Catalysis Today 239 (2015) 17–24

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes

José M. Pinazo[a], Marcelo E. Domine[a,*], Vasile Parvulescu[b,*], Filip Petru[c]

[a] Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain
[b] University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, Bdul Regina Elisabeta, 4-12, Bucharest 030016, Romania
[c] "Costin D. Nenitzescu" Center of Organic Chemistry of the Romanian Academy, Spl. Independentei 202B, Bucharest 060023, Romania

ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form 29 April 2014
Accepted 1 May 2014
Available online 1 July 2014

Keywords:
Succinic acid
Biomass fermentation
Biomass derivatives
Sustainability
Green metrics

ABSTRACT

Biomass-derived succinic acid (Bio-SA) has been described as a strategic platform chemical, due to its potential as the C4 building block in industrial organic chemistry. Sustainability of SA production via fermentative synthesis was studied through two different processes (Myriant and Reverdia cases) and compared with the corresponding petrochemical route. Four groups of parameters, namely material efficiency, economics, energy efficiency and land use were considered. Green metrics results show that energy efficiency for Bio-SA production is slightly higher while material efficiency is rather lower when compared with the petrochemical counterpart. Remarkably, Bio-SA calculated costs (≈1040€/MT in the worse case) are quite lower than the actual prices for Petr.SA and close to the price of maleic anhydride used as raw material. Thus, bio-based SA production appears to be competitive with petrochemical route for MAN. Competitiveness of Bio-SA can be boosted by optimization of fermentative process, as well as by the Bio-SA upgrading to high added value chemicals.

1. Introduction

Succinic acid (SA) is the conventional name of butanedioic acid. This has been described as a compound of a strategic importance in a future chemical industry based upon renewable raw materials, and it can be found in the priority "Top 10" list of biomass-derived compounds, elaborated by the Energy Department of the USA [1–3]. Despite its uses in agricultural, food and pharmaceutical industry [4], SA has been considered a niche product and never a relevant intermediate in the chemical industry, mainly due to its high price [5,6].

Succinic acid production from renewable feedstock is getting growing attention in the last years due to a combination of factors, such as the continuously increasing oil prices, improvements in fermentation and recovery technologies, and most importantly, its potential as the future C_4 building block in industrial organic chemistry [7,8].

Certain concern about the future importance of succinic acid has been found in literature as early as in the 1990s. In this sense, production of biomass-derived succinic acid (or BioSA), *via levulinic acid*, was evaluated as potentially competitive with the petrochemical route. However, known processes were still not efficient enough and BioSA was considered subject of long-term research [9]. For instance, whilst historical prices of succinic acid lie between 6 and 9$/kg SA [4,5], costs of 0.55–1.10$/kg BioSA [10] were predicted and communicated in 2003, and reported to be close to competitiveness short time later [11]. In 2006, the BREW Project, dealing with Green Metrics, concluded that succinic acid would be competitive with respect to its petrochemical alternative only in a scenario where the highest oil prices and lowest renewable feedstock prices were considered [12].

From 2008 on and right after the peak oil prices in 2007, a number of corporations and joint ventures (such as BioAmber [13], Myriant [14], DSM & Roquette joint venture, Reverdia [15] or BASF&Purac, subsidiary of CSM [16]) showed their interest on BioSA production at an industrial scale [17]. As a consequence, at least two industrial units with 4000 MT/year and 10,000 MT/year capacities for BioSA production have been built up and they are actually

* Corresponding authors at: Instituto de Tecnología Química (UPV-CSIC), Avda. Los Naranjos S/N, 46022 Valencia, Spain, Tel.: +34 963879696; and University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, Bdul Regina Elisabeta, 4-12, 030016 Bucharest, Romania, Tel.: +40 214100241.
E-mail addresses: mdomine@itq.upv.es (M.E. Domine), vasile.parvulescu@g.unibuc.ro (V. Parvulescu).

http://dx.doi.org/10.1016/j.cattod.2014.05.035
0920-5861/

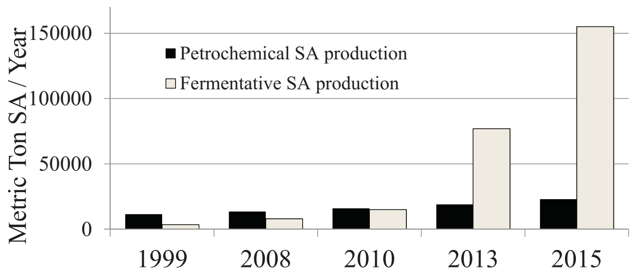

Fig. 1. Evolution of worldwide succinic acid production, in metric ton per year.

running. At this point, it can be said that succinic acid production from biomass-derived raw materials is nowadays very close or even reached the threshold of profitability from industrial point of view. Nevertheless, mid-term feasibility of the deployment of succinic acid technologies will strongly depend on its introduction as a real alternative to petrochemical intermediate compounds such as maleic anhydride (MAN), and also on the development of downstream technologies for products like 1,4-butandiol (1,4-BDO) and poly-butylene succinate (PBS) [18].

Worldwide SA production has grown from 15,000 MT a year in 1999 [4], to the 35,000 MT in latest communications available by end 2011, in which a 10% yearly increase was reported [19]. The reason of this increase is the growing BioSA, since petrochemical production has remained stable for years [5,13,20]. Actual situation is the turning point at which fermentative SA production overcomes its conventional production, in order to progressively grow up to a total 180,000 MT a year predicted by 2015, as it is shown in Fig. 1.

2. Production

2.1. Petrochemical process

Processes for the synthesis of succinic acid starting from fossil resources are based on catalytic hydrogenation of 1,4-dicarboxylic unsaturated C4 acids or anhydrides, and in a lesser extent via oxidation of 1,4-butanediol [21,22]. Carbonylation processes starting from ethylene glycol, ethylene, acetylene, dioxane or unsaturated C3 carboxylic acids or β-propiolactone are also leading to succinic acid or its esters [22].

Most direct petrochemical route to succinic acid is liquid-phase maleic anhydride hydrogenation to succinic anhydride (SAN) followed by the hydration of the later to succinic acid. This two-step process can be schematized like it is shown in Fig. 2 [21].

Maleic anhydride (MAN) hydrogenation takes place in the liquid phase at temperatures ranging from 120 to 180 °C with hydrogen pressures between 0.5 and 4.0 MPa, commonly employing metallic redox catalysts based on Ni or Pd. Succinic anhydride yields are close to the theoretical, with impurities such as non-reacted maleic anhydride, and γ-butyrolactone. The hydration step takes place directly when succinic anhydride is dissolved in hot water. Succinic acid is afterwards separated by crystallization, filtration and drying.

Input and output of a typical succinic acid production system was quantified following a factory gate-to-gate approach starting

Table 1
Inventory per metric ton SA produced via maleic anhydride hydrogenation and hydration.

Input		Output	
Maleic anhydride	890.08 kg	Succinic acid	1000.00 kg
Hydrogen	254.31 kg	Waste (generic)	319.00 kg
Water	304.62 kg		
Nitrogen	72.88 kg		
Palladium catalyst	0.01 kg		
Natural gas	101.72 kg		
Electricity	356.03 kW h		
Total	1319.00 kg 356.03 kW h	Total	1319.00 kg

from bibliographic data [21]. It is necessary to point out that literature data comprise only the first step of succinic acid production (i.e. maleic anhydride hydrogenation). Therefore a reasonable series of hypotheses was needed for the calculations to be performed, including data for hydration to succinic acid step as well as some other values by considering the overall process (see also Supporting information). By hypothesis, refrigeration water and steam were considered to be recycled within the process, at a cost included in the energy sources consumption. Water in the hydration tank was also considered to be recycled, the total consumption being twice the stoichiometric amount needed for succinic anhydride hydration. Recycling and in situ purification of water in the hydration tank was considered to raise electricity consumption by 20%. A hypothetical 50% raise was also applied to nitrogen and methane consumption due to the addition of the hydration step to the system. Palladium catalyst loss was considered to be 0.001 wt% respect to the succinic acid produced. The resulting inventory, which was directly employed as the basis for metrics calculation, is shown in Table 1.

2.2. Bio-based processes

Efforts made up until today on succinic acid synthesis by a purely chemical process with renewable feedstock include a heterogeneous catalytic process employing levulinic acid as starting compound [23]. As mentioned above, this process has never been considered of an industrial interest [9].

Most important process for succinic acid production from renewable feedstock is microbial fermentation of different glucose sources. Succinate producers include micro-organisms such as genetically engineered *Escherichia coli*, *Actinobacillus succinipro-ducens* and *Anaerobiospirillum succiniproducens* [4,7,9,11]. Eq. (1) is the theoretical chemical equation for this fermentative process.

$$C_6H_{12}O_6 + 0.86HCO_3^- \rightarrow 1.71(COO^-)CH_2CH_2COO^- + 1.74H_2O + 2.58H^+ \quad (1)$$

2.2.1. Base case: Myriant succinic acid biorefinery

Myriant's succinic acid biorefinery in Lake Providence (Louisiana, USA) employs grain sorghum grits as its saccharificable starting material. A gate-to-gate inventory similar to the petrochemical succinic acid one was elaborated starting from

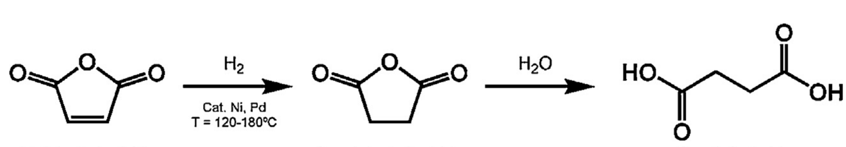

Fig. 2. Succinic acid production starting from petrochemical-derived maleic anhydride.