



Green upgrading of succinate using dimethyl carbonate for a better integration with fermentative production



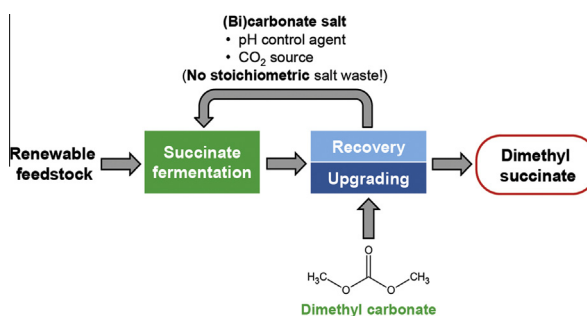
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HIGHLIGHTS

- Anion exchange resin was used for succinate sorption from neutral aqueous solutions.
- The resin released (bi)carbonate, which is required in succinate fermentation.
- The sorbed succinate was converted into dimethyl succinate using dimethyl carbonate.
- This reconverted the resin from succinate to (bi)carbonate form.
- This closes all loops, while using dimethyl carbonate as green solvent and reagent.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we present a new process alternative comprising bio-based succinate production, its recovery by ion exchange and further upgrading to dimethyl succinate via *O*-alkylation by direct downstream catalysis. The use of dimethyl carbonate as alkylating agent permits the *in-process* generation of a mobile bicarbonate anion, playing the role of counter-ion during succinate capture and then transported upstream where is used as inorganic carbon source and neutralizing agent required for most bacterial succinate fermentations. Succinate recovery using a strong anion exchange resin in the bicarbonate form presented good equilibrium characteristics and column performance. Subsequently, dimethyl succinate was produced in high yield (96%) using dimethyl carbonate as a solvent and reagent and the kinetics of the system were described by a pseudo-first order model. Throughout the reaction and in the presence of water, it was verified that the resin is effectively regenerated to its bicarbonate form maintaining its ion exchange capacity. As a main advantage, the validated concept leads to an improved bio-based process for succinate to ester derivatives where no stoichiometric waste is produced, contrary to conventional acidification–esterification operations.

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1. Introduction

Succinic acid is an attractive renewable platform chemical due to its chemical functionality and valuable derivatives [1]. Among them, succinate esters are considered to be precursors for many petrochemical products and can be used as a monomer for a wide range of polymers [2]. To realize such platform potential, research

efforts have focused on its biotechnological production [3–5], downstream processing [6,7] and chemical modification [8,9]. Although the results of such advances are applied by many industrial enterprises around the world [10–13], there are still many challenges concerning undesired salt production [14]. Waste production and chemicals consumption can still be reduced significantly for improving the sustainability of a succinate-producing biorefinery.

Bio-based production of succinic acid using bacteria runs most efficiently at neutral pH. The base addition required to maintain

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neutral pH leads to production of divalent succinate salt [15–18]. The salt should be converted back into the acid and purified thoroughly, involving the consumption of mineral acid and stoichiometric production of waste salt, before traditional methods can be applied for the upgrading of succinic acid to derivatives, e.g. esters [19], or polymers. Dimethyl succinate (DMS) is a promising alternative to petrochemical dibasic esters with direct applications as solvent and polymer additive and will be produced shortly from bio-based succinic acid [20]. As a polymer platform, DMS offers advantages over succinic acid since can be polymerized using current transesterification polymerization methods, which are simpler than the direct melt polymerization methods required for succinic acid [2,21,22]. To achieve this, DMS should be produced efficiently and it is believed that integration of green chemical transformation routes into succinate recovery may improve production economics and efficiency [23].

In a previous publication [24] we applied the concept of direct downstream catalysis to integrate recovery and chemical upgrading of succinate without intermediate acidification. In that study, we proposed and validated experimentally a new route for diethyl succinate production from a succinate salt via *O*-alkylation using chloroethane as alkylating agent and a commercial macroporous strong anion exchange as both sorbent and catalyst [24]. Although the calculated overall atom efficiency and E-factor demonstrated the advantages of the integrated process over the conventional acidification–esterification route, the halogenated alkylating agent is not considered to be green and led to chloride salt as by-product, reducing the attractiveness of that particular reaction system.

We believe that the above mentioned issues can be overcome by the use of dimethyl carbonate (DMC) as alkylating agent. DMC is a nontoxic, biodegradable solvent currently produced from syngas and methanol [25,26] and in the future from carbon dioxide and hydrogen [27] which makes it a true green reagent. Compared to other alkylating agents, it is efficient in terms of atom economy and waste generation, producing carbon dioxide and methanol as by-products [28], in which the latter may be recycled to its synthesis. In spite of the above mentioned benign characteristics, the reactivity of DMC is low and depends on reaction conditions, undergoing methylation reactions with a large number of nucleophilic substrates [29] at temperatures ranging from 90 to 175 °C depending on the catalyst used [30–32]. Under the direct downstream catalysis approach, dimethyl succinate formation using DMC could permit cascade up integration to fermentation, leading to an improved bio-based succinate production process. However, the feasibility of such reaction system has not been reported in literature and should be demonstrated first.

The objective of this work is therefore to verify the main reaction features allowing the realization of a new conceptual process. The alkylation stoichiometry and in particular the nature of the resin counter-ion after alkylation was addressed. Furthermore, it was established that quaternary ammonium functional groups such as found in commercial strong anion exchange resins were able to act as a catalyst under mild temperature conditions. The temperature effects on the reaction kinetics were interpreted by a pseudo-first order kinetic model. Finally, based on our previous experience [24], the effects of water on methylation yield and rate were determined.

2. Process conception

According to the state of the art description for reactions using DMC, it is possible to assume that carbon dioxide-related species, i.e. carbonates, produced during alkylation could play the role of mobile anion within our proposed process. Having that in mind, it is possible to describe the new integrated route as consisting of

two reactive stages. Firstly, the succinate anion is captured from an aqueous solution such as produced by fermentation by means of a strong anion exchange resin in a (bi)carbonate form (Fig. 1) releasing the respective (bi)carbonate salt. Next, sorbed succinate is *O*-alkylated at both its carboxylate groups by DMC. The reaction is catalyzed by the quaternary ammonium functional groups (Q^+) to which succinate anion is electrostatically bound. As a result of the reaction, dimethyl succinate is formed whereas the anion exchange material is left in a proper ionic form in order to keep electroneutrality. During this stage, several reactions might occur as depicted in Fig. 2. In the absence of water, the methoxycarbonate anion (DMC leaving group) could remain attached as a whole to the basic functional group (Fig. 2a) in a similar manner as reported for *N*-methylations [33]. Although not reported before, methoxycarbonate might also react further and participate in a second methylation reaction yielding a resin in a carbonate form (Fig. 2b). In the presence of water, the decomposition of the bound methoxycarbonate anion could lead to the formation of bicarbonate anion and methanol with the former remaining bound to the resin (Fig. 2c). Moreover, water might hydrolyze DMC in a side reaction (Fig. 2d).

It is possible to foresee the impact of both ion exchange sorption and *O*-alkylation DMC-based stoichiometries on the sustainability of the overall bio-based dimethyl succinate process. From a recovery perspective the anion exchange material is regenerated in the (bi)carbonate form through the alkylation process. Therefore it can be used in a new succinate sorption cycle. Then, the (bi)carbonate anion is released in aqueous solution and its use can be extended further to the fermentation process, playing the role of neutralizing agent required for maintaining optimal production pH, as described elsewhere [34,35]. Additionally, the best bacterial succinate fermentations require carbonate species as carbon source in addition to carbohydrates to achieve optimum yields [34]. In such cases, the (bi)carbonate obtained from DMC will also provide (at least partially) the necessary carbon for biosynthesis of succinate. A similar combined effect has been reported [36], avoiding the need of gaseous carbon dioxide supply. The complete block diagram for this alternative process can be seen in Fig. 3.

Our process alternative has various advantages when compared to a conventional acidification–esterification route (Fig. S1). The number of operations has been reduced and new intensification opportunities are possible since succinate sorption, resin drying and DMS production operations may be carried out in the same process unit. Moreover, the chemicals consumption and waste production are also reduced as alkylation by-products derived from the decomposition of the DMC leaving group can be recycled, maximizing the carbon usage. Overall, a process without stoichiometric waste production has been conceived.

3. Materials and methods

3.1. Materials

All chemicals were analytical grade (Sigma–Aldrich) and were used without any purification. Aqueous solutions were prepared using deionized water from a Mili-Q water purification system (Millipore). Succinate solutions were adjusted to pH 7.00 ± 1.0 in two steps, first using solid sodium hydroxide to a pH around 6 and to neutral pH with 1 mol/L aqueous NaOH solution. In a previous study [24], the resin Dowex Marathon MSA was selected due to its capacity and catalytic activity. The resin is a strong anion exchanger, with a type I quaternary ammonium functional group, macroporous structure and monodisperse bead size. According to its commercial specification, it has a mean particle size of $640 \pm 50 \mu\text{m}$ and a

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