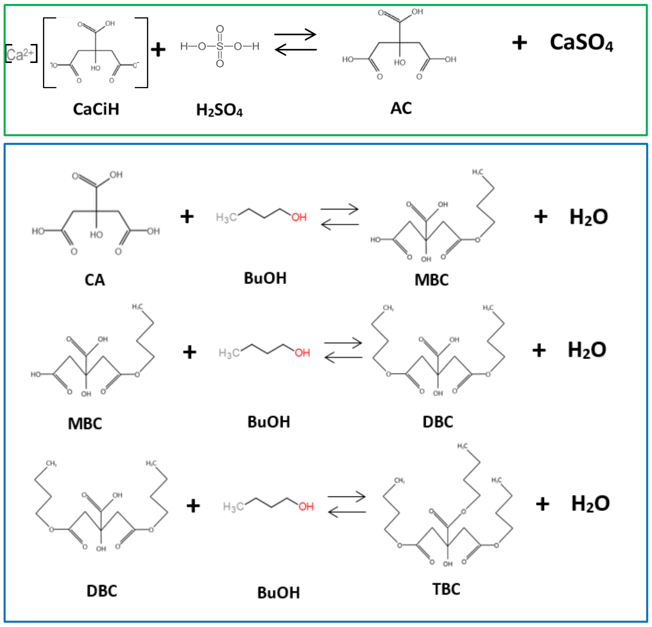

Figure 3: Scheme of reactions during the proposed simultaneous acidification-esterification of calcium citrate in 1-butanol using sulfuric acid. a) (top) acidification. b) (bottom) esterification.

Reaction Kinetics: SAE Process

As previously mentioned, the acidification occurs between solid calcium citrate and liquid H_2SO_4 in an alcoholic media. Then, released CA undergoes esterification with BuOH (Figure 3). The remaining or excess sulfuric acid acts as a catalyst in this reaction. As a result, a certain degree of conversion to intermediate citrates is achieved (i.e., monobutyl citrate - MBC and dibutyl citrate - DBC). This would facilitate the recovery of CA and reduce the time required for complete esterification [4, 10].

The corresponding kinetic model of the simultaneous acidification-esterification process was previously reported and was used to simulate the process (10). As the esterification to TBC is incomplete, this is finished in a subsequent reactor using MSA as catalyst (4). The kinetics of the acidification-esterification reaction and the corresponding kinetic parameters are presented in the supplementary material.

TBC Production Conventional Process

The simulation of the conventional process was carried out considering the two main sections involved in the production of TBC. First, there is CA production from precipitated calcium citrate. This section relies upon highly energetic demanding separation stages (e.g., evaporation, crystallization, and drying). Then, the esterification stage, where CA is transformed into the desired plasticizer via a fed-batch operation. Here, reactants loading and operating temperature change follow a pre-programmed protocol as performed in the industry (11).

Citric Acid Production

The details of the CA process and the production capacity (30,000 tons/year) corresponded to those of an existing industrial plant (11). For simplicity, it is assumed that all the commercialized CA corresponds to the anhydrous form. Approximately 95% of produced CA is sold directly; the remaining fraction is used to produce citrate esters. This small portion corresponds to the remnant CA that doesn't meet specifications regarding particle size or that is recovered from equipment walls like hoppers, filters, centrifuges, or dryers. CA is produced from submerged aerobic fermentation of sugarcane molasses using *Aspergillus niger*. The produced acid is released into the aqueous medium, so precipitation is carried out using $CaOH_2$ to generate insoluble calcium citrate. This process separates the citric acid in salt form and allows its extraction from the culture medium via filtration. For comparative purposes, both the modeling of the conventional process and the proposed process considered the resulting stream of precipitated and filtered calcium citrate as the raw material in the TBC production process. As the precipitated calcium citrate corresponds to an intermediate stream in the CA process, its commercial price is unknown. This price was estimated at $0.43/kg, based on the cost of the raw materials necessary to generate the calcium citrate. Although all high energy-intensive steps in the synthesis of CA were included in the model, polishing the acid and TBC using activated carbon absorption to remove colors and other impurities is not considered.

- **Acidification reaction:** The CA recovery from calcium citrate in an aqueous medium occurs by ion exchange with a stoichiometric amount of H_2SO_4. This solid-liquid reaction is carried out in a stirred reactor at 30 °C with a residence time of 3 hours. As a result, the stoichiometric amount of solid gypsum is produced, and the obtained liquid effluent corresponds to a 30% wt. CA aqueous solution.

- **Filtration:** Conveyor belts or rotary filters are commonly employed to separate the solid gypsum (i.e., calcium sulfate) from the effluent CA solution generated in the acidification process. The filters are connected to vacuum pumps to facilitate filtration and enhance liquid phase recovery. In the simulation a separator filter module is used to describe $CaSO_4$ removal.

- **Evaporation:** the aqueous solution is processed in an evaporation train to concentrate up to the crystallization point of the organic acid. Since the process is energetically demanding, multiple interconnected stages are typically employed (1 to 4 steps, depending on the production capacity) to reduce steam consumption. Here, a triple-effect co-current configuration is considered for a capacity of 30,000 tons/year of CA (Figure 4). Multi-effect evaporators were simulated via Heater modules that serve as calandrias for the condensation of the steam, releasing latent heat. This heat is provided to flash vessel modules, where concentration of CA is performed. A vacuum profile in the effects is assumed (0.89, 0.67, and 0.40 bara). The final concentration of the solution depends on the desired hydrated form of CA in the crystallization stage.

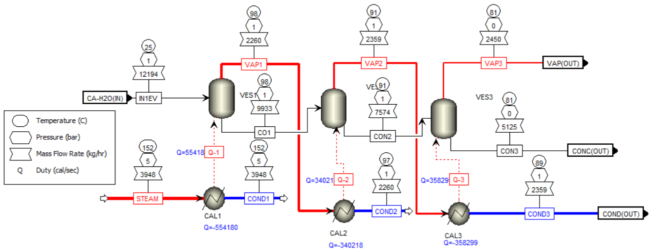

Figure 4: Triple-effect evaporation configuration

- **Crystallization:** CA can precipitate as anhydrous or monohydrate depending on the concentration and temperature. An operating temperature of 45°C is set to obtain anhydrous CA crystals. In this case, a concentration of ≥70% wt. of CA is required to ensure the saturation of the mixture at the operating temperature. Aspen Plus® Crystallizer model and CA solubility data in water (12) were used for the calculation of the saturation conditions in the crystallization modeling.

- **Centrifugation:** The use of two-stage centrifuges is common for the separation of crystallized solids. CFuge model that simulates centrifuge filters (rotating baskets), with no residual solids in the outlet filtrate, is used to separate crystallized CA from the liquor. A residual moisture of 10% by weight on a wet basis was assumed.

- **Drying:** Continuous fluidized bed dryers enable a low moisture content in the final product (< 5% wt.). Steam was used as heating utility to provide the required heat duty for the drying air that is in direct contact with the fluidized crystals. A conveyor belt coupled to a vibratory system allows better air-solid contact and prevents agglomerated solids. In this case, a convective dryer type in the dryer module is used, with a crossflow (through-the-bed) air-solid arrangement.

  Vacuum was provided using a steam-jet ejector system. The steam required for the vacuum system can be calculated considering the air leakage in the vessels. This can be determined by knowing the operation pressure and the volume of the vessel (13).

Citric Acid Dissolution-Esterification

Once anhydrous CA is obtained, it is sieve-classified, and the fines fraction is rejected according to market specifications. Additionally, it is common to find solid CA fines adhered to equipment or clumps in some units. First, this material is fed to a 23.7 m^3 dissolution tank alongside with BuOH, to enhance a total homogeneous reaction mix. Afterwards, the mix, together with the catalyst is fed to SS316 jacketed reactor with a capacity of 26 m^3 to perform the esterification reaction. During esterification, removal of produced water is desired to shift the chemical equilibrium. For this reason, the reactor is coupled to a distillation column that operates at the bubble temperature of the BuOH-H_2O mixture. As the reaction proceeds, a vapor stream of BuOH-H_2O is generated, and it is separated in the rectifying column up to the azeotropic condition. Since this azeotrope is heterogeneous, two immiscible phases are generated and separated in a decanter after condensing the column's top vapor. The BuOH-rich organic phase is returned to the column as reflux, whereas the aqueous phase is removed from the system to overcome chemical equilibrium limitations. The process of transforming CA into TBC can be divided into three stages:

- **Dissolution:** Due to the low solubility of CA, dissolution must be carried out by dosing the fed solids under heating and constant agitation. In this case, an excess of BuOH and the catalyst (MSA) are added to promote the reaction and to facilitate the dissolution of CA in the alcohol.

- **Esterification:** Once the necessary CA has been dissolved, the temperature of the reactive mixture is increased up to its bubble point to promote reaction. At this point, the vapor outlet line of the reactor is opened to connect with the distillation column, seeking to encourage water removal. The progress of the reaction is monitored through the measurement of the acid value of the mixture over time.

- **Purification:** Once the desired acid value is reached, separating the excess BuOH in the final mixture is necessary. For this, the system's pressure is reduced in the same reactor, and evaporation of all the remaining alcohol and water is carried out. Finally, the catalyst is neutralized using a sodium hydroxide solution.

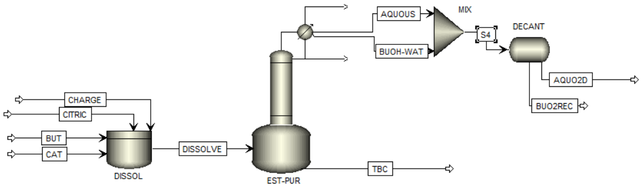

Figure 5: Batch and BatchSep module for esterification and acidification-esterification stage modeling.

Based on the above-described stages, the simulation of the citric acid dissolution-esterification stage was performed using both RBatch and BatchSep modules (Figure 5), enabling the dissolution of CA in BuOH, catalyst adding, temperature profile programming, and purification stages as reported in a previous study (11). The CA production is estimated considering a maximum processing capacity of 8t CA per batch. It is also assumed that 180 batches could be processed in a year. According to this, it is estimated that ~ 1440 t/yr of CA fines are generated in the production plant which are used for further esterification.

Proposed SAE Process

Unlike the conventional process, the proposed process involves directly using calcium citrate from the precipitation stage with $CaOH_2$ and its subsequent acidification in BuOH, as seen in Figure 2. A pre-treatment stage is considered in which the calcium citrate is washed to remove impurities and ions from the culture medium. Subsequently, it is filtered and dried to avoid the presence of water in the reactive medium. For these pre-treatment stages, the acquisition of new equipment is not considered since these processes can be carried out

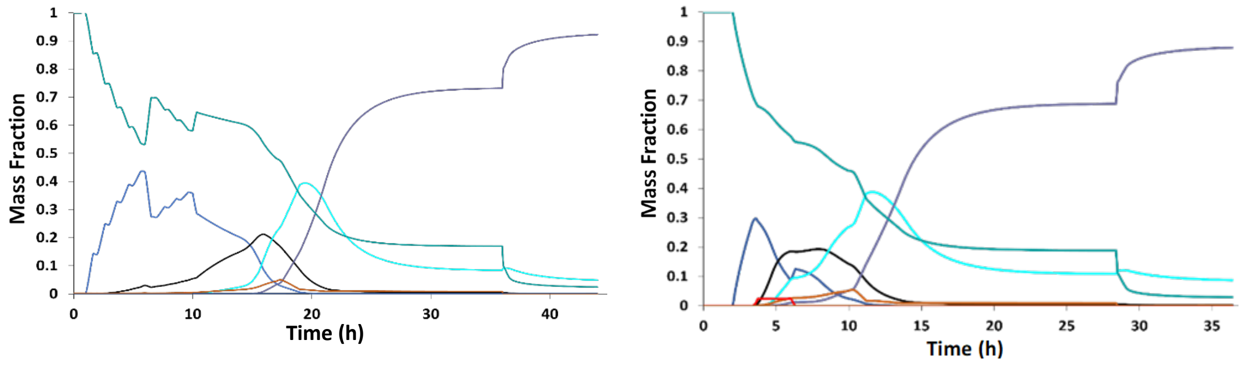

Figure 6: Mass fraction profiles **a)** conventional process, **b)** SAE process. (—) BuOH, (—)CA, (—) MBC, (—) DBC, (—) TBC, (—) H_2O, (—) H_2SO_4

Table 1: Utility costs per batch in the production of TBC for the conventional and novel processes

Utility	Conventional process		Novel Process
	Citric Acid Production	Dissolution - Esterification	Acidification - Esterification
Steam	$266.58	$66.88	$106.914
Electricity	$107.09	$244.27	$209.41
Process Water	$43.04	$4.81	$18.46
Cooling Water	$2.28	$0	$6.15
Solid Waste Disposal	$310.53	$0	$270
TOTAL	$1045.514		$610.94

within existing equipment in the CA plant (stirred tank, filters, and fluidized bed dryers).

- **Washing:** Contact with water (1 kg water / 1 kg calcium citrate) is done to remove impurities from the precipitated calcium citrate. A contact time of 1 hour is considered. The batch module is considered to perform the mixing.
- **Filtration:** Conveyor belt filters separate calcium citrate from the washing water.
- **Drying:** The remaining moisture from the calcium citrate is removed through the fluidized bed dryers. This ensures that no water enters the acidification-esterification stage.

Similar to the filtration and drying steps in conventional CA production, solid separator and crossflow convective dryer modules are used to simulate these operations in calcium citrate pretreatment. When the clean calcium citrate is obtained, it is fed into the simultaneous acidification-esterification process. This process is assumed to be carried out in the same dissolution vessel and esterification reactor used in the conventional process. Considering that, as experimentally verified in the solid-liquid reactive system, the solubility of the evolved citric species in alcohol is rapid (10), the dissolution stage of CA in BuOH is not required. Therefore, the time of addition of the citric species will depend on the feeding capacity of the reactor. Then, a feeding rate of calcium citrate of 4126 kg/h is considered. This feeding rate can be achieved through hoppers coupled to screw conveyors. The mass of calcium citrate fed to the reactor (9583.33 kg) is equivalent to the same citrate moles considered in the previous section.

Once the calcium citrate is introduced into the BuOH, sulfuric acid is added to the reactor to promote the release of CA. A slight excess of H_2SO_4 ensures complete acidification and facilitates the esterification reaction. The process is halted when the amount of MBC (Monobutyl Citrate) produced is equal to that generated in the dissolution stage of the conventional process. Once this point is reached, a stoichiometric amount of calcium citrate is added to neutralize the slight excess of sulfuric acid. This addition ensures that no residual H_2SO_4 remains in the subsequent stages of the process.

Subsequently, the acidified and partially esterified mixture is filtrated to remove the calcium sulfate that is produced. It is assumed that the remaining solid fraction, discarded as waste, constitutes 4% by weight of the reactive mixture. This assumption is made because separation in a filtration process is not 100% efficient. Therefore, two additional batches must be processed to achieve the same amount of TBC production. After filtering the reactive mixture, it is returned to the esterification reactor, and MSA is added. Once the esterification process is completed, the pressure within the system is reduced to remove the remaining BuOH and water. Operating conditions are presented in the supplementary Information.

Similar to the simulation of the CA dissolution and esterification in the conventional process, the novel process is performed using the RBatch and the BatchSep modules. These modules enabled the implementation of the simulation for the novel process and its specific operating policies (e.g., single feeds or scheduled feed configuration) using the same equipment. RBatch module enables modeling mixed, batch, and fed-batch operation conditions employed in the industrial production of TBC. On the other hand, the BatchSep module allows the modeling and scheduling of batch distillation columns when connected to the batch reactor.

Continuous water removal is possible because the more volatile compounds (H_2O-BuOH) are distilled off from the reactive media during the esterification when operating at the bubble point of the mixture. Nevertheless, BuOH removal is not desired since the reaction driving force would be diminished, striking esterification performance. Thus, assessment of the impact of simultaneous reaction and water removal is paramount to identifying the best operating policies to improve TBC yield.

With all previous considerations, we present a TBC production cost analysis focused on the utility costs of the conventional process concerning those of the SAE process. Capital costs were not considered because it is assumed that the same equipment is used in both processes and they are already available in the studied industrial facility. A composition profile of the two scenarios was merged, allowing the comparison with previous reports on the behavior of the conventional process. Also, a novel fed-batch operating policy developed during the experimental evaluation of simultaneous acidification-esterification (10) was tested and analyzed for the SAE process.

RESULTS

TBC Production Conventional Process

The mass concentration profiles over time during the production of TBC using the conventional industrial process are illustrated in Figure 6a. These profiles match those reported in a previous study (11) where a dilution stage (t < 18h) enabled MBC production as the main citrate ester and accumulation of water is observed. Due to the low solubility of CA in the medium, alternating feeding is required to ensure all the acid dissolves. A high temperature (~60°C) is also necessary to accelerate the dissolution process.

Once the CA dissolution is completed, the temperature of the reactive medium is increased to the bubble point of the mixture (~130 °C). From this point, the production of DBC and TBC is increased and a vapor stream is generated, allowing for the removal of water from the top of the distillation column. However, there are differences compared to the previous report (11), as a higher concentration of DBC was observed in the reactor. This difference is caused by the remaining water in the reactive liquid, limiting the conversion towards TBC. Therefore, the final product will have a higher acidity content than required (acidity > 0.5 %p). The results coincide with what is reported for the industrial process, as the reactor effluent usually requires a subsequent neutralization stage to remove the remaining citric acidity and the catalyst. As observed, the process includes CA loading, dissolution, and esterification and the process lasts around 45 hours.

Regarding the costs derived from the utilities required in the production of TBC, it can be seen that the stage of obtaining anhydrous citric acid constitutes ~72% of the overall operating costs. This result was expected considering the significant dilution of CA in the fermentation broth and the large amount of water to be evaporated from the CA crystals. Another substantial cost is the handling of solid waste generated in the acidification of the calcium citrate. Notably, a large amount of low-added value gypsum is produced during acidification in the existing industrial process. Although the obtained gypsum could be a salable by-product, purification to meet commercial specifications involves significant costs. So, in this case, this stream was assumed to be a waste and the disposal costs were estimated and internalized.

TBC Production Proposed Process

As observed in Figure 6b, the direct feeding of calcium citrate reduces dissolution times to carry out the esterification reaction. Additionally, the recovery of the citric species can occur at lower temperatures (e.g., 40 °C). Using an excess H_2SO_4 ensures that the esterification process concurs as CA is released. As a result, the process with calcium citrate achieves a concentration of 18% wt. MBC in the liquid phase in 6 hours of reaction. In contrast, during the dissolution in the conventional process, 15 hours are required to achieve the same MBC content.

After the acidification-esterification stage, conventional esterification is carried out with MSA as a catalyst, and vacuum purification enables excess BuOH and remaining water removal (Figure 6b). As in the conventional process, achieving the purity required to commercialize the TBC would be difficult, and a neutralizing stage is needed to remove the remaining acidity. While the process would be completed in 36 hours, the system seems to reach equilibrium in about 18 hours, considerably shorter than the 25 hours required for reaction in the conventional process, counting for a reduction by about 25% in reaction time to reach equilibrium condition.

Finally, as presented in Table 1, it is observed that the cost related to steam consumption for CA purification presented a higher difference. It can be seen that the steam-related costs are the lowest for the novel process compared to the conventional configuration related to the 68% reduction in steam usage per unit of citrate esterified in the SAE process. This is mainly attributed to the direct use of calcium citrate as the CA backbone carrier for TBC synthesis, avoiding all concentration stages commonly used in the purification of CA. The concentration stages in pure CA production (e.g., evaporation, crystallization, and drying) need a great amount of energy to evaporate close to 10 kg of water per kg of CA, to achieve the purity conditions necessary to perform esterification. As seen in Table 1, the cost associated with pure citric acid production accounts for ~70% of the utility costs in the conventional process. The other utility costs in the conventional process summarized in Table 1 do not show a massive reduction compared with the SAE process (mixing, vacuum, solid disposals, etc.) since these operations remain almost unaltered.

Despite both processes generating calcium sulfate, the one obtained from the novel process is in the form of a semi-hydrated form. This form may have potential as a valuable industrial by-product. Moreover, by crystallizing in an organic medium, the particle size distribution and the purity of the obtained crystal may generate commercial interest (14). The cost associated with the utilities used in the SAE process reflects cost savings of 41% compared to those of the conventional process. Such reduction allowed a 1.8% decrease in the TBC operating costs.

The SAE process could also be helpful in a possible continuous configuration for TBC production. As reported previously, continuous reactive distillation (RD) has arisen as a promising alternative for TBC production(5)(10). Since RD allows for the simultaneous esterification reaction and water removal, inherent equilibrium limitations are overcome. In these works, it has been identified that using a pre-reactor stage is beneficial to reduce RD column size or increase TBC production capacity (5). This pre-reaction stage could be performed via SAE processes. As described, this process has a fed-batch configuration. Also, some stages like calcium citrate feed and calcium sulfate removal would make it difficult to couple the SAE process with RD. Some strategies like equipment redundancy or using tanks for pre-reacted mixture storage, could help to overcome these issues. This configuration will be evaluated in future work.

CONCLUSIONS

This work presented a comparative assessment of a conventional and innovative process for the industrial production of TBC. The novel SAE process employs calcium citrate as raw material instead of CA to produce citric acid esters. Based on experimentally established reaction kinetics and validated thermodynamic models, it was possible to simulate the solid-solid-liquid reaction occurring during the simultaneous esterification-acidification stage in the SAE process. Reduction in the utility costs and in the time to perform the esterification reaction could lead to a significant increase in TBC's production and capacity, alongside an increase in the economic viability of TBC (1.8% cost decrease due to operating costs) using the existing industrial infrastructure. Moreover, although not quantified in this work, the reduction in process units also leads to potential capital cost reduction. As a follow-up to this work, an optimization-based cost analysis will be carried out to minimize the total (fixed and operational) process costs for a new industrial facility using the novel SAE process. This analysis can also be done to retrofit an existing TBC production plant using the conventional process.

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DIGITAL SUPPLEMENTARY MATERIAL

The supplementary material can be found with the LAPSE ID: 2023.36926

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