FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

Polyester Materials from Cosmetic Raw Materials

Executive Summary

CBI Project Course – Autumn 2020

Partner: schwan cosmetics

PROJECT COURSE
SEPTEMBER 2020

CBI
ERLANGEN

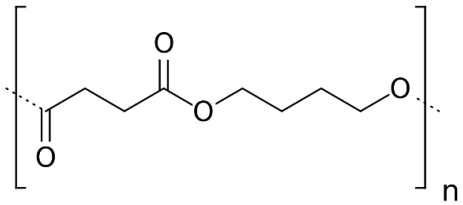
Introduction

The project course is a **joint project for all students of the master programs** Chemical and Biological Engineering (CBI), Chemical Engineering (CEN) and Life Science Engineering (LSE).[1] The main focus of the project course lies on the practical application of the students' knowledge within the project period of three weeks. The course is organized by the Department of CBI at Friedrich-Alexander-University of Erlangen-Nuremberg (FAU) in close cooperation with partners from industry, *schwan cosmetics.*[2] The company's headquarters are located in Heroldsberg near Nuremberg. The company invented the cosmetic pencil over 90 years ago and has since then become the market leader in the production of cosmetic pencils, with over 600 million pencils sold worldwide each year. The overall goal of the project course is to develop and produce innovative polyester materials for cosmetic products from sustainable, cosmetic-compliant raw materials. The plant design is based on a production rate of 100 tons of pure polymer per year. The framework for selecting suitable polymers are biodegradability and diffusion resistance to chemical ingredients. Moreover, the final product will be a suitable candidate for injection molding as well as additive manufacturing.

Results

The **management** team developed a timeline, including different project phases and milestones due to the tight time schedule of the project. A central and accessible data collection was set up to guarantee an open information flow between the groups. As suitable platform Microsoft Teams was chosen as a daily communication and data sharing platform.

A **suitable polymer** had to be determined regarding the defined requirements. From a comparative search including several polymers, poly(butylene succinate) (PBS) is the most suited polymer for production, since it can be synthesized from reactants of non-fossil origin, is biodegradable, compoundable, conforms to the required criteria and provides a wide range of scientific literature.

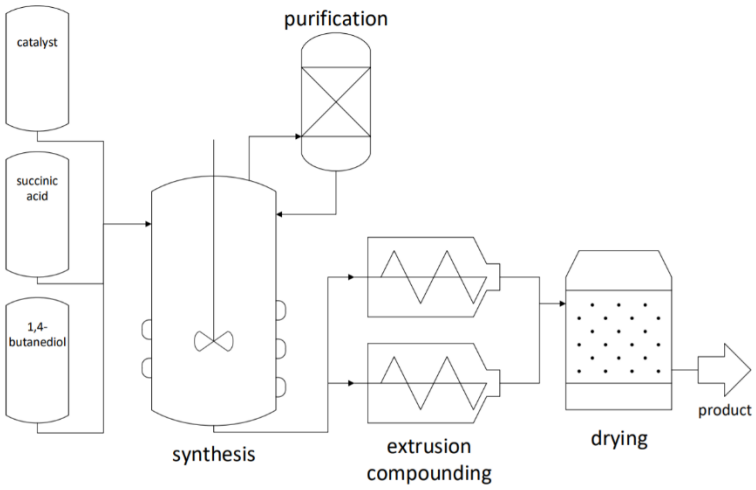


The product synthesis for PBS consist of two consecutive reactions, an esterification for 3.5 hours followed by a polycondensation for 8 hours, with a 3 hours heat adjustment phase in between.[3] The reactants are 1,4-butanediol and succinic acid, brought together in a stoichiometric molar ratio with 1,4-butanediol being delivered in an excess of 10 % to counteract the evaporation of the diol throughout the reaction. The whole **process is operated**

[1] www.cbi.tf.fau.de
[2] www.schwancosmetics.com

[3] Longo, J.M., DiCiccio, A.M., Coates, G.W. (2014) Poly(propylene succinate): a new polymer stereocomplex. *Journal of the American Chemical Society*, **136** (45), 15897–15900.

batch-wise in a 1,200 L reactor. The required reactor volume was estimated from the reactants considering the largest volume is found at the beginning of the reaction. The temperature for the esterification is set at 190 °C with atmospheric pressure. No specific catalyst is added since 1,4-butanediol acts as a catalyst for this reaction-step. During this process, water is being accumulated and constantly removed from the reactor. For the switch from esterification to polycondensation the pressure is reduced to below 1 mbar, the temperature is increased to 230 °C and the catalyst titanium n-butoxide is added. PBS is being formed from oligomers until the final **molecular weight of 45,000 g mol^{-1}** is reached. The reaction timing and parameters were established by modelling the reaction process in MATLAB by using kinetic data from scientific literature. Therefore, it is now possible to monitor the amount of reactants and product at every timestep during the reaction, as well as the reaction volume and the required heating energy for the reaction to run properly. A simplified process flow schem is depicted here.



For the esterification a **distillation column** was designed to remove as much coproduct as possible. With that setup it is possible to distillate 99.5 % of the water in the head of the column, which is produced in the first reaction step and thereby remove around 191 kg of water and 13.5 kg of tetrahydrofuran. With this set-up a minimal reactant loss in the first step can be maintained while the maximum amount of byproduct is removed. During the transition to the second reaction step a vacuum of 1 mbar is applied. A condenser is installed to condensate the 1,4-butanediol, water traces and 1-butanol resulting from catalyst decomposition. The process design allows the removal of 2.7 kg additional water formed in the second step, the remaining 1 kg of water from the first step, as well as 68.5 kg 1,4-butanediol and 3.3 kg 1-butanol.

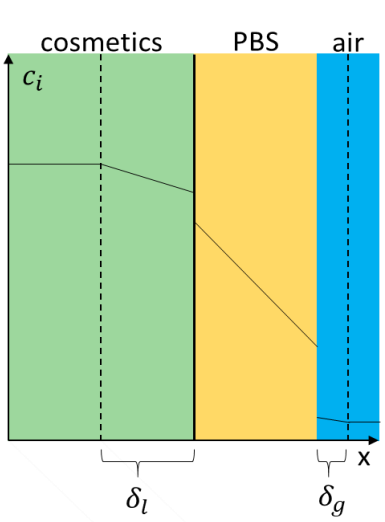
To achieve optimal water and reactant concentration the partial pressure of 1,4-butanediol is further reduced by a nitrogen stream to 0.036 Pa, which is equal to 0.3 ppm of the 1,4-butanediol vapor pressure. Taking all steps into consideration the estimated water content amounts to be lower than the 1,4-butanediol content (> 0.3 ppm). **Final purification via adsorption** allows a low energy consuming removal of remaining substances. Due to the elimination of all pollutants the remaining nitrogen can be discharged into the atmosphere while 1,4-butanediol, 1-butanol and water remains bound to the activated carbon allowing easy

handling and waste disposal. This allows to purify the exhaust gas of 26 batches during 3 months of production time before it needs to be regenerated or filled with new activated carbon. The 1,4-butanediol which is recovered in the second step is distilled after ten batches in either a second column or by using the existing reactor and column system. The **purity of the regenerated 1,4-butanediol is 99.5 %**. This recovery is estimated to cause **energy and labor costs worth about 0.57 € per kg 1,4-butanediol** whereas the newly purchased reactant is at the price of 2.50 € per kg. The comparison demonstrates that with a further purification step not only the environmental impact can be reduced but there is also a significant reduction in reactant costs possible. Taking all parameters into consideration the process designed **meets all given requirements** regarding product purification. Thereby it is achieved that at the end of the reaction the product PBS is suited for compounding, pelletizing and drying.

For the final product, **addition of additives** will increase the modulus of elasticity, to adjust the color or to stabilize the end product (e.g. UV radiation, temperature, etc.). After the synthesis the polymer is liquid at around 230 °C. This state is used to mix in the additives without any additional energy input. For this purpose, two compounders with a throughput of 800 kg per hour and an operating temperature of 140 °C were designed. The compounders have several inputs for the polymer and the additives, an additional internal degassing unit and their own water management system for the cooling bath. In addition, a guided strand pelletizer is connected in order to shape the polymer strand into pellets of the same size after homogeneous mixing with the additives. After pelletizing, the product is first stored in an intermediate container before it is passed on to the dryer. After a residence time of 4-6 hours, the pellets with a maximum **residual moisture of 0.03 %** are removed from the dryer and stored in a silo.

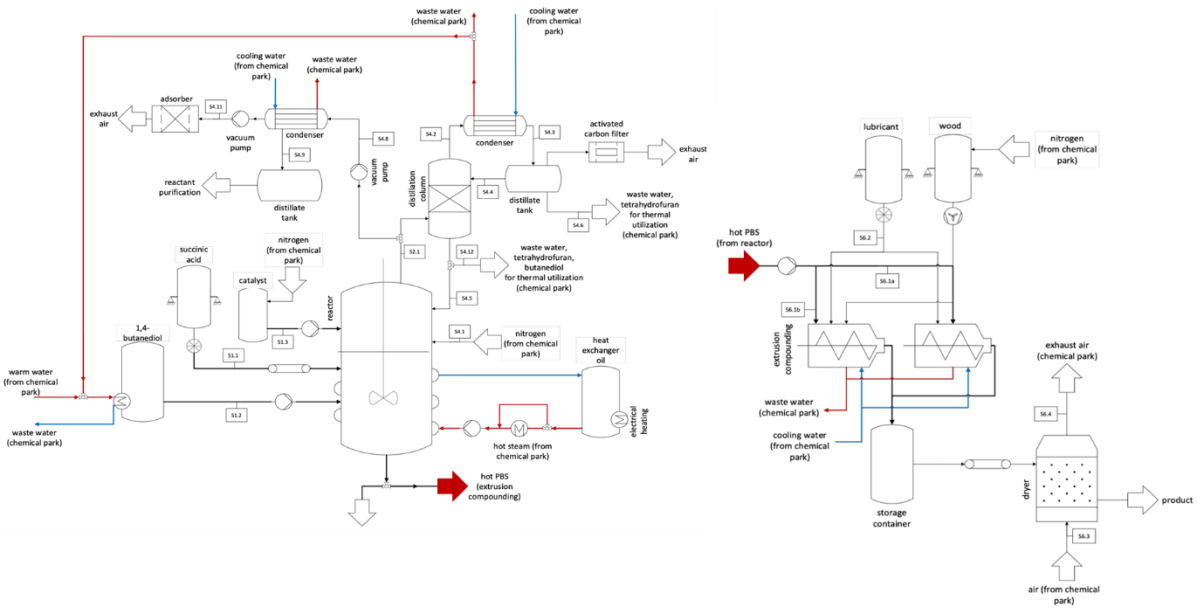
For mass production purposes, **injection molding** is preferred due to its rapid production potential.[4] Additionally, a wood plastic composite (WPC) is a suitable compound for injection molding. As an additional additive the lubricant *Licowax PE 190 P* is used. According to the formulation of material, a dosage range of 60 to 70 wt.% PBS, 30 to 40 wt.% hardwood and 1 to 2 wt.% lubricant is feasible, in order to reach the required Young's modulus and processability. In contrary, **3D printing** is considered as a technology for personalized products.[5] In the case of PBS, a suitable method for 3D printing is selective laser sintering since for this approach a semi-crystalline thermoplastic is required. Pure PBS has this physical property and is therefore suited to be processed by 3D printing.

[4] BONNET, M. (2016) Kunststofftechnik: Grundlagen, Verarbeitung, Werkstoffauswahl und Fallbeispiele, **164**.
[5] Fraunhofer Umsicht. https://www.umsicht.fraunhofer.de/de/forschung-fuer-den-markt/selektives-lasersintern.html last visited on October 1st, 2020



The **diffusion properties** were estimated in a porous system of a wooden plate. At first a model is considered in which on the inner side is the cosmetic which is surrounded by PBS and on the outer side is air. Thereby the concentration gradient is decreasing from the cosmetic to outer direction (see below). The aim is to calculate the necessary time for the diffusion of the cosmetic through the PBS. For this task a few assumptions are made. The concentration gradient over the PBS film is simulated as a step function. The film is divided into a number of layers over which the concentration is considered constant. For simplification and due to a lack of data, the substance inside the pen is assumed to be pure water, while for the starting time there are no water molecules inside the polymer. The diffusion through the polymer (PBS) is assumed to be the rate determining step. The applied diffusion coefficients are valid for water in PBS and for the calculation the first Fickian law is used. Afterwards the time for the diffusion through the boundary layer is calculated for pure PBS and 70 % PBS. The calculated duration until **complete diffusion out of the pen is 22 years for 70 % PBS and 47 years for pure PBS**.

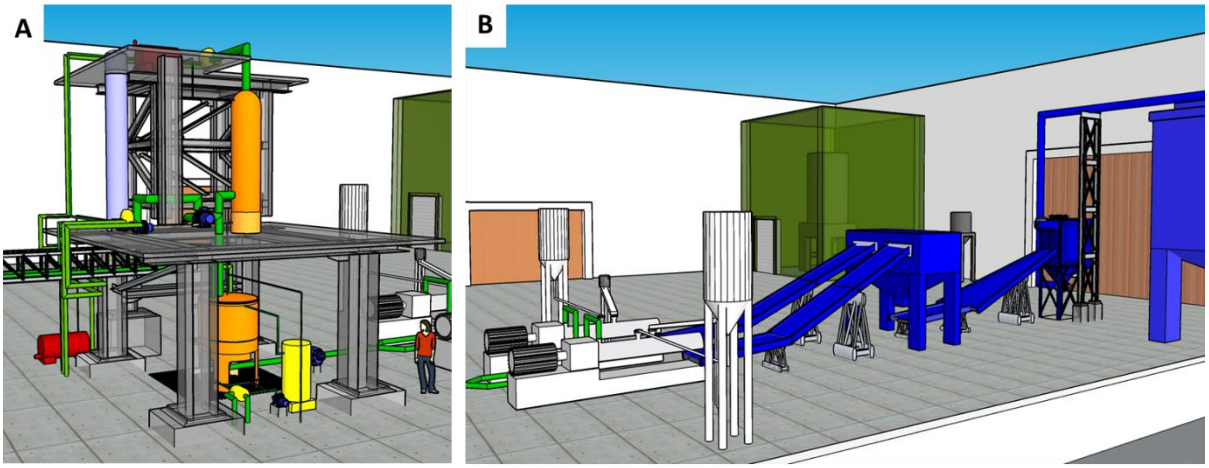
For the overall process including reactor, pipes and pumps, heat management a **plant automation concept** was introduced. The process flow charts for the PBS synthesis and all the further processing steps are shown below. The development of an automation plan is essential to ensure a safe operation mode of the individual plant components and of the whole plant itself. Therefore, every single component has to be considered. First of all, sensors for pressure, temperature, flow, levels etc. are used to measure the controlled values and compare these with setpoint values. If the controlled variable differs from the setpoint value, which can occur due to disturbances and fluctuations during the operation, the measuring instrument adjust the respective instruments or valves.



Moreover, regulations have to be designed in order to prevent or fix potential failures of the system, for example the malfunction of the heating system or of the stirrer. Furthermore, piping and instrumentation diagrams were developed in which the automated process steps are described.

The **design of the components** for reactor and separation column was carried out using CAD software *Creo Parametric 5* and put together in an assembly. After choosing a non-continuous batch reactor for the polymerization, the components are mainly dimensioned with the AD 2000 standards for pressure tanks and DIN standards, e.g. for the apparatus feet, flanges etc. In addition, the reaction conditions, such as vacuum and high viscosity, were taken into account to determine all requirements for the special reactor design and the components, such as the stirrer. The choice of the apparatus material is stainless, non-corrosive steel (1.4571). The final design of the reactor inlets, outlets and heating are established in close cooperation with the groups for pipes and heat management.

The **assembly plan was visualized in 3D** with the design software *SketchUpPro 2020*. The model was designed considering the minimum safety distance between each unit, safety requirements and based on the process flow chart. Based on this true scale arrangement, it was possible to estimate the room consumption of each part of the process (reaction and separation shown in part A, compounding, pelletizing and drying shown in part B) and the route of the pipelines as well as calculate and design the length and branching of the pipes.



For **dimensioning the piping system**, firstly the material of the pipes was selected. Criteria for the material selection are the chemical, thermal and rheological properties of the fluid which is transported by each pipe. Carbon steel was selected for the majority of the pipes. For fluids with high corrosion potential, stainless steel was chosen. The nominal diameter was iterated to achieve a maximum flow rate of the fluid in the pipe and a minimum pressure drop for each pipe. By calculating the pressure loss of each pipeline, it was possible to evaluate whether pumps are necessary for pressure compensation. In most cases, there was no need for pressure compensation. In the case of considerable pressure loss, suitable pumps were chosen from different retailers. Additionally, isolation requirements and thermal compensation for the pipes were calculated.

For the **heat management** the heating of the reactor with a maximum temperature of 230 °C was identified as the most crucial part. Because of the limited steam temperature of 200 °C at the chosen production site, an electrical heating system with a heat transfer fluid (HTF) was selected as the appropriate heating utility. A heat exchanger for heating the HTF up to the temperature limitation with onsite steam utility can be used. For the first reaction 263 kWh thermal energy with a peak of 115 kW is required. That includes heating of the reactants, reactor and HTF from 20 to 190 °C as well as the evaporation of approximately 191 kg water and tetrahydrofuran. The second step with an energy demand of 47 kWh consists of a subsequent temperature increase to 230 °C and the evaporation of small amounts of water, butanol and butanediol over a period of 11 h. An overall heat loss of 19 kWh with an insulation of 2 cm mineral wool needs to be compensated. The two cooling tasks are the condensation of the vapors after the distillation and between the two vacuum pumps. During the first reaction, the stream needs to be cooled from 110 to 60 °C, whilst the vapor in the second reaction step needs to be cooled from 230 to 20 °C. The last task is the heating of the butanediol storage tank to prevent it from solidification at 20 °C. Thus, the warm cooling water (80 °C) exiting the first condenser should be used to keep the insulated tank between 25 and 35 °C. In order to ensure liquid state throughout the year, the tank will have an additional line for external warm

water. In this batch process **heat recovery and integration is restricted** due to suitable streams not existing at the same time. The streams that do exist simultaneously do not meet temperature requirements. Heat storage is also not beneficial for the rather small heat requirement since it is expensive and complicated.

The **biodegradability** is influenced by the properties of the polymer such as size, shape or chemical structure, and by the biotic and abiotic exposure conditions. Countless studies have demonstrated good biodegradability of poly(butylene succinate) in industrial composting processes.[6] Moreover, **PBS is not ecotoxic** since it first hydrolyses to monomers in the soil and is then metabolized by microorganisms to CO_2 and H_2O. For a precise determination of the real biodegradation rate of the specific product, it must be experimentally investigated in its final shape and composition, since the polymer properties have a huge impact on the rate of biodegradation. A **bio-based production is possible** and, additionally, PBS has similar **good mechanical properties** as Polyethylene (PE) or Polypropylene (PP). Biodegradable alternatives to PBS are Poly(butylene succinate-co-butylene adipate) (PBSA), Poly(hydroxybutyrate) (PHB), Poly(lactic acid) (PLA) and many others available on the market.

A **life cycle assessment** (LCA) consists of three main parts: environmental, cost and social evaluation.[7] In the following the environmental part is examined. The environmental assessment consists of many different factors such as land and water consumption, ecotoxicity and many more. Due to the time frame and the task, only the Global Warming Potential (GWP) is considered. All emissions are converted into carbon dioxide equivalents. To make these assessments more comparable, they are carried out according to **ISO norm 14040**. There are three steps: goal and scope, system boundaries and evaluation of the results. The goal is to quantify the specific greenhouse gas emissions that occur during the production of PBS, the functional unit is 1 kg PBS, the local and time frame is Germany in 2020. Only the production of pure PBS from **Cradle-to-Gate** is considered since a quantitative consideration of the end-of-life scenarios is not possible due to the lack of sufficient data. The mass and energy flows have been collected over the course of the project and then entered the software *OpenLCA*. *Ecoinvent* was used as database. The software then automatically calculates the GWP in relation to the functional unit 1 kg PBS. The preliminary result of the LCA is that **PBS is comparable to existing polymers in terms of GWP with the advantage of biodegradability**.

[6] Umweltbundesamt (2018), Gutachten zur Behandlung biologisch abbaubarer Kunststoffe; https://www.umweltbundesamt.de/sites/default/files/medien/421/publikationen/18-07-25_abschlussbericht_bak_final_pb2.pdf

[7] Guinée, Jeroen. "Life cycle sustainability assessment: what is it and what are its challenges?." Taking stock of industrial ecology. Springer.

For the **location of the plant** the chemical park *Bitterfeld-Wolfen GmbH* was chosen as this park offered similar media as other available parks but was significantly cheaper with costs of 15 € per m^2 for purchase compared to 1.50 to 2.00 € per m^2 per month for rent in other parks.[8] The park offers important media for the plant, e.g. power, water, steam and nitrogen. Furthermore, services like a wastewater treatment plant, a thermal treatment plant and a fire department are already available. Locations of *schwan cosmetics* were also considered as potential sites as the plant is limited in size and the transport routes would be minimized. Sites in Heroldsberg and Cesky Krumlov are potential candidates as open spaces seem to be available around the existing buildings.

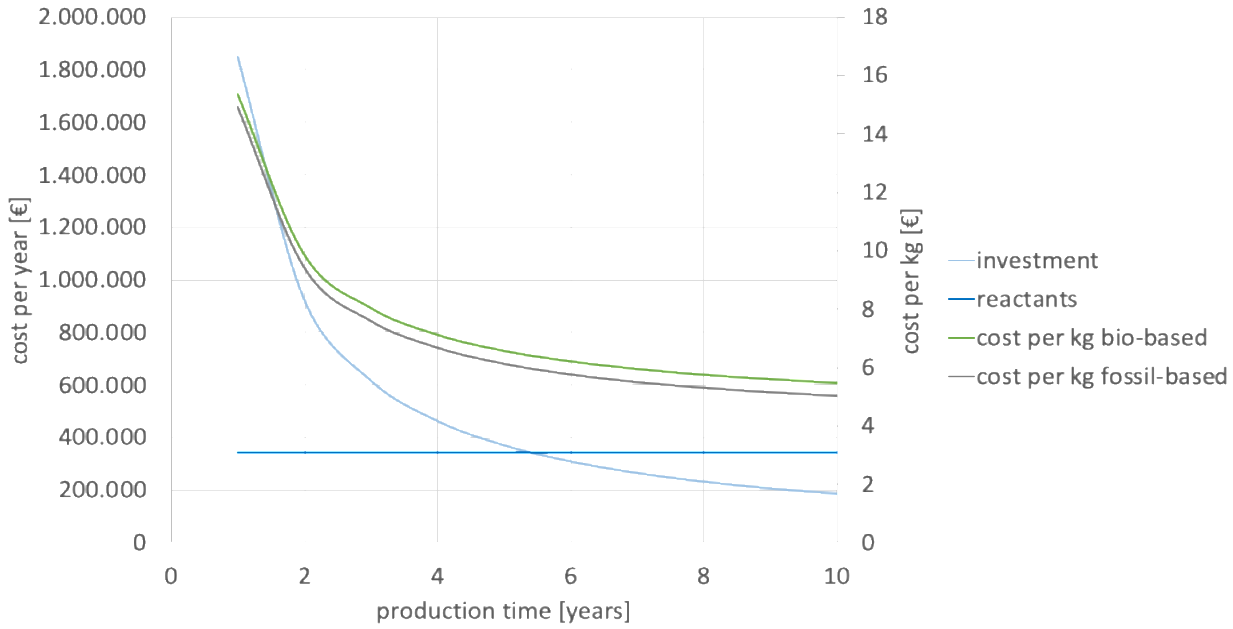
For the **approval of the plant** the requirement for permission has to be checked according to § 4 BImSchG and 4. BImSchV. As the planned process involves synthesis of polymers it requires permission (4. BImSchV, Anhang 1, 4.1.8). For the approval process information about the plant, protective measures, waste treatment and energy efficiency have to be submitted to the responsible authorities. In addition to that, the requirement of a *Umweltverträglichkeitsprüfung* (UVP*,* engl. environmental impact assessment) has to be evaluated. As the proposed site is in a chemical park which is already UVP-approved, no full UVP would have to be carried out. Additionally, the park also offers services supporting the plant operators during the admission procedure. According to BImSchG § 10, the process may take a maximum of 7 months if there are no further objections.

The **plant safety** was evaluated and planned according to the *MIndBauRL* (fire protection) and the 12. BImSchV (*Störfallverordnung*, engl. hazardous incident ordinance). Important subjects of the *MIndBauRL* include planning of storage for flammable materials, escape routes, fire extinguishing systems etc. The *Störfallverordnung* is for protecting employees and securing the process, e.g. by limiting exposure to substances and introducing alert systems, respectively. In the scope of this project potential failures of the plant were worked out and security protocols for these failures were implemented. An example for this is the potential failure of the reactor heating. Due to the increasing viscosity of the reactor content, the stirrer should be stopped to prevent damages. After repairing the malfunctioning parts, the quality of the reactor content has to be evaluated by an employee to decide if the process can be continued.

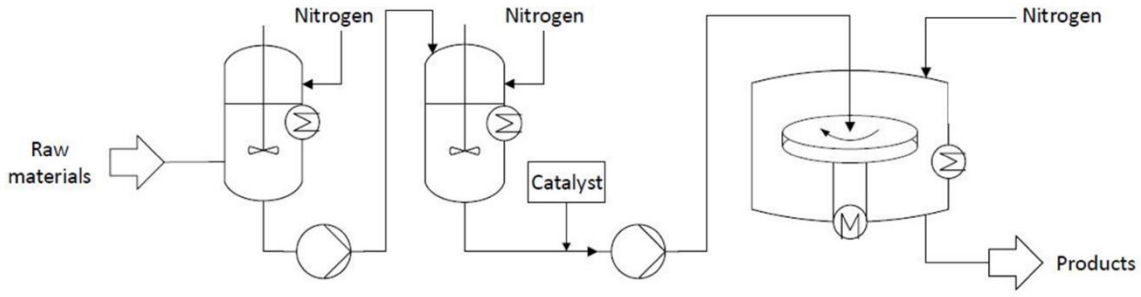
For the **detailed cost estimation**, the method of Miller and Guthrie was used.[9] The estimation is based on the price of plant components or equipment which is multiplied with additional factors for piping, controlling, assemblage etc. The factor calculated in this project was 2.98

[8] www.chemiepark.de/en/homepage/
[9] Kunysz, David Oliver: Kostenschätzung im chemischen Anlagenbau. Cost Estimation Basics, Wiesbaden 2020

which led to **total investment costs of 1.8 million Euro**. With the consideration of reactant costs, operation costs, investment costs and salary the price of the product is about 6 € per kg after 5 years with linear amortisation.



In addition to the main concept a **different reactor concept**, a Spinning Disk Reactor (SDR), for the polycondensation was selected. Therefore, the process needs to be divided into a discontinuous part in which the esterification is performed inside a batch reactor and a continuous part for the polycondensation within the SDR. Both parts are connected through a storage tank.



The oligomers from the storage tank are mixed with the catalyst and transported into the SDR where they are spread over the spinning disk due to the high rotation of the disk. A thin reactant layer is formed and within seconds the polycondensation takes place. The polymer is pushed against the wall as a result of centrifugal forces and slides downwards where it is removed. The molecular mass can be adjusted through the residence time of the reactants on the disk and the number of disks. The advantages of the SDR include a higher heat and mass transfer, a lower viscosity due to the high shear rates and a much higher reaction rate during the polycondensation. Given that the polycondensation is continuous, smaller volumes for the

batch process are needed. Therefore, the safety of the process is increased. On the other side, no comparable polyester synthesis is yet performed by using a SDR and further research and experiments within lab scale are needed.

By using different studies, a **comparison of biotechnological and petrochemical production** of the two reactants 1,4-butanediol and succinic can be carried out. The sustainability assessment includes carbon and water footprint as well as prices. Both ways of production are established in Europe. The biotechnological production proves to be more carbon dioxide- and water-saving. Petrochemical production seems to be cheaper at the moment. However, this statement refers to just a few studies. Nevertheless, the LCA shows that the reactants have a wide impact on the carbon dioxide footprint of the production of Poly(butylene succinate). Compared to the data acquired form the LCA, a potential decrease of 50 % CO_2 could be calculated while using biotechnological instead of petrochemical reactants. Therefore, the reactant recovery out of biotechnological sources should be considered.

Resumé

The overall goal of developing and producing new sustainable polyester materials from cosmetic raw materials could be demonstrated. The layout of the process and the construction of the plant meet the requirements and the whole process was evaluated according to the legal, ecological and economic framework conditions. It could be shown that the **production of biodegradable and as well as bio-based polyesters is possible**, although the production costs of PBS based on fossil reactants are still significantly lower than those based on renewable raw materials. Considering sustainability as a megatrend of the 21st century, the need for saving resources and new inventions in biotechnology could ultimately lead to lower reactant prices and therefore lower the overall production costs of PBS in the future, while reducing the global warming impact.

Imprint

For the design of the logo, we have been given the approval of *schwan cosmetics* to mimic the company's design, which is a silhouette of a swan. Our design includes a green leaf as the swan's wings, which symbolizes the concept of green chemistry and environmental protection.

Participants

Authors/Students

Ming-Yu Lee, Susann Müller, Pegah Pojhan, Jakob Scholl, Katharina Bär, Mohamed-Amr Boumiza, Eric Geelen, Robert Goik, Lea Römling, Theresa Rogge, Claudia Seeberger, Franziska Spies, Elisabeth Herzinger, Marlena Kaufmann, Markus Leidenberger, Lukas Popp, Moritz Moß, Marco Dürsch, Abeer Al-Ani, David Brüggemann, Oleksandra Solomchenko, Tim Karl-Kraus, Fernanda Luísa Paterno, Isabel Schönauer, Helin Üstün, Johanna Wiesner, Agustin Gallo, Melissa Ghetina, Franziska Seidl, Theresa Siegmund, Michael Jaschko, Levin Winzinger, Hannah Moldan, Tim Prölß, Sophie Wüstefeld, Jiexi Li, Sehr Ahmad, Ina Baumeister, Daniel Esau, Marco Blasius, Cheng Cai, Jakob Iser, Johanna Rieger, Katharina Dehm, Anne Grosser, Benedikt Bornschein, Ruth Luber, Anna-Lena Schmidt, Ramírez Andrea Camacho, Julia Höhn, Xinyi Zeng, Franziska Brodwolf, Fei Ding, Bernd Ottmann, Steidle Susanne

Supervisors

Martin Kriesten, Dr. Detlef Freitag, Moritz Langer, Timo Rüde, Philipp Rothgängel, Frederik Mayer, Dr. Holger Hübner, Tobias Beck, Phillipp Bräuer, Bastian Lehnert, Benedikt Berchtenbreiter, Dr. Ing. Andreas Michalka, Johannes Reinhard, Alexander Hauser, Tanja Schneider, Dr. Stefanos Georgiadis, Dominik Haspel, Maximilian Uttinger

Erlangen, October 2020