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Review

Succinic Acid: A New Platform Chemical for Biobased Polymers from Renewable Resources

Succinic acid is predicted to be one of the future platform chemicals that can be derived from renewable resources. The improvements in biotechnological succinic acid production are presented. Chemical conversion pathways to γ-butyrolactone, tetrahydrofuran, 1,4-butanediole, and pyrrolidones are reviewed. An overview of possible new biopolymers (e. g. polyesters, polyamides, and poly(ester amide)s) based on succinic acid and its derivatives is given. Nevertheless, industrial processes using purified succinic acid from fermentation broths are not state of the art yet. Further improvements are needed until succinic acid-based chemical production will be economically favorable.

1 Introduction

For more than 150 years, the chemical industry has been producing a large variety of products from coal, gas, and oil. The resources in these fossil raw materials are limited and if these resources will further be used with the present consumption rates, they will be running out in the forthcoming 100 years. The remaining oil resources are estimated to be $165 \cdot 10^9$ tons. If crude oil consumption remains on the same level as today (in 2002, $3.3 \cdot 10^9$ tons) they will be depleted in a period of 50 years [1]. Beside the limited repository, the use of fossil resources leads to worldwide environmental problems and increasing CO_2 concentrations in the atmosphere. These problems initiated an increasing demand for new CO_2 neutral resources for the future.

Nature offers a wide range of resources mainly from plants due to fast biomass building with low efforts. In comparison to the contemporary naphtha chemistry, only a few industries (e.g. biofuels, wood, and paper processing) are using this immense reservoir of resources. Still the diversity of biomass feedstocks and the lack of conversion technology routes prevent an increased utilization of natural resources. Nevertheless, biobased platform chemicals – building blocks for numerous chemical intermediates and end products [2] – are recognized as a burning issue in research, politics, and the industry in the last decade.

Several countries have evaluated the potential of biobased chemicals [3–7] or biobased polymers [8] by governmentally-funded projects. The main aspects of these reports – e.g. national availability [3], integrated biorefinery concepts [7] or white biotechnology [6] – led to the identification of different types and numbers of building blocks. In all these reports, succinic acid was identified as one of the most important platform chemicals. The suitability of succinic acid as a platform chemical is based on the ease of its biotechnological production and on the huge variety of chemicals that can be produced from it by chemical conversion (compare Fig. 1).

2 Biotechnology

Succinic acid has been used in the food industry since Robert Koch proved that it has a positive influence on the human metabolism without a risk of accumulation in the human body.

Today, succinic acid is mainly produced by chemical process from *n*-butane/butadiene via maleic anhydride, utilizing the C4-fraction of naphtha in quantities of about 15,000 tons per year with a price range of about 6–9 \$/kg. Beyond fossil-based chemistry, derivatives of succinic acid are announced to have a potential of hundreds of thousand tons [6, 7, 9].

Succinic acid is an intermediate of the TCA cycle (tricarboxylic acid cycle, citric acid cycle) and one of the fermentation end-products of anaerobic metabolism. The fact that carbon dioxide (CO_2) is needed by the microorganisms for succinic acid production is another interesting feature.

Many different microorganisms like fungi (different *Aspergillus stc.*, *Byssochlamys nivea*, *Lentinus degener*, *Paecilomyces*

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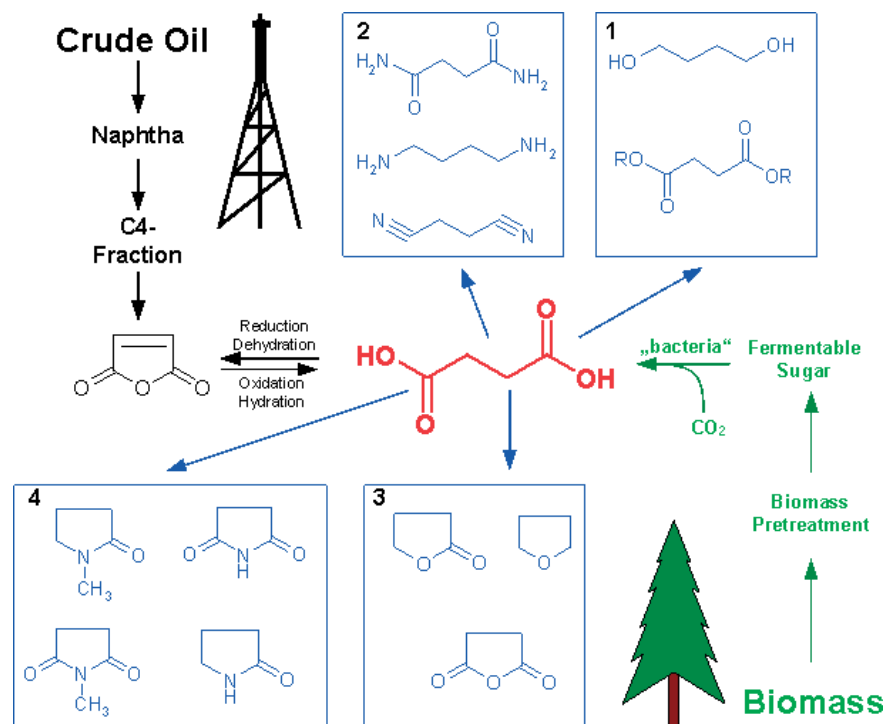
Figure 1. Possible pathways for succinic acid production and products derived by chemical conversion: 1) Acylic O-containing, 2) acyclic O,N-containing, 3) cyclic O-containing, 4) cyclic O,N-containing.

varioti, Penicillium viniferum [10, 11]), yeast (*Saccharomyces cerevisiae*), and Gram-positive bacteria (*Corynebacterium glutamicum, Enterococcus faecalis*) have been screened and studied for succinic acid production. Most intensively studied are *Anaerobiospirillum succiniciproducens* [12] and *Actinobacillus succinogenes* [13] due to their ability to produce a comparatively large amount of succinic acid. More recently, *Mannheimia succiniciproducens* MBEL55E was isolated as a natural succinic acid overproducer from bovine rumen by Lee et al. [14]. Additionally, there have been great efforts in developing recombinant *Escherichia coli* strains, which are capable of enhanced succinic acid production under aerobic and anaerobic conditions [15–17].

2.1 Natural Overproducers

A. succiniciproducens and *A. succinogenes* were the first identified natural succinic acid overproducers.

A. succiniciproducens was isolated from the throat and feces of a beagle dog [18]. This microorganism produces succinic and acetic acid as major fermentation products, and ethanol and lactic acid as minor ones under strictly anaerobic conditions [19]. *A. succiniciproducens* can utilize glucose, glycerol, sucrose, maltose, lactose, and fructose as carbon sources. Lee et al. [20] reported the use of glycerol as carbon source which leads to an increased succinic acid yield (1.33 mol/mol) and a higher ratio of succinic acid to acetic acid compared to glu-

cose-based cultivation. In addition, a possibility for cost-effective succinic acid production has been presented using untreated whey, wood hydrolysate, and corn steep liquor, which are much less expensive than refined carbohydrates and yeast extract, respectively [21, 22]. Lee et al. [19] reported a maximum succinic acid yield of 0.91 mol/mol and a maximum productivity of 1.8 $gL^{-1}h^{-1}$.

Meynial-Salles et al. [23] observed growth inhibition caused by the endproducts, succinic acid and acetic acid. The introduction of a coupled mono-polar electrodialysis for removing the end products from the fermentation broth enhanced growth, productivity, and final product concentration. Biomass concentration could be increased to 42 gL^{-1}, the maximum productivity reached 10.4 $gL^{-1}h^{-1}$ and a final concentration of 83 gL^{-1} could be achieved. The yield of 1.35 mol/mol is even higher than Lee et al. [20] reported using glycerol as carbon source. One of the workpackages in a research project concerning succinic acid utilization as a platform chemical conducted at Fraunhofer UMSICHT is the optimization of fermentative production with *A. succiniciproducens* [24].

A. succinogenes was originally isolated from bovine ruminal contents. This organism metabolizes glucose to succinic acid, acetic acid, and formic acid [25]. The *A. succinogenes* 130Z strain and its variant strains were able to produce larger amounts of succinic acid and were more resistant to succinic acid than any other previously reported succinic acid producers [26, 27]. Strain 130Z produced 66.4 gL^{-1} succinic acid by consuming 98.3 gL^{-1} of glucose after 84–h fermentation. The batch cultivations were performed with 15 gL^{-1} of yeast extract and corn steep liquor. The main problems of *A. succinogenes* fermentation are the high concentrations of byproducts like acetic acid, propionic acid, and pyruvic acid which lead to high costs for product separation.

2.2 Recombinant Producers

More recently, a new succinic acid overproducing strain, *M. succiniciproducens* MBEL55E, was isolated from bovine rumen [14]. A succinic acid productivity of 3.9 $gL^{-1}h^{-1}$ could be achieved, the highest value that has been reported so far. Furthermore, the efficient and economical production of succinic acid was possible by fermentation of *M. succiniciproducens* using a whey-based medium containing corn steep liquor instead of yeast extract [12]. Metabolic engineering led to increased succinic acid production and yield with simultaneous reduction of byproduct formation. The metabolic engineered strain produced 52.4 gL^{-1} succinic acid in 29 h in a fed-batch

process. The yield is reported by Lee et al. [28] with 1.16 mol/mol. Nevertheless, a growth stop after 19.5 h was observed when the succinic acid titer reached 36 gL^{-1}.

A wild-type strain of *E. coli* primarily produces ethanol, formic acid, acetic acid, and lactic acid together with merely trace amounts of succinic acid from glucose under anaerobic conditions. The succinic acid yield on glucose typically obtainable was no more then 0.2 mol/mol. A mutant strain, AFP111, could grow on glucose with a succinic acid yield of 1.0 mol/mol and a productivity of 0.87 gL^{-1}h^{-1}. Further metabolic improvement resulted in an enhanced productivity. The dual-phase fermentation comprised of an aerobic growth phase followed by an anaerobic production phase led to a succinic acid concentration of 99.2 gL^{-1} and a productivity of 1.3 gL^{-1}h^{-1} [15].

Recently, a metabolically engineered *E. coli* strain, capable of aerobically producing succinic acid through the glyoxylate pathway and the oxidative branch of the TCA cycle, has been developed. The aerobic fed-batch fermentation of this strain resulted in the production of 58.3 gL^{-1} succinic acid in 59 h with a succinic acid yield of 0.85 mol/mol glucose. However, the production of pyruvic acid (6.1 gL^{-1}) and acetic acid (3.0 gL^{-1}) could not be avoided [16, 17].

2.3 Downstream Processing

The downstream purification cost for fermentation-based processes normally amounts to more than 60 % of the total production costs. In the case of succinic acid purification, the separation of byproducts like acetic acid, formic acid, lactic acid, and pyruvic acid have a crucial effect on process costs. Furthermore, most specialty and commodity applications of succinic acid require the free acid form rather than the salt form. Several methods for purification of succinic acid, including electrodialysis, precipitation, and extraction have been reported.

Glassner et al. [29] investigated the purification of succinic acid by coupled electrodialysis, consisting of conventional electrodialysis followed by water-splitting electrodialysis membrane stacks, which removed most of the salt cations and produced a high purity acid stream. In order to separate the residual cationic, anionic and amino acids, cation and anion exchange resins were integrated into the above process as the final step. A succinic acid purity of 80 % could be achieved.

The purification of succinic acid by precipitation was reported by Datta et al. [30]. According to their method, succinic acid can be precipitated directly into the fermentation broth by addition of calcium dihydroxide, which simultaneously neutralizes the fermentation broth. Calcium succinate was recovered by filtration and converted to succinic acid by adding sulfuric acid. Succinic acid was recovered by filtration and further purified by acidic and basic ion exchangers. With this downstream processing method, a purity of 95 % could be achieved.

The extraction of succinic acid with an amine-based extractant (tri-*n*-octylamine and 1-Octanol as diluent) has been investigated by Huh et al. [31]. This process is based on a reversible reaction between extractant and extracted carboxylic acid. The selective separation of a specific acid from fermentation

broths containing mixed acids could be achieved based on the pKa values of the acids and the operating pH. The overall process contains additional steps, such as vacuum distillation and crystallization for high purity succinic acid production. Byproduct acids were effectively removed by reactive extraction as primary separation step. In addition, crystallization was applied without adding any salts to produce highly purified succinic acid. Succinic acid with 99.8 % purity and 73.1 % yield was obtained.

3 Chemical Conversion

Succinic acid has long been recognized to undergo a variety of reactions. Therefore, extensive literature on reactions of succinic acid exists. The general chemistry is summarized in [32].

Succinic acid is often called a "Green" platform chemical because it represents a potential building block (see Fig. 1), which can be transformed into several commodity or specialty chemicals [7, 33]. The succinic acid-derived products discussed which have industrial applications can be divided in 4 classes:
- acyclic O-containing: 1,4-butanediol, succinic acid esters
- acyclic O,N-containing: 1,4-butanediamine, succinamide, succinonitrile
- cyclic O-containing: tetrahydrofuran (THF), succinic acid anhydride, dihydrofuran-2(3*H*)-one (γ-butyrolactone)
- cyclic O,N-containing: pyrrolidin-2-one (2-pyrrolidone) and derivatives, pyrrolidine-2,5-dione (succinimide)

It is obvious that many of these compounds differ in the degree of hydrogenation or that they can be transformed by substitution of O/OH with NH/NH$_2$.

As shown in Fig. 1, succinic acid can be produced (and is produced today) by oxidation of fossil-derived maleic acid (anhydride). In biobased chemistry, succinates will be fermented from carbohydrates like sugar. Nevertheless, only a few articles consider the fermentative nature of "green" succinic acid.

Taking the neutral and salty nature of fermentation broth into account, diammonium succinate (DAS) was identified as a raw material for chemical syntheses. The production of 2-pyrrolidone (2-PDO) from DAS in aqueous media by hydrogenation using active metal catalysts has been described by Werpy et al. [33]. Hydrogenation in the presence of methanol using rhodium catalysts yields about 50 % N-methyl-2-pyrrolidon (NMP) and 30 % 2-PDO. Using N-methylsuccinimide as starting material and appropriate catalysts (2.5 % Rh/2.5 % Re/C) and reaction conditions (200 °C, 8 h, 130 bar H$_2$), nearly pure NMP (NMP:2-PDO = 67:1) could be obtained [33, 34–37]. This method of production of pyrrolidones is also described in [38]. It is claimed that the reactant composition can be derived from fermentation broths and that the transformation to pyrrolidones can be done as a one-step or two-step reaction. Direct hydrogenation of an aqueous diammonium succinate solution containing methanol and a Pd/ZrO2/C catalyst at 265 °C and 130 bar H$_2$ produces 2-PDO and NMP in a ratio of about 1:2 and up to 90 % yield. In the two-step reaction, the diammonium succinate or succinimide reacts with methanol, preferably at 280–320 °C without a catalyst followed by hydrogenation at preferably less than 230 °C with a carbon/metal oxide catalyst at 130 bar H$_2$.

The same working group has also developed a series of textured metal catalysts for the hydrogenation reactions in hydrothermal conditions [39]. These catalysts include a porous hydrothermally-stable support, a metal oxide precipitated on the support and a catalyst component. Highly selective aqueous phase hydrogenation of succinic acid to γ-butyrolactone (GBL) is shown as an example. Operating temperatures of 150–175 °C with pressures ranging from 56–140 bar and succinate concentrations of 5–25 wt % have also been reported [33]. It is said that fermentation byproduct, acetic acid, is not being reduced to ethanol. Additionally, a route from succinic acid to 1,4-butanediole (BDO) via GBL is mentioned. The purified GBL can be catalytically hydrogenated over bimetallic catalysts (Ni and Pd coupled with Rh) supported by carbon. The catalysts yielded selectivities greater than 95 % of BDO from GBL. Operating temperatures range from 150–200 °C with hydrogen pressures from 70–140 bar.

Some of the above noted results were published at an ACS symposium [40].

Considering the disadvantages of purifying steps that are needed using the process described in [38], Fischer et al. have presented a method for the production of succinimide and related compounds by reactive distillation of nitrogen-containing succinate salts in fermentation broths [41]. The distillation can take place with the addition of ammonia or diammonium succinate or primary amines for the production of succinimide or N-alkylated succinimides. Heat transfer media acting simultaneously as diluting agents are recommended. The distillate fractions can be reduced to 2-pyrrolidones and derivatives.

Without special considerations of the characteristics of fermentative succinic acid, the conversion of succinates into the interesting bulk chemicals, THF, GBL, and BDO has been described in early publications, e.g. the reduction of succinates over Cu-Cr oxide by Wojcik and Adkins in 1933 [42]. Consequently, many publications can be found. A previous review is given in [43]. Here, only the last five years are summarized. Alkylesters of polycarboxylic acids were manufactured by reactive distillation of ammonium salts of polycarboxylic acids with monoalkanols, e.g. dibutylsuccinate which was used for gasphase hydrogenation to THF in a reactor at 250 °C and 13 bar using CuO/Al_2O_3 as catalyst [44]. A process using a hydrogenation catalyst comprising one or more active hydrogen catalyst components on a rutile support for the production of GBL, THF, and BDO is described by Bhattacharyya [45]. A two-stage gas-phase hydrogenation process for the preparation of THF, BDO, and GBL from C4 dicarboxylic acid is presented in [46]. In the first stage, catalysts consisting of 5–95 % Cu oxide and 5–95 % of an oxide with acid centers are used to produce an intermediate stream mainly consisting of GBL and THF. The by-product succinic acid anhydride can be separated by partial condensation. THF, GBL, and water remaining in the gaseous phase are hydrogenated in a second reactor. Its products, THF, GBL, BDO, and water are separated by distillation; a GBL rich flow is optionally returned into the second reactor and the product ratios can be adjusted by varying the temperatures in the two hydrogenation reactors as well as the GBL reflux.

A homogeneous process is described for the hydrogenation of dicarboxylic acids and/or anhydrides in the presence of a catalyst comprising of Ru, Rh, Fe, Os or Pd and an organic phosphine. The reaction is carried out in the presence of ≥ 1 % water at a pressure of 35–140 bar and the product is stripped out of the reactor with hydrogen at 200–300 °C [47]. Improved bimetallic catalysts of Ru-Mo or trimetallic catalysts of Ru-Mo-Sn or Pt-Re-Sn with an inert support are used for hydrogenation of precursors (γ-butyrolactone, maleic anhydride, maleic acid, succinic acid) in an aqueous solution to produce BDO and THF [48, 49]. BDO can be produced from succinic acid anhydride using Raney-type catalysts in the form of hollow spheres [50].

A small review of current fossil-based technology for the production of BDO, THF, and GBL starting with acetylene, propylene oxide or butane/butadiene is given in [33]. The majority of GBL produced by cyclic dehydrogenation of BDO is used for the production of NMP.

4   Polymerization

In addition to succinic acid, the production of polyamides (PA), polyesters, and poly(ester amide)s requires components like diamines or diols. These products can also be obtained by chemical conversion of succinic acid (Section 3).

4.1   Polyamides

Polyamides are technical plastics with high performance levels. Their properties are characterized by high durability, and high hardness and rigidity simultaneously.

Carothers was the first researcher to perform systematic investigations of the polycondensation of dicarboxylic acids with diamines [51, 52]. Methods for the production of polyamides by polycondensation of aliphatic diamines and dicarboxylic acids or the polyaddition of lactams are described on a large scale in the literature. These articles are mostly dedicated to standard polyamides, from which the two "commodity polyamides", PA 66 and PA 6, constitute the predominant contingent. The established technical polyamides, PA 46, PA 11, and PA 12 as well as special polyamides like PA 610, can also be widely found.

PA 44 based on succinic acid and 1,4-butanediamine has up to date only been manufactured on the laboratory scale [53, 54]. A technical synthesis of PA 44 has not been described in the literature yet. Publications can be found concerning polyamides, either on the basis of 1,4-butanediamine (PA 4n) [55–58] or on the basis of succinic acid (PA n4) [56, 59–62]. These polyamide types show interesting and unexpected properties.

For example PA 24 possesses the same properties such as both silk proteins and commercial polyamides regarding IR absorption, solubility, and thermal behavior [62]. A short-chain aliphatic PA 42 manufactured by polycondensation of 1,4-butanediamine with diethyl oxalate could be interesting for use as fibers [56].

PA 46 was first produced in 1938 by Carothers [57] and is now distributed by DSM under the trade name Stanyl®. Carothers reported a melting point of 278 °C, which later was confirmed by Coffman et al. [58]. Other authors present a range

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of the melting point of PA 46 as a function of the thermal history from 283 °C to 319 °C [63–65].

Katsarava et al. [59–61] suggested a new polycondensation method for the synthesis of high-molecular weight polysuccinamides on mild reaction conditions.

4.2 Polyesters

Some homo- and copolyesters of succinic acid are manufactured industrially and are currently being introduced into the polymer market. Mitsubishi Chemical Corporation (Tokyo, Japan) has developed a new biodegradable plastic with the trade name GS Pla®, i.e. a poly(butylene succinate). Their goal is to produce a "Green Sustainable Plastic" using succinic acid produced by bacterial fermentation of corn and 1,4-butanediol [66].

Bionolle® (Showa Denko) is produced by polycondensation of glycols such as ethylene glycol and 1,4-butanediol together with aliphatic dicarboxylic acids such as succinic acid and adipic acid [67]. Bionolle® with a production capacity of 10,000 t/a is in the introductory market phase [68].

Polyester blown films have similar mechanical properties to the widely-used films from high-pressure polyethylene (LDPE). The most important factors for the biodegradability of polyester films are the structure and physical properties of the polymer, for example the morphology of crystals, the degree of crystallinity and their orientation, as well as the thermal and mechanical properties [69–71].

Polyesters (homo- and copolyester) can be manufactured by polycondensation of dicarboxylic acid esters with diols [70, 72–74]. A second way is the direct polycondensation of dicarboxylic acids with diols [63, 75–79] High-molecular weight polyesters are obtained by chain extensions from low-molecular weight polyesters with hexamethylene diisocyanate as a chain-extender.

4.3 Poly(ester amid)es

Biodegradable polyesters have attracted industrial attention as environmentally degradable thermoplastics used for a wide range of applications. Although polyesters are nowadays the most important family of biodegradable polymers in general, their thermal and mechanical properties are not optimal for industrial applications. Attempts have been made to regulate the physical properties and biodegradation rate of polyesters by copolymerization with various monomeric units. The properties of the polymer can be improved by the introduction of amide groups into the main chain, since these comonomers give rise to strong intermolecular hydrogen-bond interactions.

The physical properties, such as melting temperature and tensile strength of poly(ester amide)s, show a strong dependence on both the content and the distribution of the amide units in the polyester chains.

The first works were carried out in 1979 and were based on the amide-ester interchange reaction that takes place if a polyamide/polyester mixture is heated at temperatures near 270 °C [80]. Different biodegradable poly(ester amide)s were commercialized (BAK®) with a wide range of applications due to

their performance and processing facilities. For example, BAK1095 is manufactured from ε-caprolactam, adipic acid, and 1,4-butanediol. BAK2195 is a mixture of polyamide on the basis of 1,6-hexamethylenediamine and adipic acid with a polyester from adipic acid and 1,4-butanediol [81]. The production of BAK was stopped in 2001 due to economic reasons.

Novel biodegradable copolymers derived from succinic acid dialkyl ester, 1,4-butanediol, and 1,4-butanediamine were synthesized by two-step polycondensation reactions. The materials obtained had a periodic sequence structure consisting of ester and amide units. Melting temperatures of the periodic copolymers increased with an increase in amide content [82].

The favorable combination of properties of poly(ester amide)s is used with the development of new thermoplastic materials with good mechanical properties, processibility, and complete degradability.

5 Discussion and Conclusions

In this paper, a review of processes for succinic acid fermentation from renewable resources, its chemical conversion, and the production of polymers based on succinic acid were presented.

5.1 Biotechnological Production and Downstream Processing

Regarding literature today, four strains (*A. succinogenes*, *M. succiniciproducens* MBEL55E, *A. succiniciproducens*, and *E. coli*) are potential candidates for industrial succinic acid production. Many problems like slow growth, high by-product formation, and low yield could be solved partially by metabolic engineering. Nevertheless, a complete suppression of the by-products has not been achieved yet. Another problem for industrial application is the inhibitory effect of the cultivation product, succinic acid itself. Lee et al. [28] reported a growth stop after 19.5 h for the metabolic engineered strain of *M. succiniciproducens* when the succinic acid titer reached 36 gL^{-1}. Meynial-Salles et al. [23] made an energetic characterization of *A. succiniciproducens*. Based on the very low Y_{ATP} values, they assumed that the succinate export mechanism is ATP dependent. The *A. succinogenes* strain 130 Z has a higher tolerance for succinic acid and a concentration of 66.4 gL^{-1} could be achieved [26, 27].

Different methods were used for in-situ product removal to overcome the inhibitory effect of succinic acid during fermentation. Guettler et al. [26, 27] added high amounts of $MgCO_3$, Meynial-Salles et al. [23] coupled a mono-polar electrodialysis to a cell recycle bioreactor. A final succinic acid concentration of 83 gL^{-1} could be reached this way.

The subsequent problem of the biotechnological process is product purification (downstream processing). Regarding the rising energy prices, electrodialysis may probably not the best suited method. The power consumption is rather high for an intended bulk chemical. A second method for purification (Datta et al. [30]), precipitation, has the disadvantage of producing large amounts of waste. In the case of in-situ precipitation using calcium hydroxide not only succinic acid, but also

phosphate and sulphate will be precipitated from the fermentation medium.

Actually, the reactive extraction (tri-*n*-octylamine) reported by Huh et al. [31] seems to be the most promising method. In comparison to other processes, it requires less energy and produces less waste. Nevertheless, the long-term stability of such a combined process has to be proved because of the possible toxic or inhibitory effects of extractant and solvent for the microorganisms.

In order to get competitive with oil-based succinic acid production, further improvements in the composition of the fermentation medium have to be made. Regarding the media compositions reported in the literature, especially costly factors like peptone and tryptone must be removed from the raw materials. Furthermore, the amount of yeast extract should be reduced.

Screenings for cheaper carbon sources than glucose have already been performed. Literature shows that it is possible to use glycerol and wood hydrolysate as cheap carbon sources.

Summarizing the above, the future of fermentative production of succinic acid is promising considering the increasing acceptance of renewable raw materials, a large potential market size, the advantage of carbon dioxide fixation in the fermentation, and advances in the development of strategies for strain improvement, fermentation, and downstream processing.

5.2   Chemical Conversion

The utilization of N-containing succinates from fermentation broths for the production of N-containing derivatives of succinic acid seems to be a favorable method. Nevertheless, the above noted patents (see Section 3) for the production of pyrrolidones are not describing processes with real fermentation broths because:

- The separation of proteins and contaminants [38] or the use of "processed" aqueous fermentation solutions [41] is recommended.
- Extraction with (chlorinated) organics of semiproducts e.g. succinimide prior to hydrogenation is preferred [38].
- In an example in [41], the fermentation broth containing about 13 gL^{-1} diammonium succinate has been enriched with a fourfold amount of synthetically diammonium succinate.

It has to be revealed if the conversion reactions described will work in technical processes, or if the downstream processing of succinate fermentation broths will lead to other solutions in terms of energy, sustainability, and cost efficiency. It is one of the challenges to develop new integrated processes. The development of new catalysts providing water resistance, stability, and high transformation rates is very important for new raw material feedstocks from fermentation. Energy- and time-consuming processes for water removal thus could be avoided.

5.3   Polymerization

Polyamide: Although only a few works in the field of PA 44 have been published in the literature to date and the process chain biomass – C4-chemistry – high-performance polymers on the basis of the key component succinic acid with the final product PA 44 has not been pursued intensively, some characteristics of PA 44 can be forecasted.

From aliphatic high-melting PA 46 and PA 66, it is well-known that they have a relatively small time and temperature range during processing. Thus, a narrow processing window is also to be expected for PA 44.

The academic literature describes the melting temperature of PA 44 ambiguously. In the fundamental publication about PA 44 by Dreyfuss [54], a melting temperature of > 260 °C is reported. Other papers state that PA 44 – as well as PA 42 – will decompose before reaching the melting point [83]. However, Koning et al. reported a melting temperature of PA 42 of 390 °C [84]. Our work in this area at Fraunhofer UMSICHT, where PA 44 is being synthesized, indicated a range of the melting point between 300 and 350 °C [85].

The technical synthesis of PA 44 cannot be easily performed. Due to economic criteria, a mass polymerization is preferable, since the reactants are present as acid and amine. Concerning 1,4-butanediamine, it is well-known that a critical secondary reaction, the formation of the cyclic pyrrolidine, takes place and thus the stoichiometry of the polymerization is changed. However, this side reaction can be reduced like the industrial synthesis of the PA 46 (Stanyl®, DSM) reveals; or like it is also described by Pipper et al [55]. If the synthesis of high-molecular weight polysuccinamides runs over special esters of succinic acid, the chain growth stopping reaction of the aminolysis can almost be suppressed completely [59–61].

The properties of the homo polyamide are determined by the strong polar amide groups along the polymer chain in regular consequence and the hydrocarbon residues. The water absorption depends on the structure and the processing of the polyamides.

Gaymans et al. [65] examined the water adsorption of cast films from PA 42 and showed that the material was very hygroscopic (7.5 % at 65 % RH). PA 42 with a crystallinity of 70 % has exhibited lower water absorption (3.1 % by 50 % RH) [56]. From these results we can assume that PA 44 will show similar behavior concerning water absorption.

Polyester: The properties of polyesters depend on their composition. Pure aliphatic polyesters have low melting points and are mostly crystalline. The melting points increase with increasing number of methylene groups between the ester functions. On the other hand, polyesters which are composed of aromatic or cyclic-aliphatic dicarboxylic acids and diols, possess different properties [86].

For example, Bionolle® (Showa Denko) is a typical thermoplastic polyester with good manufacturing properties, flexibility, and tenacity, which are comparable to those from LDPE [67]. GS Pla® (Mitsubishi Chemical Corporation, Japan) is a poly(butylene succinate) (PBS) [66]. It is flexible, has high heat-seal strength and is permeable to oxygen and moisture. It is more flexible and has higher tensile elongation and notched izod impact than PLA, according to Mitsubishi. It has recently been introduced in Japan, where it is currently used in agricultural applications. GS Pla® is reported to be as soft as polyethylene but can be made harder like polypropylene by adding fillers. It can also be processed to fibers, suggesting non-wovens and synthetic papers as applications.

The properties of polymers can be changed by copolymerization with aromatic monomers. The increasing content of the phenyl side chain reduces the melting temperature and crystallinity, but increases the glass transition temperature of the aliphatic polyesters. The tensile strength, the elongation, and the tear resistance of polyester-26 decreased with an increase of the phenyl content. However, the increase in the phenyl content increased the elongation and tear resistance of polybutylene succinate considerably [78, 79, 87].

Poly(ester amide): Succinic acid and their derivatives are not only basic molecules for polyesters and polyamides, they can also be used for the synthesis of poly(ester amide)s.

Novel biodegradable copolymers with a periodic sequential structure of ester and amide groups could be synthesized by two-step polycondensation reactions from dimethyl succinate, 1,4-butanediol and 1,4-butanediamine [82]. These periodic copolyester-amides have high thermal stability comparable with the PBS homopolyester. This suggests that the copolyester-amides form different chain packing structures due to the formation of the intermolecular hydrogen bonds coming from the periodic amide units introduced into the polyester chains. The melting temperature of the periodic copolymers increased with an increase of the amide content from 140 °C for homopoly(butylene succinate) to 260 °C for poly(butylene succinamide).

The introduction of ester segments can lead to the reduction of crystallinity of the polyamide as a function of size and concentration of the ester segments. The combination of good physical properties, biocompatibility, and controlled degradability of poly(ester amide)s makes it possible to use these materials in medicine as absorbable seams or temporary implants.

Like PET, semicrystalline polyamides are only very slowly biodegradable. In contrast, aliphatic poly(ester amide)s are biodegradable with sufficient ester content and a statistic distribution of the amide and ester functions. Copolymers of ε-caprolactam (approx. 60 wt %), adipic acid, and 1,4-butanediol exhibit similar mechanical properties and melting points as LDPE and are suitable for applications like films. Due to their higher strength, copolymers from 1,6-hexamethylenediamine, adipic acid, 1,4-butanediol, and diethylene glycol (amide content 40 wt %) are suitable for injection moulding articles, like flower pots or one-way cutleries, as well as fibers.

Polymers like polyamides, polyesters, and poly(ester amide)s based on succinic acid and its derivatives today are fossil-based products. For economical and ecological reasons, it is advisable to substitute oil-based polymers in as many applications as possible. In order to be competitive with fossil-based materials, all biopolymers need to have a good processibility on conventional machines and a broad and excellent range of characteristics.

As an example, PA 44 based on fermentative succinic acid offers an alternative to oil-based polyamides for use in special applications. Regarding the properties of PA 44, three product groups seem to be interesting:

- Parts demanding high thermal stability and mechanical strength, for example for oil-immersed gearbox parts, pumps parts, and abrasion-resistant gear wheels.
- Tearproof fibers with high water absorption, for example for blended fabrics for the use in outdoor clothes.
- Hydrophilic, modifiable, mechanical resistant polymer membranes, for example for filtration techniques.

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