Agricultural University of Athens

Postgraduate Study

Bioprocess design and techno-economic evaluation of 1,4 – butanediol production with final application in biopolymer production

Department of Food Science and Human Nutrition
Laboratory of Food Process Engineering
Food Science and Technology & Human Nutrition

Sofia-Maria S. Ioannidou

Supervisor: Apostolis Koutinas
Associate Professor

Athens, February 2019

Agricultural University of Athens
Department of Food Science and Human Nutrition
Laboratory of Food Process Engineering
Food Science and Technology & Human Nutrition

Postgraduate Study

Bioprocess design and techno-economic evaluation of 1,4 – butanediol production with final application in biopolymer production

Sofia-Maria S. Ioannidou

Supervisor:
Apostolis Koutinas, Associate Professor

Athens, February 2019

Postgraduate Study

Bioprocess design and techno-economic evaluation of 1,4 – butanediol production with final application in biopolymer production

Sofia-Maria S. Ioannidou

Supervisor:
Apostolis Koutinas, Associate Professor

Examination Committee:
Apostolis Koutinas, Associate Professor
Ioannis K. Kookos, Professor
Seraphim Papanikolaou, Associate Professor

Athens, February 2019

Acknowledgments

The present thesis was carried out at the Department of Food Science and Human Nutrition, Agricultural University of Athens, in the Food Process Engineering Laboratory during the academic year 2018-2019. A number of people deserve acknowledgment for their help and support. It is, therefore, my pleasure to express my gratitude to them in this section.

First of all, I would like to express my gratitude to my thesis Advisor, associate professor Apostolis Koutinas, who believed in me and gave me the opportunity to conduct my study as a member of his research group. His support and guidance were valuable to the completion of my thesis. I would also like to express my appreciation to the members of my examination committee, Professor Ioannis Kookos and Associate Professor Seraphim Papanikolaou for their insightful comments and encouragement, as well as for the questions which incented me to widen my research from various perspectives.

I am also especially grateful to Dr. Dimitrios Ladakis for his help during the whole period of this thesis composition. His patience and comments were really enlightening, whenever I needed help. The collaboration with him gave me motivation and increased my knowledge on the subject. Moreover, I would like to thank all the members of the laboratory for their support and help any time I needed it.

Last but not least, I would like to thank my family and friends for their support and encouragement throughout all this year and my life in general.

Athens, February 2019

Περίληψη

Η αξιοποίηση ανανεώσιμων πρώτων υλών καθώς και βιομηχανικών αποβλήτων με σκοπό την παραγωγή προϊόντων προστιθέμενης αξίας είναι ένα αρκετά αμφιλεγόμενο θέμα στις μέρες μας το οποίο προσελκύει όλο και μεγαλύτερο ενδιαφέρον στο χώρο της έρευνας. Οι επιστήμονες αναζητούν εναλλακτικές πρώτες ύλες οι οποίες θα μπορούν να είναι πιο οικονομικοί και πιο φιλικοί προς το περιβάλλον. Η παρούσα διπλωματική εργασία πραγματεύεται τη μελέτη παραγωγής της 1,4 - βουτανοδιόλης (1,4 - BDO) από την καθαρή γλυκόζη και από γλυκόζη που προέρχεται από απόβλητα καλαμποκιού, καθώς και την παραγωγή του βιοπολυμερούς πολύ-ηλεκτρικού βουτυλεστέρα (PBS) από ανανεώσιμες πρώτες ύλες. Επιπλέον, στην εργασία πραγματοποιείται αξιολόγηση κύκλου ζωής των διεργασιών αυτών, προκειμένου να αξιολογηθούν οι περιβαλλοντικές τους επιπτώσεις.

Αρχικά, αξιολογείται η διαδικασία παραγωγής της 1,4 - βουτανοδιόλης. Η διεργασία αυτή αποτελείται από δύο μέρη, το upstream και το downstream. Το upstream είναι το τμήμα στο οποίο λαμβάνει χώρα η παρασκευή και η αποστείρωση των πρώτων υλών καθώς επίσης και η ζύμωση τους προκειμένου να παραχθεί το επιθυμητό προϊόν. Συγκεκριμένα, το upstream αποτελείται από ένα σύστημα αποστείρωσης και έναν συγκεκριμένο αριθμό βιοαντιδραστήρων ανάλογα με την επιθυμητή δυναμικότητα της διεργασίας. Το υπόστρωμα της ζύμωσης αποτελείται από γλυκόζη, άλατα αμμωνίου ως πηγή αζώτου και άλλα θρεπτικά συστατικά. Ο μικροοργανισμός που χρησιμοποιείται για την παραγωγή 1,4 - BDO είναι το γενετικά τροποποιημένο βακτήριο Escherichia Coli, καθώς αυτή η ουσία δεν παράγεται φυσικά μέσω της βιοχημικής οδού του μικροοργανισμού. Κατά τη διάρκεια της ζύμωσης, παρέχεται αερισμός στο σύστημα με ρυθμό 0.02 vvm έτσι ώστε να επιτευχθούν μικροαερόβιες συνθήκες. Η ζύμωση διεξάγεται για 36 ώρες σε θερμοκρασία 37 ° C και το τελικό προϊόν περιέχει 1,4 - BDO σε συγκέντρωση $125\ g \cdot L^{-1}$. Στη συνέχεια, το προϊόν ζύμωσης προχωρά στο τμήμα ανάκτησης και καθαρισμού (downstream). Συγκεκριμένα, το προϊόν διαχωρίζεται από τα ανεπιθύμητα συστατικά, όπως για παράδειγμα τα κύτταρα της βιομάζας, χρησιμοποιώντας φυγοκεντρικό διαχωριστή. Στη συνέχεια, το ρεύμα εισέρχεται στις ρητίνες προκειμένου να απομακρυνθούν τα παραπροϊόντα της ζύμωσης και στον εξατμιστήρα έτσι ώστε να συμπυκνωθεί το ρεύμα. Τέλος, χρησιμοποιείται μια στήλη απόσταξης για να ανακτηθεί το επιθυμητό προϊόν από το υδατικό του διάλυμα (καθαρότητα μεγαλύτερη από 99,5%).

Το επόμενο βήμα είναι ο σχεδιασμός του πολυμερισμού του βιοπολυμερούς. Η 1,4-βουτανοδιόλη που παράγεται από την προηγούμενη διεργασία μαζί με βιοτεχνολογικά παραγώμενο ηλεκτρικό οξύ χρησιμοποιούνται ως πρώτες ύλες για την παραγωγή του PBS. Το πρώτο βήμα της διαδικασίας είναι η προετοιμασία των πρώτων υλών με την ανάμιξή τους. Το ρεύμα που προκύπτει εισέρχεται στον αντιδραστήρα εστεροποίησης και μετά από 3 ώρες δημιουργείται ο εστέρας. Ο πολυμερισμός του εστέρα είναι μία αντίδραση πολυσυμπύκνωσης παρουσία τετραβουτοξειδίου του τιτανίου ως καταλύτη. Το τελικό προϊόν είναι το βιοπολυμερές PBS με μοριακό βάρος 70,000.

Ακολούθως, πραγματοποιείται τεχνικοοικονομική αξιολόγηση των διεργασιών παραγωγής 1,4 - BDO και PBS από καθαρή γλυκόζη για διάφορες ετήσιες δυναμικότητες, έτσι ώστε να επιτευχθεί η μοντελοποίηση των διεργασιών αυτών. Μετά την ανάλυση χρηματοροών, εκτιμάται ότι και οι δύο διεργασίες είναι εφικτές και αποδοτικές και ότι η ελάχιστη τιμή πώλησης των 1,4 - BDO και PBS είναι $1.3\ \$\cdot kg^{-1}$ και $2.5\ \$\cdot kg^{-1}$, αντίστοιχα.

Στη συνέχεια, αξιολογείται η αξιοποίηση αποβλήτων καλαμποκιού ως ανανεώσιμη πρώτη ύλη. Η προεπεξεργασία των αποβλήτων αυτών αποτελείται από δύο τμήματα: την αρχική προεπεξεργασία με χημική υδρόλυση και το στάδιο της ενζυματικής υδρόλυσης. Μετά το σχεδιασμό των σταδίων αυτών, διεξάγεται η τεχνικοοικονομική αξιολόγηση της διαδικασίας προεπεξεργασίας προκειμένου να εκτιμηθεί η τιμή των εκχυλισμένων σακχάρων. Η τιμή αυτή χρησιμοποιείται για την επαναξιολόγηση των οικονομικών της παραγωγής 1,4 - BDO.

Το τελευταίο στάδιο της μελέτης είναι η αποτίμηση κύκλου ζωής των διεργασιών. Η αποτίμηση του κύκλου ζωής (LCA) έχει γίνει μια από τις πιο συστηματικές τεχνικές για την αξιολόγηση μιας διεργασίας σε σχέση με την περιβαλλοντική απόδοση του κύκλου ζωής της. Η ανάλυση απογραφής, διαδικασία που συμπεριλαμβάνεται στη συνολική μεθοδολογία του LCA, πραγματοποιείται για τις δύο υπό μελέτη διεργασίες και στη συνέχεια γίνεται σύγκριση των αποτελεσμάτων με αυτά που προκύπτουν από την πετροχημική βιομηχανία. Το αποτέλεσμα αυτών των συγκρίσεων αποδεικνύει ότι οι διεργασίες βιοτεχνολογικής παραγωγής παρουσιάζουν πλεονέκτημα σε σύγκριση με τις πετροχημικές.

Λέξεις κλειδιά: 1,4 – βουτανοδιόλη, Πολύ – ηλεκτρικός βουτυλεστέρας, Γλυκόζη, Απόβλητα καλαμποκιού, Τμήμα Παραγωγής, Τμήμα ανάκτησης, Τεχνοοικονομική Αξιολόγηση, Αποτίμηση Κύκλου Ζωής

Abstract

Currently, the conversion of industrial waste streams into chemicals or fuel production is a controversial issue and attracts increasing interest in research. Scientists seek alternative resources that can be more cost – effective and environmentally friendly. This thesis deals with the study of 1,4 – butanediol production from pure glucose and glucose derived from corn stover, as well as the production of the biopolymer poly – butylene succinate from biobased raw materials. Moreover, a life cycle assessment is carried out, in order for the environmental impact of the processes to be evaluated.

Firstly, the production process of 1,4 – BDO is evaluated. This process consists of two parts, upstream and downstream sections. The upstream is the part of the process, where the preparation of the raw materials and the fermentation take place in order to produce the desired product. Specifically, the upstream consists of a sterilization system and a number of fermentors, depending on the desired capacity. The feedstock is composed of glucose, ammonium salts as nitrogen source and other nutrients. The microorganism used for the production of 1,4 – BDO is genetically engineered Escherichia Coli, because this substance is not produced naturally via the biochemical pathway of the microorganism. During the fermentation process, air is supplied to the system at a rate of 0.02 vvm because this fermentation is a microaerobic process. The fermentation is carried out for 36 h at a temperature of 37 °C and the final product contains 1,4 – BDO in a concentration of 125 $g \cdot L^{-1}$. Next, the fermentation product proceeds in the downstream section. In this section, the isolation and purification of the product take place. Specifically, the product is separated from the undesired components, such as the biomass, using a centrifugal separator. Then, the stream enters the resins in order for the by – products of the process to be removed and the evaporator so as for the stream to be condensed. Finally, a distillation column is employed in order for the product to be recovered from its aqueous solution (purity greater than 99.5%).

The next step is the design of the polymerization of biopolymer. 1,4 – butanediol which is produced from the previous process along with biobased succinic acid are used as raw materials for the production of PBS. The first step of the process is the preparation of the raw materials by mixing them. The liquid outflow enters the esterification reactor and after 3 h the ester is generated. The polymerization of ester is a polycondensation reaction in presence of titanium tetrabutoxide as catalyst. The final product is PBS with Molecular Weight 70,000.

Afterwards, the techno – economic evaluation of 1,4 – BDO production and PBS production from pure glucose is carried out for various annual capacities, so as a modelling of the processes for multiple capacities to be demonstrated. After the discounted cash flow analysis, it is estimated that both processes are feasible and profitable and the minimum selling price of 1,4 – BDO and PBS are 1.3 $\$ \cdot kg^{-1}$ and 2.5 $\$ \cdot kg^{-1}$, respectively.

Next, corn stover as renewable raw material is evaluated. The pretreatment of corn stover consists of two sections: the initial pretreatment by chemical hydrolysis and the stage of enzymatic hydrolysis. After the design of the stages, the techno – economic evaluation of the pretreatment process is carried out in order for a price of the extracted sugars to be estimated. This price is used for the re-evaluation of the economics of 1,4 – BDO production.

The final step of this study is the life cycle inventory analysis of the process. Life Cycle Assessment (LCA) has become one of the most systematic techniques for the evaluation of a process with respect to its life cycle environmental performance. Therefore, the inventory analysis is performed for both processes under study and a comparison to the counterpart petrochemical production processes is made. The result of these comparisons proves that the biotechnological production processes are at an advantage comparing to the petrochemical ones.

Key Words: 1,4 – butanediol, Poly – butylene succinate, Glucose, Corn Stover, Upstream, Downstream, Technical and Economic Evaluation, Life Cycle Assessment

Table of Contents

1 Introduction

Nowadays, due to environmental pollution, the limited fossil fuel sources, carbon dioxide (CO_2) and other Greenhouse gases emissions, the main interest of the science is focused on “green” and sustainable methods of producing these chemicals from renewable sources (Jang et al., 2012). The biomass feedstock used for production of platform chemicals and bio-polymers by fermentation is based on the exploitation of carbon from industrial by-product stream. Any industrial byproduct stream that is produced in significant quantities is considered as a valuable resource rather than as a waste stream. Waste and by-product streams from existing industrial sectors can be used as a renewable resource for the production of fermentation feedstocks used as carbon source. The potential of utilizing waste and by-product streams from current industrial activities for the production of chemicals via microbial bioconversion opens numerous possibilities to connect industrial product lines with existing agricultural production units.

The resources are utilized in laboratory scale equipment to investigate the potential of the production of a variety of intracellular or extracellular product such as important platform chemicals (i.e., selected C2–C6 metabolic products and single cell oil) and biopolymers via bioconversion (Cho et al., 2014). In industrial or white biotechnology (i.e. the application of biotechnology for the processing and production of chemicals, materials and energy) enzymes and micro-organisms are used to make products in sectors such as chemistry, food and feed, paper and pulp, textiles and energy (European Commission, 2015, Koutinas et al. 2014), (Werpy et al., 2004). The possibilities have been expanded by the potential to utilize metabolically engineered microbial host that overproduce industrially useful chemicals, increasing the selectivity of the desired product.

1.1 Biorefineries

Most of the platform chemicals can be produced by the different steps of fractionation of crude oil. However, some of them can be produced by bio-based methods, through the use of biorefineries. The term “biorefinery” describes all these physical or chemical processes, that have as a result the conversion of biomass into a commercial context for the production of fuels, chemicals, polymers, materials, food, feed and value-added chemicals (Koutinas et al.,2014). The goal within the biorefinery concept is to start with a biomass feedstock-mix, to produce a multiplicity of products by a technology-mix in a systematic and technologically feasible way so as to improve economics and environmental performance (Kamm and Kamm, 2004). These biotransformation processes will take place through biotechnology, especially through white biotechnology, using enzymes, microorganisms and fermentation (Liguori et al. 2013).

1.2 Bioplastics & Biopolymers

Most plastic products used nowadays such as polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET) are derived from petrochemical resources. Fossil fuels and natural gas are the main raw materials in order for the petroleum based polymers to be synthesized (Gumede et al., 2018). These polymers have excellent mechanical and thermal properties, thus they are suitable for wide applications in the packaging industry (bottles, plastic bags, etc.). However, these materials enter municipal waste streams at the end of their service life, because their composition complexities together with contamination during use often render recycling uneconomic compared with disposal in landfill (Song et al., 2009). As a result, there is a growing necessity for the development of polymers with similar properties to those that are petroleum based, but susceptible to microbial action.

Currently, bioplastics represent only 1% of the about 320 million tons of plastic produced annually, their market is rapidly growing at about 20 – 100% per year. Bioplastics production is expected to increase from around 4.2 million tons in 2016 to approximately 6.1 million tons in 2021. Such consistent increment is driven not only by the growing awareness of the impact of plastic materials on the environment, but also by the need to reduce their dependence on non-renewable fossil resources (Guidotti et al., 2017).

New types of bioplastics are of particular interest nowadays, which were developed in the past 30 years. Institute for Bioplastics and Biocomposites refers to the so called “New Economy” bioplastics as opposed to “Old Economy” bioplastics (earlier materials developed before petrochemical bioplastics emerged, but still exist on the market) (Biopolymer facts, 2017). “New Economy” bioplastics are separated into two main groups. On the one hand, there are those biopolymers which have a new chemical structure virtually unknown in connection with plastics until a few years ago, on the other hand there are biopolymers that are called “drop-ins”, which they have the same chemical structure as the existed polymers, yet they are bio-based. Both types have been studied as potential biomaterials for a variety of applications such as biomedical devices, biodegradable packaging, adhesives, agricultural areas, auto-motion and construction. Table 1.1 presents some bioplastics separated into the two categories.

Biobased poly – butylene succinate (bioPBS) is one of those polymers which belongs to the “drop – in” class. PBS is a thermoplastic polymer resin of the polyester family. The most common way for its synthesis is the direct esterification of succinic acid (SA) with 1,4 – butanediol (1,4 – BDO). In this study, the PBS production process which is evaluated, is derived from biobased raw materials. Important information for succinic acid and 1,4 – butanediol, as well as more detailed description of bioPBS are presented in the next sections.

Table 1.1 “Old Economy” and “New Economy” bioplastics (Biopolymer facts, 2017).

Bioplastics		
“ Old Economy”	**“ New Economy”**	
	Chemical Novel	**“Drop – in”**
Rubber	Poly – lactic acid (PLA)	Bio Poly – amides
Regenerated cellulose	Poly – hydroxyalkanoates (PHA)	Bio Poly – ethylene
Cellulose acetates	Poly – ethylene furanoate (PEF)	Bio Poly – ethylene terephtalate
Linoleum	Starch blends	Bio Poly – butylene succinate

1.3 Succinic Acid (SA)

Succinic acid is a C4 platform chemical which its properties are presented in Table 1.2. It has a broad range of applications, from high-value niche applications such as personal care products and food additives (used in the food and beverage industry as an acidity regulator), to large volume applications such as bio-polymers (for example PBS), plasticizers, polyurethanes, resins and coatings (European Commission, 2015).

Common industrial routes of its synthesis include partial hydrogenation of maleic acid and carbonylation of ethylene glycol. In living organisms, succinic acid takes the form of an anion called succinate, which has multiple biological roles as a metabolic intermediate. Succinate is a key intermediate in the tricarboxylic acid cycle (TCA), a primary metabolic pathway used to produce chemical energy. Succinate can be formed by reverse activity of the enzyme succinate dehydrogenase (SDH). Under anaerobic conditions certain bacteria (Table 1.3) run the TCA cycle in reverse and convert glucose to succinate through the intermediates of oxaloacetate, malate and fumarate (Cheng et al., 2013, Pateraki et al., 2016). Additionally, new biotechnological routes now allow the production of succinic acid based on renewable feedstock, such as glucose, sucrose and biobased glycerol and in the future also from second generation renewable feedstock (Succinity). The physical properties of biobased succinic such as density, viscosity, molar volume and surface tension are identical to those of petrochemical succinic acid, and therefore it is considered as “drop – in” with no additional investment required in new production equipment.

Regarding the market of biobased succinic acid, there is intense competition among several European and non – European companies at similar levels of development (European Commission, 2015). The most famous companies in Europe are Reverdia (Italy) and Succinity (German, Spain), while BioAmber and Myriant operate production plants in Canada and USA, respectively. In 2013, global production of biobased succinic acid was 38 kt at a total bio-based market value of 108 M$. Fossil-based succinic acid production was approximately 40 kt with a market value of 100 M$. Bio-based succinic acid has a current market price of approximately 2.86 $\$\cdot kg^{-1}$, while the fossil-based equivalent is valued at around 2.500 $\$\cdot kg^{-1}$. At larger scale (typically 50 kt), biobased succinic acid has the potential to be cheaper than fossil-derived succinic acid (European Commission, 2015).

Table 1.2 Properties of succinic acid.

Chemical formula	$C_4H_6O_4$
Molar mass	118.09 $g\cdot mol^{-1}$
Density	1,560 $g\cdot L^{-1}$
Melting point	184–190 °C
Boiling point	235 °C

Table 1.3 Succinic acid producers.

Microorganisms
Actinobacillus succinogenes
Mannheimia succiniciproducens
Basfia succiniciproducens
Escherichia coli
Corynebacterium glutamicum
Yarrowia lipolytica

Furthermore, today's technology for the production of succinic acid from biomass can lead to a significant reduction in Greenhouse gasses emissions (GHG) and in the energy consumption compared to petrochemical equivalents. BioAmber has reported over 100 % reduction of GHG with petrochemical succinic acid emitting 7.1 kg $CO_{2eq}\cdot kg^{-1}_{SA}$ compared to -0.18 kg $CO_{2eq}\cdot kg^{-1}_{SA}$ for the biobased production route on a cradle – to – gate basis. BioAmber has also reported energy consumption for biobased succinic acid is around 34.7 $MJ\cdot kg^{-1}_{SA}$ compared to the fossil-based 97.7 $MJ\cdot kg^{-1}_{SA}$.

The cost of the production process of succinic acid, as well as its environmental impact are highly dependent on the selection of the raw materials, the pretreatment stage, the performance of microorganism, the fermentation stage and the downstream stage for the separation and purification of the product, especially if it is required high purity of the final product for biopolymer formulation (Pateraki et al., 2016).

1.4 1,4 – butanediol (1,4 – BDO)

1,4-Butanediol is colorless viscous compound that its properties are presented in Table 1.4. It has industrially applications as a solvent, it is used in the manufacture for some types of plastics, elastic fibers and polyurethanes and its global market approaches two million tons per year (Burgard et al., 2016). However, despite its wide use, BDO is currently produced exclusively from petrochemical feedstocks such as acetylene, maleic anhydride and propylene oxide.

1,4 - BDO is an organic compound that is not produced naturally in any known organism, thus there are no complete biosynthetic pathways (Yim et al., 2011). The need for an efficient, sustainable process leads to genetically modified microorganisms in order for the one-step production of BDO in a fermentation process. Employing a strain of a specific microbe for the production of a heterologous compound requires, initially, a thorough knowledge of its metabolism and then the establishment of a new biochemical pathway able to produce the required product.

Microorganism Escherichia coli is the most common microorganism that can be engineered for direct production of biobased BDO at high levels from a variety of different carbohydrate feedstocks. Two artificial routes for BDO biosynthesis converge at the common intermediate 4 – hydroxybutyrate (4 – HB). Given that, the production of BDO is divided into two pathways: upstream enzymes for the production of 4 – HB and downstream enzymes for the conversion of 4 – HB to 1,4 – BDO (Yim et al., 2011, Barton et al., 2014). Both these pathways take place during the fermentation process.

Table 1.4 Properties of 1,4 – BDO.

Chemical formula	$C_4H_{10}O_2$
Molar mass	90.12 g·mol^{-1}
Density	1,017.1 g·L^{-1}
Melting point	20.1 °C
Boiling point	235 °C

As Figure 1.1 presents, steps 1 – 4 form the upstream pathway and the 4–HB production. Steps 5 – 7 constitute the downstream pathway in which 4 – HB is converted into 1,4 – BDO. Steps 2 and 7 occur naturally in E. coli, whereas the others are encoded by heterologous genes and plasmids. Depending on the strain modifications that are made, specific concentrations, productivities and yields can be achieved. After fermentation stage, a suitable downstream recovery and purification process is also important to be developed, so as to provide biobased BDO that meets industry specifications and performance requirements.

Regarding the industrial production of biobased 1,4 – butanediol, a California-based company, Genomatica, has developed a patented process, which uses a specially engineered microbe, for 1,4 – BDO production directly via fermentation of sugars (European Commission, 2015). Based on this technology, a number of companies have developed direct fermentations from dextrose. BASF and Novamont are typical examples that headquarter in Europe, while Tate & Lyle and BioAmber have developed similar processes in USA and Canada. Biobased 1,4 – BDO market is around 3 kt annually, with a price of around 3$·kg^{-1}, and a market value of 9 M$. This market share only comprises a tiny fraction of the total BDO market, which in 2013 was an estimated 1,956 kt annually. The market price for fossil-based BDO in 2013 ranged from around 1.8 $·kg^{-1} to 3.2 $·kg^{-1}, depending on the region.

Preliminary life cycle assessments indicate that biobased production process BDO may require 60 - 87% less fossil energy, and reduce CO_2 emissions by around 70 - 117% compared to petrochemical 1, 4 – BDO. Moreover, the biobased fermentation process requires no organic solvent and can use recycled water, further improving its environmental performance (Environmental Protection Agency,1993).

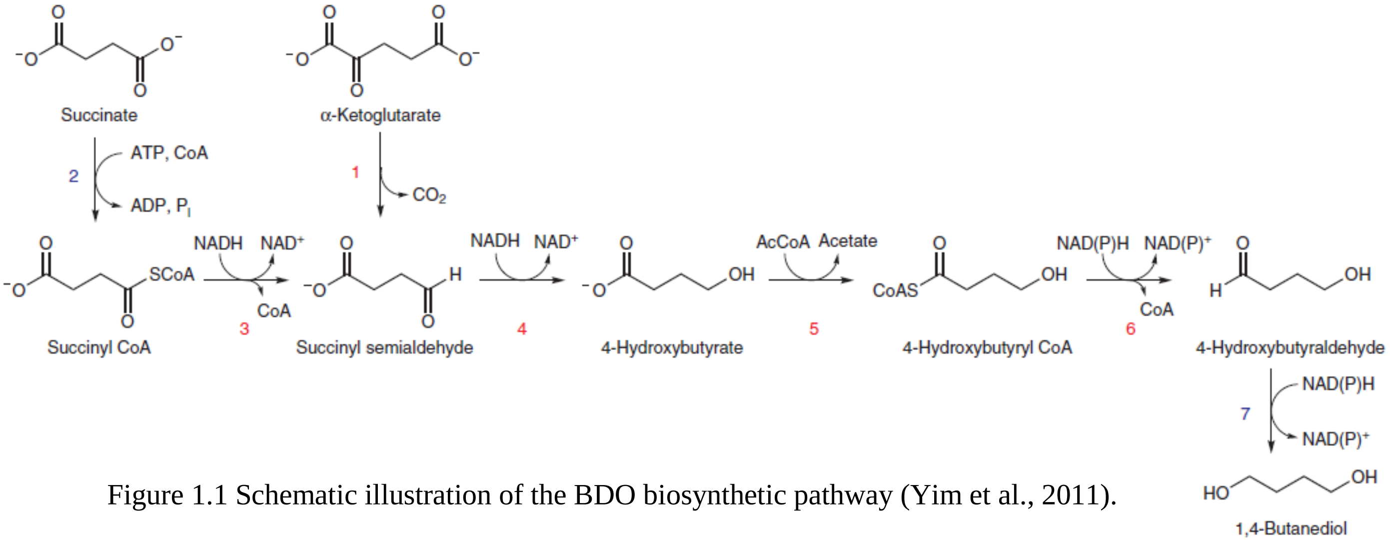


Figure 1.1 Schematic illustration of the BDO biosynthetic pathway (Yim et al., 2011).

1.5 Poly – butylene succinate (PBS)

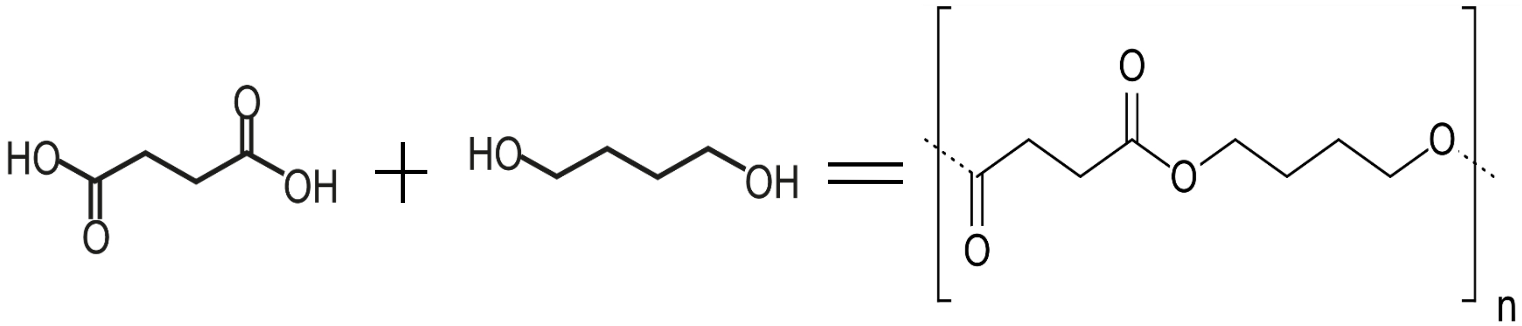
As mentioned in section 1.2, polybutylene succinate (PBS) is a biodegradable aliphatic polyester produced by the polycondensation of succinic acid (SA) and 1,4-butanediol (1,4 – BDO) (Figure 1.2) . This polymer is an interesting material regarding industrial applications, as its mechanical properties are similar to those of popular polymers.

For many years, the production of PBS was linked to the company Showa Highpolymer and was made by petrochemical sources. This polymer, which has the trade name Bionolle, is characterized by similar processability to that of conventional resins, such as polyethylene. Bionolle is one of the most suitable materials for processing into films, which can then be utilized for agricultural purposes, shopping bags and compost bags (Fujimaki, 1997). However, the lack of renewability and the rising price of fossil resources lead to the development of method based on microorganisms for the production of succinic acid and 1,4 – butanediol. Given that, PBS will be an attractive biodegradable polymer that are completely produced from renewable resources (Puchalski et al., 2018).

1.5.1 Properties of PBS

PBS is a crystalline polyester with a melting temperature exceeding 100°C, which is important for applications that require a high temperature range. However, residence time should be low in these application in order for the properties of the polymer not to be degraded (Succinity). PBS does not offer various choices regarding its mechanical properties. Mechanical properties of PBS can however be modified by various compounding routes. Among others, blending and additivation can be used to modify properties (Succipack).

An overview about the mechanical properties of PBS in comparison with other biopolymers and common petro-based polymers is shown in Table 1.5 (Xu et al., 2010). Compared with standard petro-based plastics, PBS is most similar to LDPE in its properties.



Succinic Acid

1,4 – butanediol (1,4 – BDO)

Poly – butylene sucicinate (PBS)

Figure 1.2 Production route of PBS.

Table 1.5 Comparison of properties of PBS compared to other polymers.

	PBS	PBSA	PLA	HDPE	PS	PP
Glass Transition Temperature (oC)	-32	-45	55	-120	105	-5
Melting Point (oC)	114	96	140 – 180	129	Amorphous	163
Heat Distortion Temperature (oC)	97	69	55	82	95	110
Tensile Strength (MPa)	34	19	66	28	46 – 60	33
Elongation at break (J · m^{-1})	560	807	4	700	3 – 4	415
Degree of Crystallinity (%)	34 – 45	20 – 30	0 – 40	69	0	56

1.5.2 Processing of PBS

PBS are suitable as pure materials, without equipment modifications. PBS is well adapted to the following processes:

- Extrusion
- Foil extrusion
- Thermoforming
- Injection moulding

However, there are some options so as for the PBS processability to be improved that are presented in Table 1.6 (Succipack).

Table 1.6 Improvement options for PBS.

Increasing crystallization rate	Increasing modulus at solid state and cohesion at molten state	Improving bubble stability
Blending with PLA	Blending with PLA	Blending with PBSA
Blending with talcum powder	Blending with talcum powder	Blending with PBAT
Blending with TPS		

1.5.3 Applications of PBS

PBS has various potential applications, as presented in Table 1.7 (Succinity). Using conventional melt processing techniques, it is possible to use PBS in electronics and other consumer goods applications as well as various packaging applications such as tea cups, plates and bowls. Thanks to its biodegradability, PBS can also find its way into applications where compostability is important, for instance in agricultural mulch films. A special feature of PBS is its blendability with other plastics, including both biobased and conventional polymers. Even the creation of wood plastic composites is possible because of this property. When blending PBS with PLA, its processability and mechanical properties improve (see section 1.5.2). PBS compounds with PBAT or thermoplastic starch can make its use more economical. Another interesting application for PBS is in combination with PLA for 3D printing. (Succipack)

1.6 Corn Stover

As already mentioned, due to environmental concerns and the limited fossil fuel sources, the main interest is focused on the exploitation of the biomass feedstock and the carbon from industrial by-product streams. The feedstock type and composition can have significant impacts on the overall process design and economics. Feedstock composition, from a potential sugar perspective, clearly affects the product yield.

In this study, corn stover is used as biomass feedstock, because it is the most abundant agriculture residue in the U.S. and is thus readily available (NREL, 2011). Corn stover can vary in composition and moisture content due to corn variety, region, weather, soil type, fertilization practices, harvesting, storage practices and time in storage. National Renewable Energy Laboratory has reported that the average concentrations (dry wt %) of the major stover components are 32% glucan, 19% xylan, 18% solubles and 13% lignin (corrected for protein). These data are used in order for the mass balances to be calculated.

Table 1.7 Applications of PBS.

Packaging / Disposables	**Agriculture**	**Fibres**	**Industrial/Automotive**
Food Packaging	Mulch film	Hygiene products	Wood – plastic composites
Coffee capsules	Plant pots	Fishing nets and lines	Composites with natural fibres
Food service ware			

1.7 Life cycle assessment

In 1990 Life Cycle Assessment is defined as "an objective process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment, to assess the impacts of those energy and material uses and releases on the environment, and to evaluate and implement opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process, or activity, encompassing extraction and processing of raw materials, manufacturing and distribution, use/reuse/maintenance, recycling, and final disposal" (Fava et al.,1991). To put it more accurately, Life Cycle Assessment (LCA) is a technique to assess environmental impacts associated with all the stages of a product's life from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling (life cycle of a product).

The term "life cycle" can be easier understood by the description of Figure 1.3. Raw materials, such as ores or agricultural products, are first extracted from the ground. Next, they are processed - by mixing, fermenting, reacting - and transformed into the desired product. The next step of the process is the purification and recovery of the exact product. Final products are then put in storage, packed and distributed to the markets so as to be used. The final stage is the end of life of a product, which means managing its disposition. The linear path means treating the product as waste. However, there are three more alternatives that better depict the term "life cycle". The disposal stream connects the end of life phase back to previous stages of the typical life cycle through the reuse, remanufacturing and recycling paths.

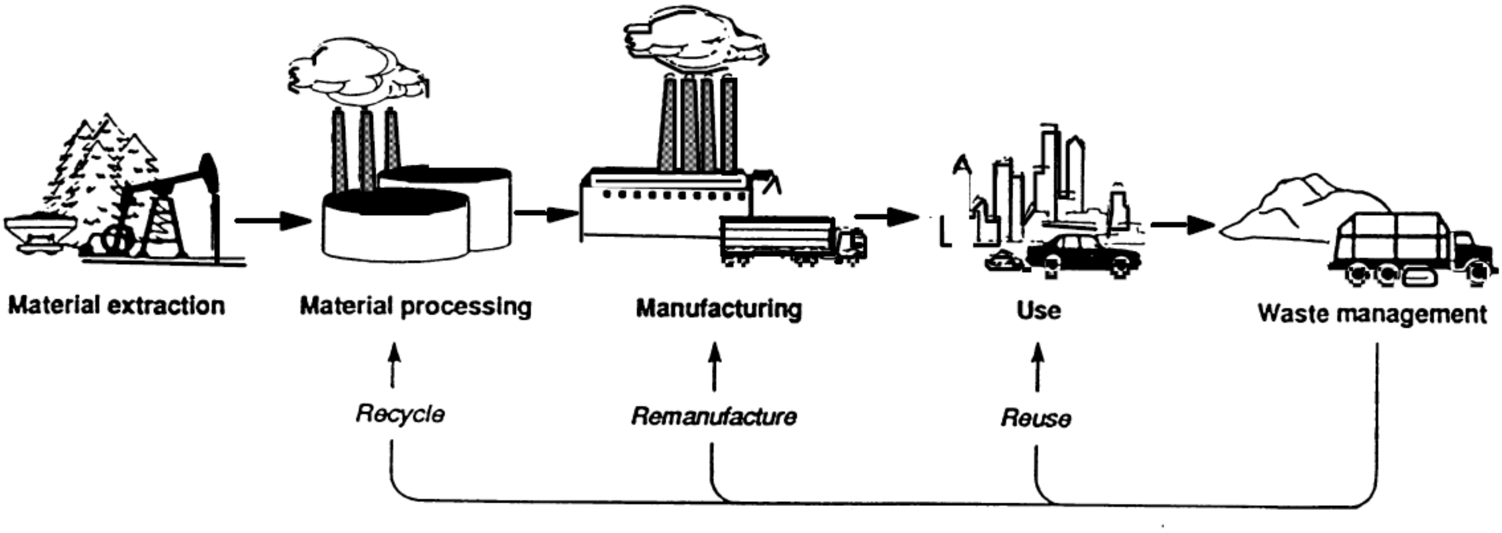


Figure 1.3 Overview of a physical product Life Cycle (Matthews et al., 2015).

1.7.1 The History of Life Cycle Assessment (LCA)

LCA appeared in the late 1960s to early 1970s. The first application of LCA can be traced back to 1969, which was carried out by Coca-Cola for the evaluation of the resource consumption and emissions associated with beverage containers. In that study, the Coca-Cola Company considered whether to replace disposable plastic containers with returnable glass bottles. By analysing the complete life cycle, from raw material extraction to final waste disposal, they were able to track the whole process from cradle to grave, which provided quantitative analysis to compare the environment-friendly conditions of each of the two choices. This study is recognized as one of the first studies of LCA and laid the basis for life cycle inventory analysis (Environmental Protection Agency, 1993).

In the early 1990s, there were various groups of researchers debating the question of "Paper or plastic?" Even these simple questions can, and should, be answered by data and analysis, rather than just a feeling that the natural product is better. The ensuing analysis ignited a major controversy over how to decide which product is better for the environment, beginning with an analysis of paper versus polystyrene cups (Hocking 1991). In the end of the analysis, there was no single agreed upon answer to the simple question of "paper vs. plastic". Even now, any study using the best data and methods available today, will still conclude with an answer along the line of “it depends” (Matthews et al., 2015).

LCA methodology is still being researched and developed since now. Society of Environmental Toxicology and Chemistry (SETAC) and the International Organization for Standardization (ISO) are actively promoting the international standards for the LCA methodology.

1.7.2 The limitations of LCA

There are many different ways of studying a process or system, not just according to the given data, but also depending on the limits being set at each time for the system. The system boundaries determine which processes to be included in the LCA study. Defining system boundaries is partly based on a subjective choice, made during the scope phase of the study, when the boundaries are initially set (see section 2.6). A very crucial fact for the system boundaries is that these are the basis for the comparison of two independent LCA studies. Specifically, comparison between two studies can be made only if they have the same system boundaries. Studies are carried out on the basis of the following categories:

- Cradle-to-grave

Cradle-to-grave is the full Life Cycle Assessment from resource extraction (cradle) to use phase and disposal phase (grave). All inputs and outputs are considered for all the phases of the life cycle.

- Cradle-to-gate

Cradle-to-gate is an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate (i.e., before it is transported to the consumer). One of the significant uses of the cradle-to-gate approach compiles the life cycle inventory (LCI) using cradle-to-gate. This allows the LCA to collect all of the impacts leading up to resources being purchased by the facility. They can then add the steps involved in their transport to plant and manufacture process to more easily produce their own cradle-to-gate values for their products.

- Cradle-to-cradle

Cradle-to-cradle is a specific kind of cradle-to-grave assessment, where the end-of-life disposal step for the product is a recycling process. This is a method used to minimize the environmental impact of products by employing sustainable production, operation, and disposal practices and aims to incorporate social responsibility into product development.

- Gate-to-gate

Gate-to-gate is a partial LCA looking at only one value-added process in the entire production chain. Gate-to-gate modules may also later be linked in their appropriate production chain to form a complete cradle-to-gate evaluation.

1.7.3 LCA Uses

LCA is mostly used to support business strategy and R&D, as input to product or process design and for labelling or product declarations. LCA will be continuously integrated into the built environment as tools which provide practitioners guidance on methods to implement LCI data into the planning and design process. Major corporations all over the world are either undertaking LCA in house or commissioning studies, while governments support the development of national databases to support LCA. LCA also has major roles in environmental impact assessment, integrated waste management and pollution studies.

1.8 Purpose of the study

This study focuses on the design and the techno – economic evaluation of the 1,4 – butanediol production process from two different substrates, pure glucose and glucose from corn stover, as well as its utilization as raw material for the production of the biopolymer poly – butylene succinate (PBS). Three different flowsheets have been evaluated concerning 1,4 – butanediol production process, the polymerization of PBS and the pretreatment of corn stover for the extraction of sugars.

First of all, the study for the production process of 1,4 – butanediol is carried out. More specifically, the fermentation process and the separation and purification stage are designed and the dimensions of the employed equipment are calculated. The final product should have purity greater than 99.5%.

Next, the production of the biopolymer poly – butylene succinate (PBS) is evaluated. 1,4 – butanediol is utilized along with biobased succinic acid as raw materials in order for the PBS polymerization to be designed. Both these processes are evaluated through a techno-economic study and a life cycle assessment.

Finally, the process for the pretreatment of corn stover is evaluated. This process is divided into two different stages. The design of these stages results in the determination of the mass balances of the process and therefore, in the correlation between the desired quantity of total sugars and the required quantity of corn stover. Moreover, the price of glucose that is extracted from corn stover is determined and therefore the economics of 1,4 – BDO are re-evaluated.

2 Methodology and process flow diagrams descriptions

The design of a process and its techno – economic evaluation are based on preliminary economic analysis (accuracy up to ± 30%) that is carried out for the estimation of its total capital investment and operating cost. In this study, the first step is the design of the process flow diagrams for the production of 1,4 – butanediol. Next, data for the production process of succinic acid are used (Ladakis, 2018) and combined with those of 1,4 – BDO in order for the production process flow diagram of PBS to be determined. After that, the process flow diagram for the pretreatment of corn stover is designed in order for the mass balances to be calculated and the required quantity of corn stover that should be converted into glucose to be defined. Finally, a Life Cycle Assessments (LCA) is carried out in order for the environmental impact of PBS production in this study to be evaluated.

The software used to develop the bioprocess design simulations is UniSim (Honeywell). Equipment sizing is performed using well known procedures and rules of thumb.

2.1 Process Flow diagram and Design of 1,4 – butanediol production (1,4 – BDO) production

The process design for the production of 1,4 – BDO is based on the experimental results provided by Burgard et al. (2016) (Table 2.1). Process Flow Diagram (PFD) of the production process is presented in Figure 2.1. The suggested production process consists of two parts, upstream and downstream sections.

The upstream is the part of the process, where the preparation of the raw materials and the fermentation take place in order to produce the desired product. Specifically, the upstream starts with the mixing of the process water and the feedstock to a mixing tank (V-101). The feedstock is composed of glucose (pure or derived from industrial/agricultural waste), ammonium salts as nitrogen (N) source and other nutrients (Table 2.2). After that, the stream enters the heat-sterilization section. The mixture is sterilized at 140 ^{o}C for 2 minutes and then cooled to the fermentation temperature (37 ^{o}C). The sterilization consists of two heat exchangers (E – 101, E – 102) and a holding tube (E – 103). The main sterilization is achieved in the well- insulated holding tube. Finally, the sterilized mixture enters the main fermentor (F – 104). The appropriate number of fermentors for the production process depends on the desired capacity and the maximum volume of bioreactors.

Table 2.1 Parameters of the 1,4 – BDO fermentation.

Bacterial Strain	E.coli
Concentration of 1,4 – BDO (g·L^{-1})	125
Yield (g·g^{-1})	0.4
Productivity (g·L^{-1} h^{-1})	3.5
Fermentation time (h)	36

Table 2.2 Nutrients for the fermentation.

Nutrient	**Concentration (g · L^{-1})**
Na_2HPO_4	6.78
NaCl	0.50
$CaCl_2$	0.01
NH_4Cl	2.00
$(NH_4)_2SO_4$	1.00
KH_2PO_4	3.00
$MgSO_4$	0.12
$NaHCO_3$	0.84

1,4 - BDO is an organic compound that is not produced naturally in any known organism, thus there are no complete biosynthetic pathways. The need for an efficient, sustainable process leads to the employment of genetically modified microorganisms in order for the one-step production of BDO in a fermentation process to be achieved. During the fermentation process, BDO fermentation is simulated under fed-batch conditions. The pH is held at 7 and the reaction is carried out in microaerobic conditions (0.02 vvm).

Next, the fermentation product proceeds in the downstream section. In this section, the isolation and purification of the product take place. Specifically, the product is separated from the undesired components, such as the biomass, using a centrifugal separator (CF – 101). The biomass free solution is fed to cationic resin columns (V-102, V-103) in order to transform organic salts to their corresponding organic acids via acidification and then to anionic resin columns (V-104, V-105) in order for the organic acids to be removed. The exit stream is concentrated using mechanical vapor recompression (MVR)-force circulation evaporator system (EV-101). The concentrated liquid is supplied into distillation column (T – 101) so as to be separated from the remaining by-products and to be recovered from its aqueous solution.

2.1.1 Mass Balances of the 1,4 – BDO production process

In order for the mass balance of the bioreactor to be derived, it is necessary to determine the formation reaction of 1,4 – BDO. For that reason, the assumption of two different stages during fermentation is made, the microbial growth stage and the 1,4 – BDO production stage. The empirical formula of the microorganism used is $CH_{1.77}O_{0.49}N_{0.24}$. Calculations and assumptions for the by – products as well as the biomass produced during the reaction are made based on Yim et. al (2011) and Burgard et. al (2016). The relevant calculations and assumptions can be found in the Appendix A. The total formation reaction is:

$$\begin{aligned}&1.7361\ C_6H_{12}O_6 + 1.6629\ O_2 + 0.15\ NH_3 \rightarrow\\&0.625\ CH_{1.77}O_{0.49}N_{0.24} + 1.387\ C_4H_{10}O_2 + 0.0154\ C_2H_6O + 0.0154\ C_4H_6O_2\\&\qquad + 0.0636\ C_2H_4O_2 + 0.0548\ C_4H_8O_3 + 2.715\ H_2O + 3.805\ CO_2\end{aligned}$$

At this point, it is possible to calculate the mass of the components entering and leaving the bioreactors for each capacity using the reaction stoichiometry. Therefore, the mass flow rates of the whole process, as well as energy requirements and utility demands are determined for any required annual capacity (Appendix A).

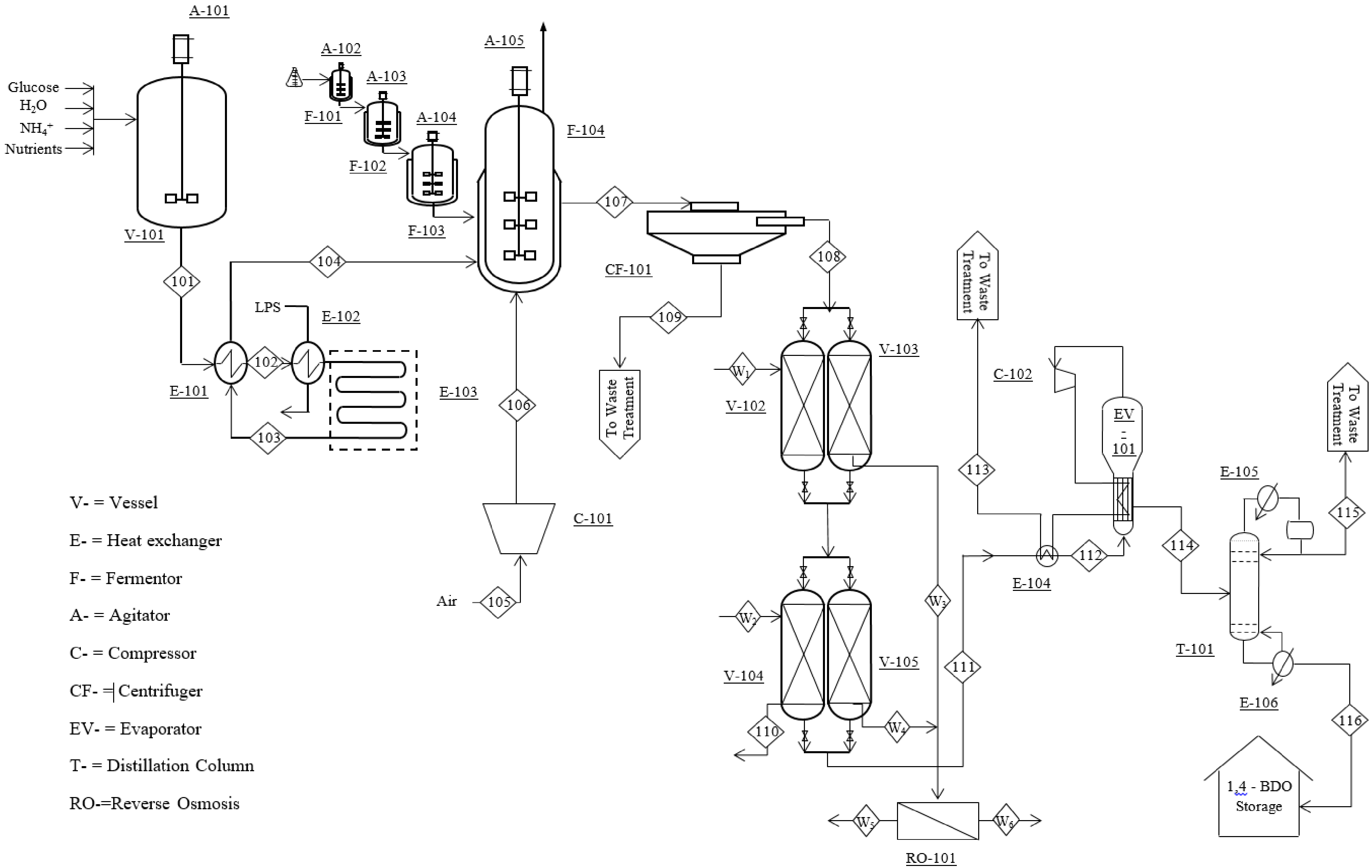


Figure 2.1 Process Flow Diagram of 1,4 – BDO.

2.1.2 Bioreactor Design

The optimal design of upstream processes is based on Dheskali et al. (2017). In order to achieve a specific annual production capacity P_y ($t \cdot y^{-1}$), an integer number of bioreactors N_f is used. The onstream time τ_y corresponds to 95% of the total annual hours (8,300 $h \cdot y^{-1}$). For a given annual production capacity P_y and given product concentration in fermentation broth c_f ($kg \cdot m^{-3}$) the total annual broth volume V_y (m^3) is determined (Eq. 1).

$$V_y = \frac{P_y}{C_f} \qquad \text{Eq. 2.1}$$

The total annual broth volume V_y is produced at an annual operation time t_y (8300 $h \cdot y^{-1}$) of the plant by bioreactors with working volume V_w (m^3). In case of batch operations the working volume V_w and the number of bioreactors N_f must meet the requirements for the accomplishment of the annual production capacity P_y. At the same time, an appropriate scheduling is applied at the fermentation stage in order to follow the continuous operation of the upstream and downstream stages. The V_w and N_f are calculated based on the methodology, previously described by Dheskali et al. 2017. This methodology is applied for the determination of scheduling characteristics loading time τ_l (h), operation time τ_f (h), uploading time τ_{ul} (h), active volume V_w (m^3), total volume V_R (m^3) and number of batches (N_b), aiming to minimize the cost of annual production capacity.

The characteristic size of bioreactor is the total volume V_R (m^3). The determination of V_R based on the bioreactor working volume V_W as shown in Equation 2:

$$V_R = \frac{V_w}{\lambda} \qquad \text{Eq. 2.2}$$

where λ is a specific fraction of working volume (V_W) to the total volume (V_R). Typically, λ is set 0.8.

The geometrical characteristics of bioreactors are estimated by the assumption of flat bottomed tank with height H (m) and diameter D (m). The H and D were estimated using the specific height to diameter ratio $\varphi = \frac{H}{D} = 3$ and Equation 3.

$$V_R = \varphi \cdot \frac{\pi \cdot D^3}{4} \qquad \text{Eq. 2.3}$$

The power requirements for agitation estimated using the assumption of 1 kW per m^3 of bioreactor working volume and efficiency of agitator 0.9. The optimal design and function for the selected capacity are shown in Table 2.1.

2.1.3 Heat – Sterilization Design

As it has already been mentioned, the fermentation medium must be sterilized before its entrance in the bioreactor. The mixture is sterilized at 140 ^oC for 2 minutes and then cooled to the fermentation temperature (37 ^oC).

First heat exchanger (E-101)

The mixture enters E-101 at 20 °C and is heated up to 130 °C. The heating is achieved by the exchange of heat between the fresh feed stream and the stream which leaves E-103. The second stream enters the exchanger at 140 °C and is cooled up to the fermentation temperature.

Second heat exchanger (E-102)

The stream which leaves E-101 at 130 °C is heated up to 140 °C. The heating is achieved by the exchange of heat between this stream and a low pressure steam at 160 °C.

Holding tube (E-103)

Basically, the sterilization takes place inside the holding tube. The temperature of the mixture is constant (140 °C) and the residence time is 2 min. According to that time, the length of the tube is calculated, so as to achieve the sterilization in the end of it.

The power requirements Q (kW) for heating a stream from an inlet temperature (T_{in}) to an outlet temperature (T_{out}) are determined by Equation 2.4:

$$Q = \dot{m} \cdot c_p \cdot \ (T_{out} - T_{in}) \qquad \text{Eq. 2.4}$$

where $\dot{m}$ is the mass flow of the stream and c_p ($kJ \cdot kg^{-1} K^{-1}$) is the heat capacity of the media.

The heat transfer area of heat exchanger equipment is estimated by Equation 2.5:

$$A = \frac{Q}{U \cdot \Delta T_{LM}} \qquad \text{Eq. 2.5}$$

where U is the overall heat transfer coefficient ($kW \cdot m^{-2} K^{-1}$) and ΔT_{LM} is the logarithmic mean temperature difference (°C) given by Equation 6. The maximum permitted heat transfer area of a heat exchanger should be up to 1000 m^2.

$$\Delta T_{LM,1} = \frac{(T_{hot,in} - T_{cold,out}) - \ (T_{hot,out} - T_{cold,in})}{\ln\left(\frac{(T_{hot,in} - T_{cold,out})}{(T_{hot,out} - T_{cold,in})}\right)} \qquad \text{Eq. 2.6}$$

The mass flow rate of the steam necessary for heating processes m_s ($kg \cdot s^{-1}$) is given by:

$$\dot{m}_s = \frac{Q}{\Delta h_s} \qquad \text{Eq. 2.7}$$

Where Δh_s ($kJ \cdot kg^{-1}$) is the latent heat of the steam and Q (kW) is the power requirement Q (kW) for heating the desired stream.

Dimensions of the holding tube are based to specifications of the holding time and determined by Equation 2.8:

$$\dot{V} = \left(\frac{L_t}{\tau_h}\right) \cdot \left(\frac{\pi \cdot d_t^2}{4}\right) \qquad \text{Eq. 2.8}$$

where $\dot{V}$ ($m^3 \cdot s^{-1}$) is the volumetric flow rate that enters the holding tube, L_t is the length (m), τ_h is the holding time (s) and d_t (m) is the diameter of the holding tube. The quotient $\frac{L_t}{\tau_h}$ is the velocity of the liquid in the tube and is considered that the maximum value is 1 $m \cdot s^{-1}$.

2.1.4 Centrifugal separator design

After the fermentation process the fermentative liquid is sent to centrifugal separator and accomplished a separation of biomass from the solution. The design of centrifuge is based on the volumetric flow rate of the inlet stream ($m^3 \cdot h^{-1}$) and the energy requirements are estimated by assuming 1 bhp per m^3.

2.1.5 Columns design

Packed columns are used for both the acidification (V – 102, V – 103) and the removal (V – 104, V – 105) of the organic salts. For the acidification, the packed material of column is the ion-exchange resin Amperlite IR-120, a cationic resin of sulfonic (SO_3H) type. For the removal, the packed material of column is the ion-exchange resin Amperlite IRA-402, an anionic resin of quaternary ammonium type.

The calculation of packed columns characteristics is based on the residence time of the applied solution in the columns and on the volumetric flow rate F_v ($m^3 \cdot h^{-1}$) of each column. The residence time is considered as 0.5 h. The volume of the packed resins used for the ion exchange is given by Equation 2.9.

$$V_{resin} = \frac{F_{acids} \cdot t_{residence}}{\text{porosity} \cdot d_{resin} \cdot \text{max capacity}_{resin}} \qquad \text{Eq. 2.9}$$

where F_{acids} ($kg \cdot h^{-1}$) is the mass flow rate of the acids that should be removed, d_{resin} is the density of the dry resins (1.25 $kg \cdot m^{-3}$), the porosity is 0.5 and the maximum capacity of resins is the assumption that 1 t of resin can convert 100 kg of organic salt to organic acids.

The volume of the columns and therefore geometrical characteristics are estimated by Equations 2.10 and 2.11.

$$V_{column} = 1.2 \cdot V_{resin} \qquad \text{Eq. 2.10}$$

$$V_{column} = h \cdot \left(\frac{\pi \cdot D^2}{4}\right) \qquad \text{Eq. 2.11}$$

where h and D are the height (m) and diameter (m) of the column respectively.

The columns operate in batches, thus the acidification unit consisted of two columns operating consecutively. While the first one is in operation, the other is being regenerated either with HCl while the acidification takes place or with NaOH while the organic acids are removed. An important assumption for the resins is that its shelf life is 3 years.

2.1.6 Preheater design

The design of the heat exchanger (E- 104) follows the same equations as the heat exchangers E-101 and E-102 (Equations 2.4, 2.5 and 2.6). The stream exits the heat exchanger with a temperature of 100 °C. The power requirements Q (kW) of the heater are satisfied from both the thermal energy of the stream F13 and a utilized LPS stream. F12 stream is the recompressed vapour fraction that exits the evaporator (EV – 101).

2.1.7 Mechanical vapor recompression (MVR) evaporator design

A mechanical vapor recompression (MVR)-force circulation evaporator system is chosen for the evaporation process. At this type of evaporator, the temperature and pressure of the secondary vapor that is produced from the liquid material rise via re-compression on a centrifugal compressor and this vapor is used as heating agent.

For the design, the recompression is assumed as an isentropic process and the work $W_{S,\Delta S=0}$ (kJ kmol^{-1}) is estimated as follows (Equation 2.12):

$$\mathrm{W_{S,\Delta S=0}} = \frac{\mathrm{R_g} \cdot \mathrm{T_s}}{\mathrm{a}} \cdot \left(\left(\frac{\mathrm{P_d}}{\mathrm{P_s}} \right)^{\mathrm{a}} - 1 \right) \qquad \text{Eq. 2.12}$$

where T_s is the steam temperature, P_s (bar) is the steam pressure, P_d (bar) is recompress pressure, R_g is the ideal gas constant (8.314 kJ-^{1}kmol^{-1} K^{-1}), a (=1-C_v / C_p) is a constant approximately equal to 0.24 for steam.

The electricity consumption W_c (kW) of compressor is estimated by the Equation 2.13:

$$\mathrm{W_c} = \frac{\mathrm{W_{S,\Delta S=0}}}{\mathrm{e_c}} \qquad \text{Eq. 2.13}$$

where e_c is the yield of compressor.

The recompress temperature of steam T_d (K) is estimated by Equations 2.14 and 2.15:

$$\mathrm{T'_d} = \mathrm{T} \cdot \left(\frac{\mathrm{P_d}}{\mathrm{P_s}} \right)^{\mathrm{a}} \qquad \text{Eq. 2.15}$$

$$\mathrm{T_d} = \mathrm{T} + \frac{\mathrm{T'_d} - \mathrm{T}}{\mathrm{e_c}} \qquad \text{Eq. 2.14}$$

where T_d' is the temperature of steam arising from isentropic increase of pressure and T is the temperature of steam that is produced by the evaporation of the inlet product.

The heat transfer area of the evaporator is determined by the Equation 2.5. Q (kW) is the power needs to evaporate a required stream fraction and calculated as follows:

$$Q = \dot{m}_{vapour} \cdot \Delta h_{vapour} \qquad \text{Eq. 2.16}$$

where $\dot{m_{vapour}}$ is the mass flow of the vapour stream of the evaporator and $\Delta h_{vap,w}$ is the latent heat of this stream. The overall heat transfer coefficient U (kW m^{-2} K^{-1}) is estimated by empirical Equation 2.17 that is used for forced circulation evaporators.

$$U = 5 + 0.25 \cdot (T_d - T) \quad \text{Eq. 2.17}$$

The evaporation is conducted under conditions of 100 °C and 1 bar. The produced steam is recompressed to 1.6 bar and the temperature rises to 159.4 °C. The temperature of saturated steam at 1.6 bar is 113.6 °C, thus the recompressed steam is superheated steam. The centrifugal compressor efficiency is assumed 0.75.

2.1.8 Distillation column design

After evaporation, the stream F114 which contains 1,4 – BDO, water and by – products, enters the distillation column T – 101, in order for the desired product to be isolated. The boiling point of 1,4 – BDO is approximately 228 °C, so it can be easily separated from the solution and recovered in the lower level of the distillation column. For the dimensioning of the distillation column, the diameter and the height are calculated. The parameters ρ_L (kg · m^{-3}), ρ_v (kg · m^{-3}), V′ (kg · s^{-1}), rr_{min} and $N_{T,min}$ are determined from UniSim (Honeywell). In order for the Equations 2.18 – 2.26 to be used, constant relative volatility is used.

The available surface of the traces, thus the diameter of the distillation column, depends on both the velocity (Eq.18) and the mass flow rate (Equation 2.19) of the gas that goes around the distillation column. (Kookos I., 2007)

$$u_v = 0.06 \left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{\frac{1}{2}} \quad \text{Eq. 2.19}$$

$$V' = u_v \cdot \rho_v \cdot A_{net} \quad \text{Eq. 2.18}$$

Assuming that traces have circular geometry, their diameter is calculated by Equation 2.20.

$$\frac{\pi \cdot D_c^2}{4} = \frac{A_{net}}{\lambda} \quad \text{Eq. 2.20}$$

where λ is the factor of the surface of the tray that is available for the fluid (considered as 0.88)

As regards the height of the column, the vital parameters are the number of traces and the Reflux Ratio. Following the below equations (Eq. 2.21 – 2.26) the height of the column is determined.

$$rr = 2 \cdot rr_{min} \quad \text{Eq. 2.23}$$

$$X = \frac{rr - rr_{min}}{rr + 1} \quad \text{Eq. 2.25}$$

$$Y = 0.75 \cdot (1 - X^{0.5668}) \quad \text{Eq. 2.24}$$

$$Y = \frac{N_T - N_{T,min}}{N_T + 1} \quad \text{Eq. 2.22}$$

$$N = \frac{N_T - 1}{E_o} \quad \text{Eq. 2.21}$$

where E_o is the total efficiency grade (considered as 0.7). TS is the distance between the trays and is considered as 0.6096 m.

$$\mathrm{H} = 1.2 \cdot (\mathrm{N} - 1) \cdot \mathrm{TS} \qquad \text{Eq. 2.26}$$

Distillation columns also consist of two heat exchangers, condenser (E – 105) and reboiler (E – 106). These heat exchangers provide a means of countercurrent contact between the rising vapor and the descending liquid. Equations 2.4 – 2.7 are used in order for the surface of the exchangers to be determined as well as the quantity of the heating/cooling agent to be calculated.

2.2 Process Flow diagram and Design of Poly – butylene succinate production (PBS)

In this study, PBS is synthesized by the esterification polymerization method. The synthetic procedure can be separated into two stages: esterification and polycondensation. The reactions starts with stoichiometric amounts of succinic acid and 1,4 – butanediol, or using an excess of 1,4-butanediol not above 10% in order for the ester to be created. After most of the water produced by esterification has been distilled off, the polycondensation is fulfilled under vacuum at a higher temperature, e.g., 200°C, to remove the butanediol formed in the reaction and polymerize the oligomers to polymer. (Chen et al., 2010)

The design and simulation of the production process of poly – (butylene succinate) (PBS) are carried out based on literature data by Kamikawa et al. (2013). The suggested production process (Figure 2.2) consists of three parts, the preparation of raw materials, the esterification and finally the polymerization of monomer and the production of the desired polymer PBS.

The first step of the process is the preparation of the raw materials by mixing succinic acid and 1,4 – butanediol in a mixing tank (V – 201). The molar ratio of 1,4 – BDO to succinic acid is 1.3:1. During the mixing, raw materials are heating up to 80 ^{o}C by employing LPS in order for the flowability of the mixture to be secured.

The liquid outflow (stream 203) enters the esterification reactor (R – 201), after its heating up to 180 ^{o}C. The reaction takes place at 230 ^{o}C and 1 bar in order for an appropriate rate of reaction to be secured and the ester of succinic acid and 1,4 – BDO is generated after 3 h. After the reaction, the vapour stream (stream 206) is distillated in order for the remaining 1,4 – BDO to be recovered and reused in the process.

The polymerization of ester is a polycondensation reaction in presence of titanium tetrabutoxide as catalyst with a concentration of 2000 ppm (with respect to succinic acid). The temperature of the reaction is 240 ^{o}C and the degree of vacuum is 2 torr. After 16.5 h of reaction, stream 210 leaves the polycondensation reaction (R – 202) containing PBS with Molecular Weight 70,000.

The vapour stream of the reactor (stream 211) is, firstly cooled up to 80 ^{o}C and then it is compressed to 0.05 bar. Precooling is necessary because if the vapour stream was compressed in its initial temperature, the final temperature would have surpassed the autoignition temperature of 1,4 – BDO (350 ^{o}C). After that, the vapour stream is cooled in E – 207 so as to liquefy and then enters P – 201 in order to return in atmospheric pressure and to be fed in T – 201.

Distillation column is used so as the remaining 1,4 – BDO to be recovered. The produced PBS (stream 210) is cooled in E – 206 and after a pelletization process (not included in this study), it is stored.

After the simulation of the polymerization process, the yield for the polymerization is 0.73 $kg_{PBS} \cdot kg^{-1}{}_{raw\ materials}$ (total quantity of raw materials). The mass flow rates of the polymerization process, as well as energy requirements and utility demands are determined for any required annual capacity. (Appendix B).

2.2.1 Preparation Tank Design

In the raw materials preparation tank, succinic acid and 1,4 – butanediol are mixed in order for the esterification reaction to take place in the next step. The residence time in the mixing tank is determined 1 h. As a result, the effective and the real volume of the tank are calculated (Equations 2.27 and 2.28).

$$V_{eff,V201} = t_{r,V201} \cdot F_{203} \qquad \text{Eq. } 2.28$$

$$V_{V201} = \frac{V_{eff,V201}}{\lambda} \qquad \text{Eq. } 2.27$$

where$t_{r,V201}$ (h) is the residence time, F_{203} ($m^3 \cdot h^{-1}$) is the volumetric flow rate of stream 203, λ is a specific fraction of working volume (V_W) to the total volume (V_R). Typically, λ is set 0.8.

The power requirements for agitation estimated using the assumption of 1 kW per m^3 of bioreactor working volume and efficiency of agitator 0.9.

During the mixing, raw materials are heating up to 80 ^oC by employing LPS in order for the flowability of the mixture to be secured. The amount of the required steam is calculated by Equations 2.4 and 2.7.

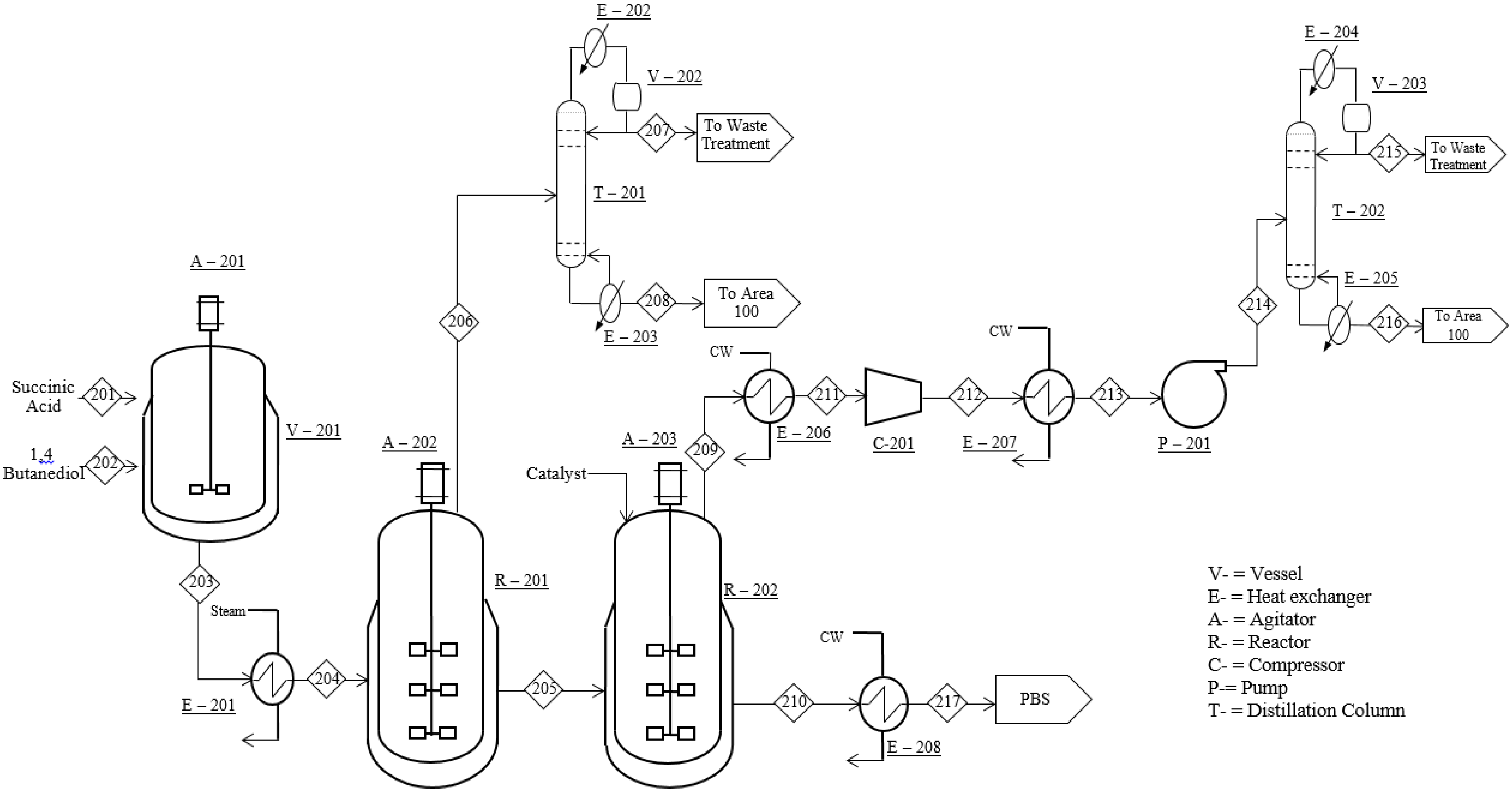


Figure 2.2 Process Flow Diagram of PBS (polymerization).

2.2.2 Esterification and Polymerization reactors Design

The liquid outflow (stream 203) enters the esterification reactor (R – 201). The reaction takes place at 230 °C and 1 bar and the ester of succinic acid and 1,4 – BDO is generated after 3 h. After that, the polycondensation reaction takes place and after 16.5 h of reaction, stream 210 leaves the polycondensation reaction (R – 202) containing PBS. Similar to the design of preparation tank, Equations 2.27 and 2.28 are used in order for the volume of the reactors to be determined and Equations 2.4 and 2.7 for the power requirements and the required steam to be calculated.

2.2.3 Heat exchanging Design

Heat exchanging is necessary during process in order for the streams 209 and 212 to be cooled before compression and stream 210 to be cooled in order to be storage. The determination of power requirements Q of these heat exchangers (E – 206, E – 207 and E – 208), as well as their heat transfer area are estimated by Equations 2.4 – 2.7.

2.2.4 Compressor Design

After polymerization, the pressure of stream 209 should be readjusted to atmospheric conditions. Stream 209 is a vapor stream, thus a compressor is used. For its design, Equations 2.12 and 2.13 are used. During compression, not only is the pressure increased but also the temperature of the stream is. P_{212} is assumed 0.05 bar in order for the T_{212} not to surpass the autoignition temperature of 1,4 – BDO. The compressor efficiency is assumed 0.75.

2.2.5 Pump Design

Stream 214 that enters T – 202 is in liquid phase, so the use of a pump is necessary. The design of a pump in order for its power Q_P (W) to be determined follows Equation 2.29:

$$Q_P = \frac{d \cdot g \cdot h \cdot F_{213}}{n} \qquad \text{Eq. 2.29}$$

where d ($kg \cdot m^{-3}$) is the density of the stream, g ($m \cdot s^{-2}$) is the gravitational constant, h (m) is the conversionof pressure change into distance, F ($m^3 \cdot s^{-1}$) is the volumetric flow rate and n is the efficiency of the pump.

2.2.6 Distillation columns design

Distillation columns are used in this process in order for the 1,4 – butanediol to be recovered after esterification and polymerization step from its aqueous solution. Their design follows the same Equations as section 2.1.8.

2.2.7 Important Assumption

It should be noted that the simulation is performed in Honeywell UniSim that has limited capability as far as polymerization reactions are concerned, thus some assumptions have been made in order for the simulation to be achieved. The first assumption is related to the thermodynamic data of the ester and the polymer of the process. These products had to be inserted as hypothetical components in the simulation because of their absence from the data of the program. As a result, their properties had to be determined by estimation methods (Joback for ester and Van Krevelen for PBS). Another assumption is the molecular weight of the final product. The products of a polymerization reaction are diverse and the chains have various molecular weight. In order for the difficulty to be surpassed, an average molecular weight is decided based on literature data (Kamikawa et al., 2013). Finally, owing to the lack of data about the specific reaction rate of the polycondensation, a stoichiometry reaction for polymerization is assumed.

2.3 Process Flow diagram for the pretreatment of corn stover

The design of the production process for the pretreatment of corn stover is based on NREL (2011). This process consists of two stages: the initial pretreatment of the feedstock and the enzymatic hydrolysis in order for the cellulose to be converted into glucose

2.3.1 Initial pretreatment

During the initial pretreatment process, chemical hydrolysis is carried out in order for the most of the hemicellulose carbohydrates in the feedstock to be converted into soluble sugars (xylose, mannose, arabinose, and glucose). The reaction that is taken place is catalysed by dilute sulfuric acid and heat from steam. .

In the first step, milled corn stover is fed to the receiving bins after its delivery in the factory. The pretreatment reactor system includes a feedstock receiving system, followed by a vertical vessel (M – 301) with a long residence time for steam-heating. The vertical presteamer tank is designed for a residence time of up to 10 minutes at a temperature of up to 165°C, though in the current study it only operates at 100°C such that no significant hydrolysis reactions occur in the presteamer. (NREL, 2011)

After that, feedstock enters the horizontal pretreatment reactor (M – 302), which operates at a higher pressure and a short residence time. Dilute sulfuric acid is added in this reactor at this point so as to control the pretreatment effluent at 30 wt % total solids. The design conditions of this tank are 158°C and 22.1 mg acid/dry g of biomass. The temperature of the reactor is maintained constant by utilizing high-pressure steam. The reactor pressure is held at the bubble point for the mixture. The residence time in the horizontal pretreatment reactor is nominally 5 minutes.

The pretreatment reactor is discharged to a blowdown tank (T – 301). The tank temperature is held at 130°C by controlling the pressure in it. Stream 303 leaves T – 201 and enters the oligomer conversion tank (T – 302), where it is held at 130°C for 20–30 minutes. After this stage, the hydrolysate slurry containing 30 wt % total solids and 16.6 wt % insoluble solids and having atmospheric pressure is sent to the tank (T – 303). Here, the slurry is diluted with water in order to ensure miscibility through enzymatic hydrolysis. Ammonia gas is mixed into the dilution water to raise the hydrolysate pH to 5. The residence time in T – 303 is 30 minutes and the dilution cools the slurry to 75°C.

This initial pretreatment section is a preliminary stage during which glucan is converted into glucose in a low percentage (9.9 %). The basic conversion of glucan is achieved in the next section. On the other hand, xylan has an almost 100 % conversion into xylose in this stage.

2.3.2 Enzymatic Hydrolysis

The next step is the conversion of cellulose into glucose by enzymatic hydrolysis. Stream 307 leaves T – 303 as a neutralized, diluted hydrolysate. This stream enters E – 301 so as to be cooled and then is fed to T – 304 after its mixing with the appropriate enzyme (cellulase) in the mixer A – 304. After the cellulase enzyme stream is mixed, the total solids loading is 20 wt % and the temperature is 48°C.

The first stage of enzymatic hydrolysis begins in a continuous, high-solids reactor (T – 304). The residence time in this first stage is 24 hours, thus a low conversion of cellulose is achieved. The continuous high-solids hydrolysis reactor (T – 304) is considered as an empty tower, with the stream entering at the top and flowing down with gravity. The amount of enzyme which is purchased and used is determined by the amount of cellulose present in the hydrolysate and the specific activity of the enzyme. In the present study, the total cellulase loading is 20 mg enzyme protein/g cellulose to achieve a 90% conversion to glucose.

As the cellulose is saccharified by the enzyme, the viscosity of the mixture drops dramatically, so as to be pumped to the next tank. Hydrolysis continues in T – 305 where the main hydrolysis is taken place. During the process, the temperature is maintained constant with cooling water. Temperature control during enzymatic hydrolysis is very important because of the optimum performance of the enzyme. After 60 hours of additional enzymatic hydrolysis in T – 305, the concentration of glucose is increased from 8.81 $kg \cdot m^{-3}$ (Stream 309) to 73.66 $kg \cdot m^{-3}$ (Stream 310). Finally, the saccharified stream is centrifuged (CF – 301) in order for the lignin to be isolated and the main stream containing sugars enters the fermentation stage.

The mass flow rates of the process are presented in Appendix C.

M – 301 Vertical Presteamer

M – 302 Horizontal Pretreatment Reactor

T – 301 Blowdown Tank

A – 301 Blowdown Tank Agitator

T – 302 Oligomer Conversion Tank

A – 302 Oligomer Conversion Tank Agitator

T – 303 Ammonia Addition Tank

A – 303 Ammonia Addition Tank Agitator

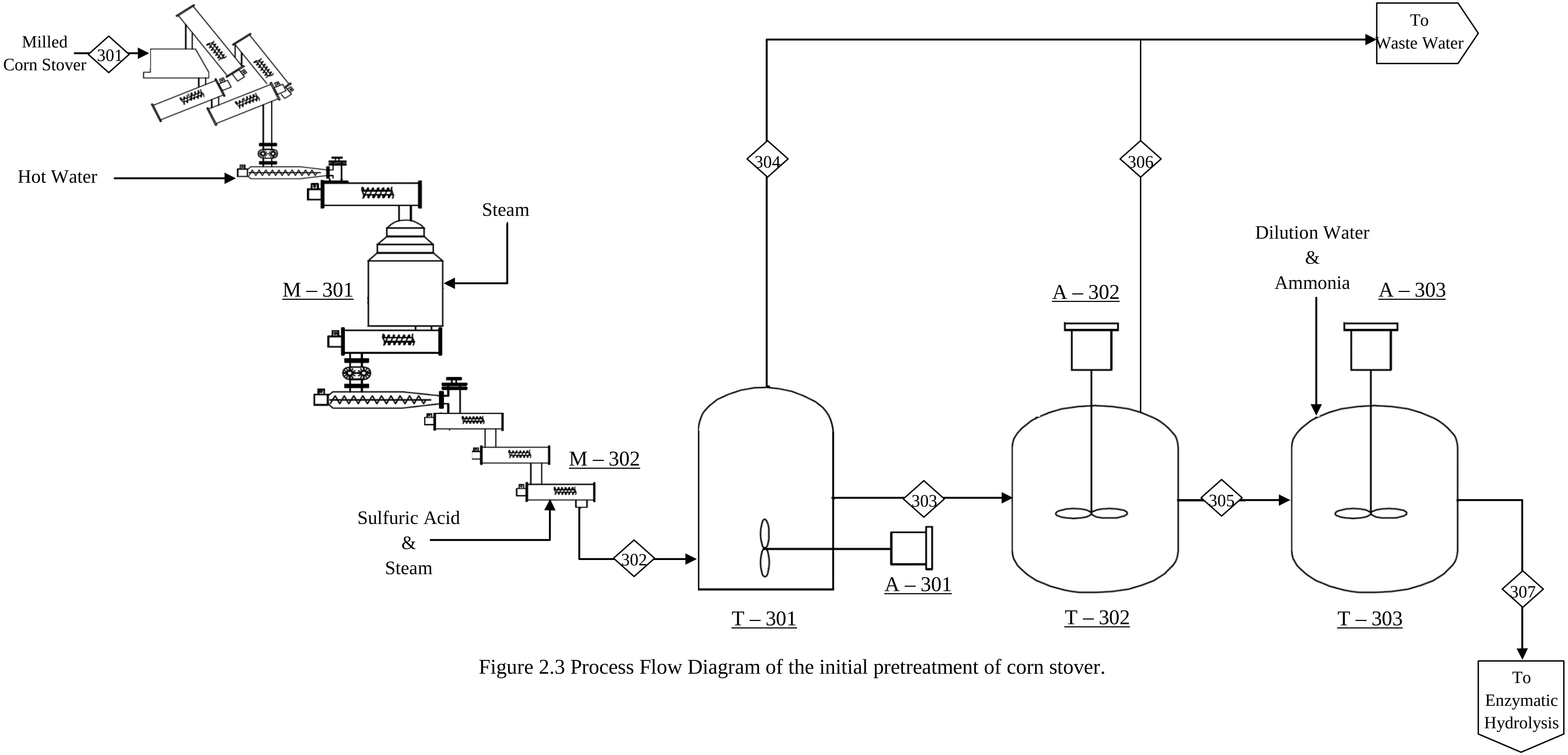


Figure 2.3 Process Flow Diagram of the initial pretreatment of corn stover.

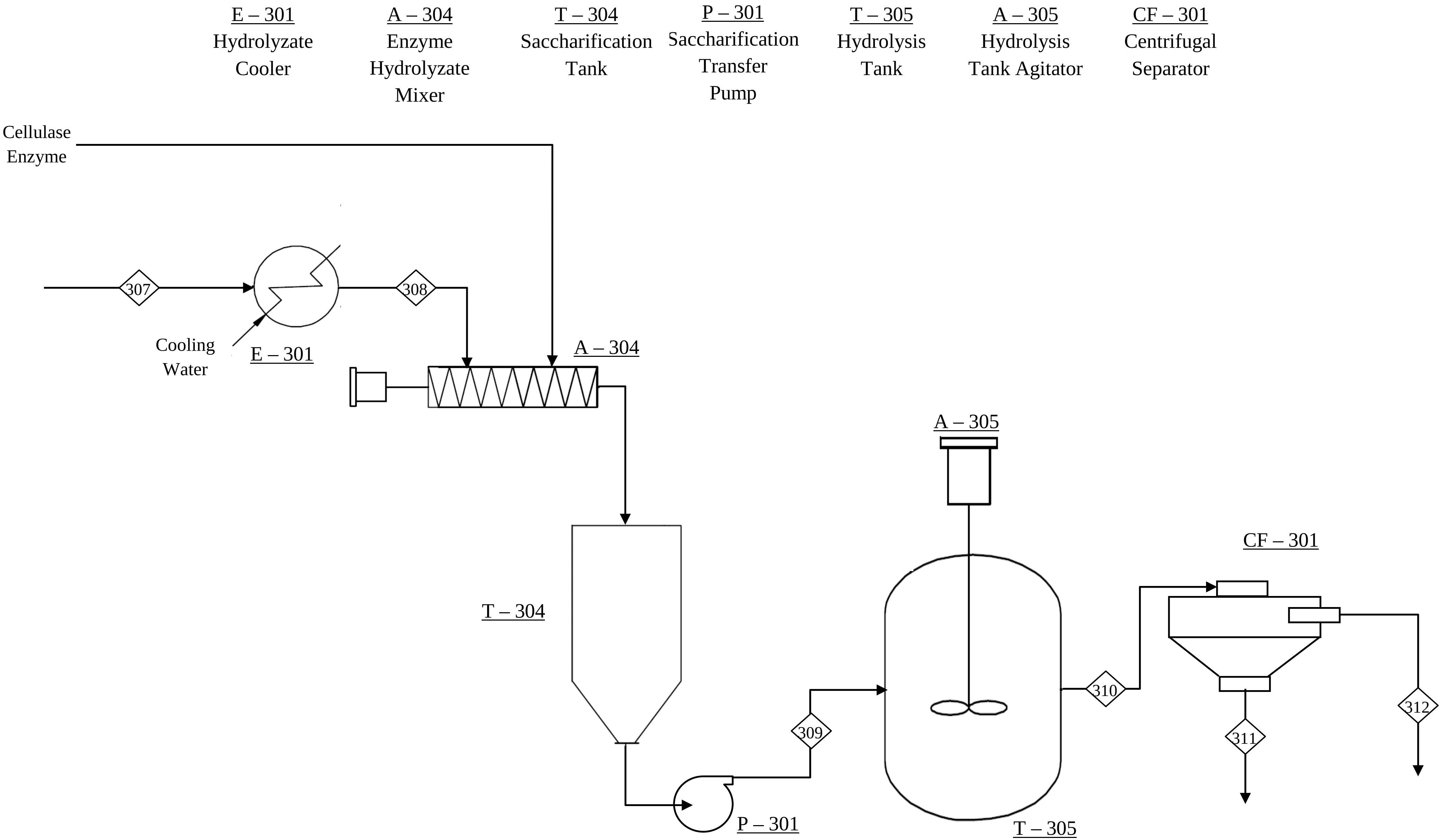


Figure 2.4 Process Flow Diagram of the enzymatic hydrolysis of corn stover.

2.4 Estimation of Process Economics

After the design of any production process, the techno – economic study is carried out so as for the cost of manufacture (COM) to be determined and the feasibility of the process to be evaluated. Cost of manufacture includes Fixed Capital Investment (FCI), the cost of utilities C_{UT}, the cost of raw materials C_{RM} and the cost of operating labor C_{OL}.

2.4.1 Fixed Capital Investment

The estimation of the Fixed Capital Investment is based on the calculation of the cost of supply and installation of the equipment that constitutes the Process Flow Diagram. For this purpose, equipment is initially dimensioned so as its characteristic size to be determined and the literature equations are used in order for the purchased and installed cost to be calculated.

Calculations for the purchased equipment cost C_p^o (\$) that is employed in upstream stage (1,4 – BDO production) as well as the cost of heat exchangers are based on Equation 2.30 (Dheskali et. al,2017).

$$\ln C_P = c_3 + c_2 \cdot \ln X + c_1 \cdot (\ln X)^2 \qquad \text{Eq. 2.30}$$

where X is the characteristic size of each type of equipment and the c_1, c_2, and c_3 are constants.

The cost of equipment employed for the separation and purification of 1,4 – BDO is determined as followed:

The cost of the centrifugal separator for the separation of biomass is calculated by Equation 2.31.

$$c_{p^o}(\$@2004) = 5.5\ 10^3 \cdot Q + 1.3\ 10^5 \qquad \text{Eq. 2.31}$$

The cost of the packed columns is based on Peters et al. (2003) and it is calculated graphically.

The purchased equipment cost of MVR-force circulation evaporator (EV-101) is estimated as the sum of the forced circulation evaporator and vapor compressor by Equation 2.32.

$$\log_{10} C_P = c_3 + c_2 \cdot \log_{10} X + c_1 \cdot (\log_{10} X)^2 \qquad \text{Eq. 2.32}$$

The c_1, c_2, and c_3 constants and given by Turton et al. (2008).

The cost of the distillation column and the traces is estimated by equations 2.33 and 2.34, respectively (Kookos I., 2007).

$$\begin{aligned} c_{p^o}(\$@1979) = {} & \exp[6.95 + 0.1808 \cdot (\ln W) + 0.02468 \cdot (\ln W)^2] \\ & + 834.86 \cdot D^{0.633} H^{0.802} \end{aligned} \qquad \text{Eq. 2.34}$$

$$c_{p^o}(\$@1979) = 278.38 \cdot \exp[0.5705 \cdot D] \cdot \max\left\{1, \frac{2.25}{1.0414^{NT}}\right\} \qquad \text{Eq. 2.33}$$

As for the equipment employed for the polymerization of biopolymer, its cost is calculated with Equations 2.35 and 2.36

The cost of agitated, jacketed preparation tank is calculated by: (Peters et. al, 2003)

$$c_p(\$@2002) = 1{,}812.5 \cdot V_{V101} + 12{,}750 \qquad \text{Eq. } 2.35$$

The cost of the agitated, jacketed reactors R – 101 and R – 102 and the cost of the pump is based on Turton et al. (2008):

$$\log_{10} C_P = c_3 + c_2 \cdot \log_{10} X + c_1 \cdot (\log_{10} X)^2 \qquad \text{Eq. } 2.36$$

The c_1, c_2, and c_3 constants are given.

A corrective coefficient is used to multiply the estimated cost, in order to calculate the cost which refers to 2017. More specifically, when the purchase cost $C_{p,0}$ of a particular type of equipment is known in year t_0, then the purchase cost C_p of the same type of equipment in a different year can be obtained using the following equation:

$$C_p = \frac{CEPCI_t}{CEPCI_0} \cdot C_{p,0} \qquad \text{Eq. } 2.37$$

where $CEPCI_t$ is the chemical engineering plant cost index in year t published monthly in the Chemical Engineering Magazine. In order for the FOB cost to be converted into fixed capital investment (FCI), a coefficient is used called Lang factor L_f (considered equals to 5).

2.4.2 Cost of Utilities, C_{UT}

The cost of utilities is an additional cost of the total cost of manufacture. During the processes, electrical energy, low-pressure steam (LPS), high-pressure steam (HPS) and cooling water are used. The total quantity of utilities used during the production of the desired product are multiplied with their unitary, thus the cost of utilities is determined. The unitary costs of utilities are presented in Table 2.3.

2.4.3 Cost of Labor, C_{OL}

The cost of labour has been calculated using the Ulrich method. This method presents an estimation of the required workers per shift for the proper operation of each unit of equipment. It should be mentioned here that every employee works 2,080 hours per year and consequently the necessary shifts per day are approximately 4.5. The salary of employees is 20 $\$ \cdot h^{-1}$.

2.4.4 Cost of raw materials, C_{RM}

The cost of raw materials, C_{RM}, is usually a large part of the total cost of production in a chemical industry. The required quantities of raw materials of the process are multiplied with their price and the total cost is determined.

2.4.5 Cost of manufacture, COM

The final cost of manufacture of the process is calculated by Equation 2.38:

$$COM = 0.18 \cdot FCI + 2.73 \cdot C_{OL} + 1.23 \cdot (C_{RM} + C_{UT}) \qquad \text{Eq. } 2.38$$

Table 2.3 Unitary cost of utilities.

Utility	Unitary Cost ($/unit)
LPS (t)	9.45
HPS (t)	9.61
Cooling Water (t)	0.0157
Electricity (kWh)	0.0674

2.5 Economic Analysis

In order to evaluate a designed production process, a discounted cash flow (DCF) analysis should be performed and the minimum selling price of the desired product should be estimated. The assumptions for performing the DCF analysis are based on the 2011 NREL bioethanol production report. More specifically, the following assumptions have been made: the discount rate (or internal rate of return) is 10%, the plant lifetime is 30 years, the equity financing is 100%, the depreciation is 7 years based on the Modified Accelerated Cost Recovery System (MACRS), the corporate tax rate is 35%, the duration of the plant construction is 3 years, the percentage of project costs is 8%, 60% and 32% for the 1st, the 2nd and 3rd year of the plant construction period respectively, the working capital is 5% and the salvage value and land purchase costs are zero.

The aim is to determine the price of the product expressed in $\$\cdot kg^{-1}$ that results in zero net present value (NPV) of the project. This is called the minimum selling price (MSP) of the product. Moreover, net present value for all capacities should be calculated so as for the feasibility of the process to be evaluated. NPV is calculated by using the present selling price of the product.

2.6 Life Cycle Assessment (LCA)

This study follows the International Standards ISO 14040 – 14043 that provides principles, framework, and methodological requirements in order to conduct the LCA study. This framework includes four discrete but interdependent phases that should be taken into consideration when performing an LCA: definition of goal and scope, inventory analysis, impact assessment and interpretation of the results (Figure 2.5) (Matthews et. al, 2015).

Table 2.3 summarizes the impact categories which are commonly used in LCA studies. It is also included the scale of impact (e.g., local or global), and the typical kinds of LCI data results that can be used as inputs into methods created to quantitatively assess these impacts. This list of impact categories is not intended to be exhaustive in terms of listing all potential impact categories for which an individual or a party might have concern, or in terms of the potentially connected LCI results.

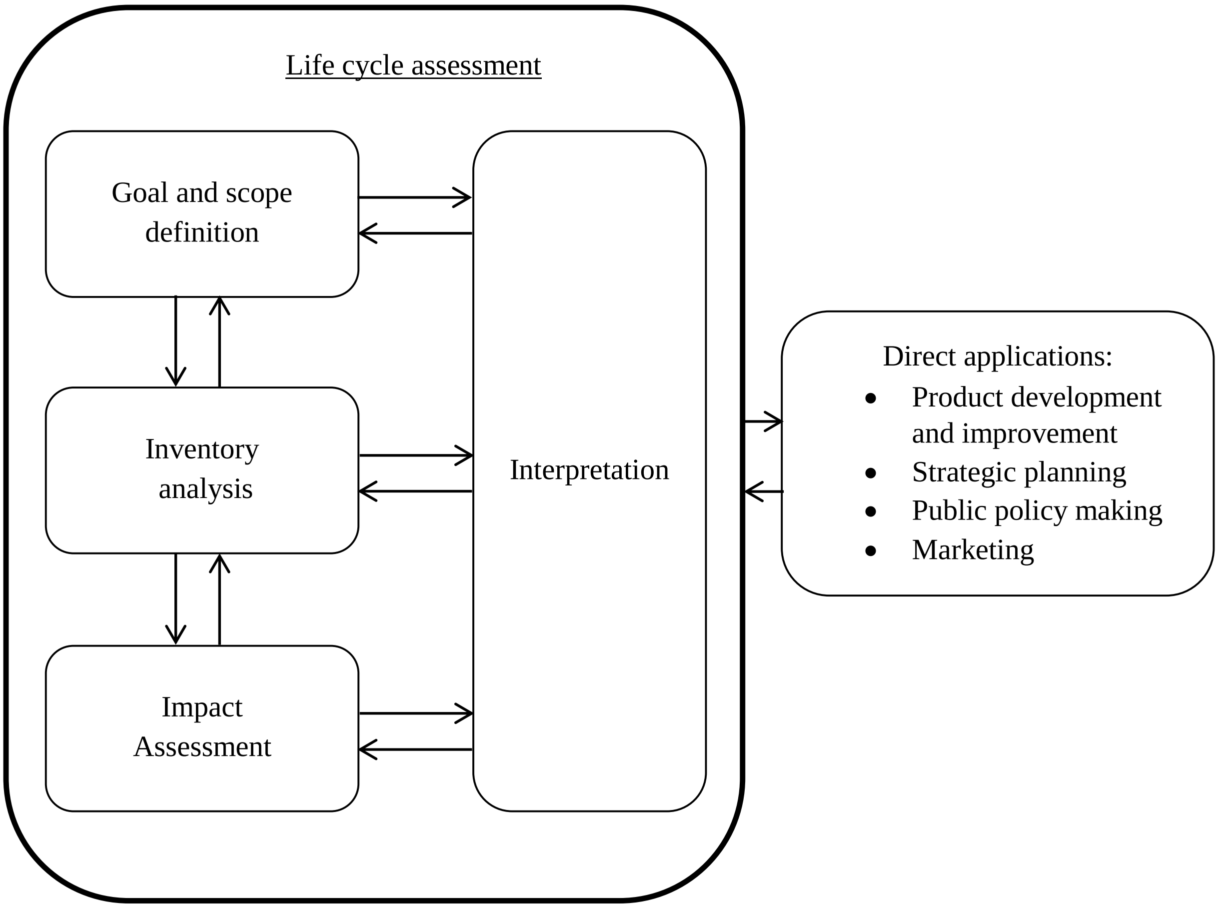


Figure 2.5 Overview of ISO LCA framework (ISO 14040:2006).

Table 2.4 Summary of Impact Categories. (US EPA 2006)

Impact Category	Scale	Examples of LCI Data
Global Warming	Global	Carbon Dioxide (CO_2), Nitrous Oxide (N_2O), Methane (CH_4), Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs),
Stratospheric Ozone Depletion	Global	Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs),
Acidification	Regional, Global	Sulfur Oxides (SO_x), Nitrogen Oxides (NO_x), Hydrochloric Acid (HCl), Hydrofluoric Acid (HF), Ammonia (NH_4)
Eutrophication	Local	Phosphate (PO_4), Nitrogen Oxide (NO), Nitrogen Dioxides (NO_2), Nitrates, Ammonia (NH_4)
Photochemical Smog	Local	Non-methane hydrocarbon (NMHC)
Terrestrial Toxicity	Local	Toxic chemicals with a reported lethal concentration to rodents
Aquatic Toxicity	Local	Toxic chemicals with a reported lethal concentration to fish
Human Health	Global, Regional, Local	Total release to air, water and soil
Resource Depletion	Global, Regional, Local	Quantity of minerals used, Quantity of fossil fuel used
Land Use	Global, Regional, Local	Quantity disposed of in a landfill or other land modification
Water Use	Regional, Local	Water used or consumed

2.6.1 Goal and Scope

The goal of the study should include a statement of the reason for carrying out the study. In the scope of an LCA, the items considered and described should be the function of the product system, the functional unit and the system boundaries.

This work presents a “cradle – to – gate” assessment for the production of 1 kg of PBS, in order for the comparison with 1 kg of polymer produced from fossil resources to be carried out. The system boundaries include the production of agricultural crops, their transportation to biotransformation facility, the extraction of raw materials, the fermentation of succinic acid and 1,4 – BDO, their recovery and the polymerization stage so as for the polymer to be created. Emissions that occur during the construction of the production facilities and the machinery and emissions due to administration, maintenance and supervision of their operation are excluded. The study evaluates the impact of glucose derived from sugar cane.

2.6.2 Life Cycle Inventory Analysis

LCIA comprises all stages dealing with the data retrieval and the required calculations. Subsequently, data are validated and related to the functional unit in order to allow the aggregation of results. A very important part during the calculation process is the allocation of flows. Most of the processes yield more than one product. Therefore, one of the major causes of the discrepancies in LCA reports is the difference in the way the environmental impacts are allocated among the co – products. Materials and energy flows regarding the process as a whole, as well as environmental impacts, should often be allocated to the different products.

In this study, all flows are allocated to the production of 1 kg of 1,4 – BDO and PBS, respectively. Two different methods are followed in order for the allocation to be made. First, a mass-based allocation method is used to determine how the used energy and the carbon emissions are attributed among the co-products regarding their mass (Pradhan et al., 2011). Another method of allocation used is the energy allocation (Huo et. al, 2008). Energy allocation is based on the calorific values of the outputs of the process. Allocation ratios are calculated according to the percentage that the product has if it is compared to the summary of the calorific values of the outputs. The energy allocation method is not applied to the PBS case because the calorific value of PBS cannot be determined.

2.6.3 Impact assessment

Life cycle assessment aims to evaluate the significance of potential environmental impacts using the results coming out from the LCIA phase. This study evaluate two different impacts, Non-Renewable Energy Use (NREU) and Global Warming Potential (GWP). These impacts are expressed via two factors, ECF and CEF respectively. Finally, the result is allocated to the desired product by multiplying the total environmental factors with the allocation ratios of the two methods (Equations 2.39 and 2.40).

2.6.4 Interpretation

The aim of the interpretation phase is to reach conclusions and recommendations in accordance with the defined goal and scope of the study. Results from the LCI and LCA are combined together and reported in order to give a complete and unbiased account of the study. The interpretation is to be made iteratively with the other phases.

3 Results & Discussion

Materials and energy balances for the three processes that have been presented and discussed in the previous section are carried out and then validated using UniSim (Honeywell). Then, sizing of equipment is performed by determining the dimensions and the characteristic size of its equipment and the purchased equipment cost is determined. In addition, the raw material and utilities consumption and cost are determined based on energy and material balance in order for economic analysis to be conducted. Finally, a LCA analysis is carried out for 1,4 – BDO and PBS production process.

3.1 1, 4 – butanediol production process

Table 3.1 presents the characteristic size of the equipment employed in Figure 2.1 as well as their purchased cost. These results are representative for an annual capacity of 40 kt 1,4 – BDO with an assumed overall downstream recovery of BDO equal to 90%. As can be observed from this table, the cost of the upstream is significantly larger than the cost of the downstream product recovery area. Moreover, the cost of fermentors, including agitation and aeration, is the most important cost and determines the final FCI necessary for the bioprocesses under study (Figure 3.1). More specifically, this cost is approximately 71% of the total cost of bioprocess. Regarding the downstream section, the most expensive parts of equipment are the centrifugal separator (CF – 201) and the total system of evaporator (EV – 101, C – 102).

To calculate the overall cost involved in producing the 1,4 – BDO, in addition to FCI, the cost of utilities C_{UT}, the cost of raw materials C_{RM} and the cost of operating labor C_{OL} should be estimated. The consumption of utilities, their annual costs as well as the labor requirements per equipment are summarized in Table 3.2. It is observed that for the fermentation section the main part of the utilities cost is related to the agitation and cooling of the fermentors. The utility cost that is more important in the downstream process is the electricity consumption of the compressor during the evaporation process. Therefore, electricity is considered as the most important utility of the process (Figures 3.2 and 3.3). The total cost of utilities (C_{UT}) is 2.276 M$\$\cdot y^{-1}$.

The cost of raw materials (C_{RM}) required for 1,4 – BDO production is estimated 31.11 M$\$\cdot y^{-1}$ (Appendix A). This cost is a large part of the total cost of manufacturing for the production of 1,4 – BDO. Finally, the total COM is determined by Equation 2.38 as 51.99 M$\$\cdot y^{-1}$.

Table 3.1 Summary of equipment specifications, purchased cost and FCI for 1,4 – BDO production.

	Specifications	**Characteristic size**	**Purchased Cost (M$@2017)**
	Upstream		
V – 101/ A – 101		Q = 21.2 kW	0.301
E – 101	U = 1 $kW\cdot m^{-2}K^{-1}$	A = 498.85 m^2	0.185
E – 102	U = 1 $kW\cdot m^{-2}K^{-1}$, LPS	A = 34.40 m^2	0.032
E – 103	Residence time = 2 min	dt = 0.19 m Lt = 210 m	0.106
F – 104-109	H/D = 3, D = 5.48 m, 6 units	V_b = 310.08 m^3	2.982
A – 105	6 units	Q = 462.36 bhp	2.138
C – 101	0.02 vvm, e=0.9	Q = 10.58 kW	0.036
		Upstream purchased cost (M$@2017)	5.780

	Downstream		
CF – 101		$\dot{V}$ = 47.43 $m^3 \cdot h^{-1}$	0.499
V – 102-103	Residence time=0.5 h, 2 units, cationic resin of sulfonic (SO_3H) type	H = 1.24 m D = 2 m	0.092
V – 104-105	Residence time=0.5 h, 2 units, anionic resin of quaternary ammonium (NR_4^+) type	H = 1.24 m D = 2 m	
E – 104	U = 1 $kW \cdot m^{-2}K^{-1}$	A = 161.24 m^2	0.063
EV – 101	T = 100 °C, P = 1bar, U = 3.82 $kW \cdot m^{-2}K^{-1}$	A = 458.67 m^2	0.307
C – 102		Q = 1,181.1 kW	0.350
T – 101	N=8 Tray Spacing = 0.61 m	D = 0.82 m H = 17.55 m	0.069
E – 105	Condenser, U = 1 $kW \cdot m^{-2}K^{-1}$	A = 16.22 m^2	0.022
E – 106	Reboiler, U = 1 $kW \cdot m^{-2}K^{-1}$	A = 59.76 m^2	0.035
		Downstream purchased cost (M$@2017)	1.437
		Total	**7.217**
		FCI	**36.085**

Table 3.2 Summary of the utilities cost and the labor requirements for 1,4 – BDO production.

	Worker/shift	**Electrical Energy ($kWh \cdot y^{-1}$)**	**Low Pressure Steam (LPS) ($t \cdot y^{-1}$)**	**High Pressure Steam (HPS) ($t \cdot y^{-1}$)**	**Cooling Water ($t \cdot y^{-1}$)**
	Upstream				
V – 101/ A – 101	0.6	176,000			
E – 101	0.1				
E – 102	0.1		6,404		
E – 103	0.1				
F – 104-109	3				3,782,584
A – 105-110	2.1	12,800,000			
C – 101	0.1	87,789			

	Downstream				
CF – 101	0.4	400,000			
RO – 101		3,200,000			
V – 102-105	0.8				
E – 104	0.1		9,800		
EV – 101	0.3				
C – 102	0.1	9,802,720			
T – 101	0.5				
E – 105	0.1				933,200
E – 106	0.1			28,040	
Total	8.5	26,466,509	16,204	28,040	4,715,784
Unitary Cost ($/unit)		0.0674	9.45	9.61	0.0157
Cost (M$ · y^{-1})	**1.622**	**1.78**	**0.153**	**0.269**	**0.074**

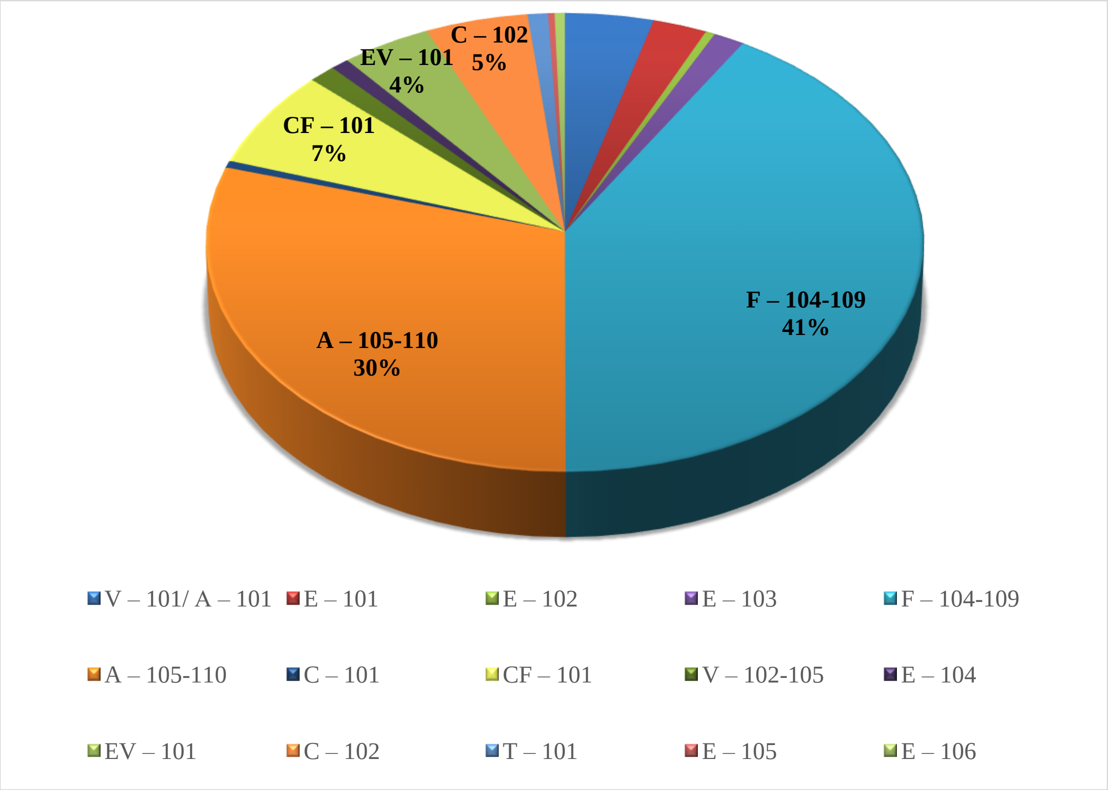


Figure 3.1 Distribution of purchase cost of equipment for 1,4 – BDO production.

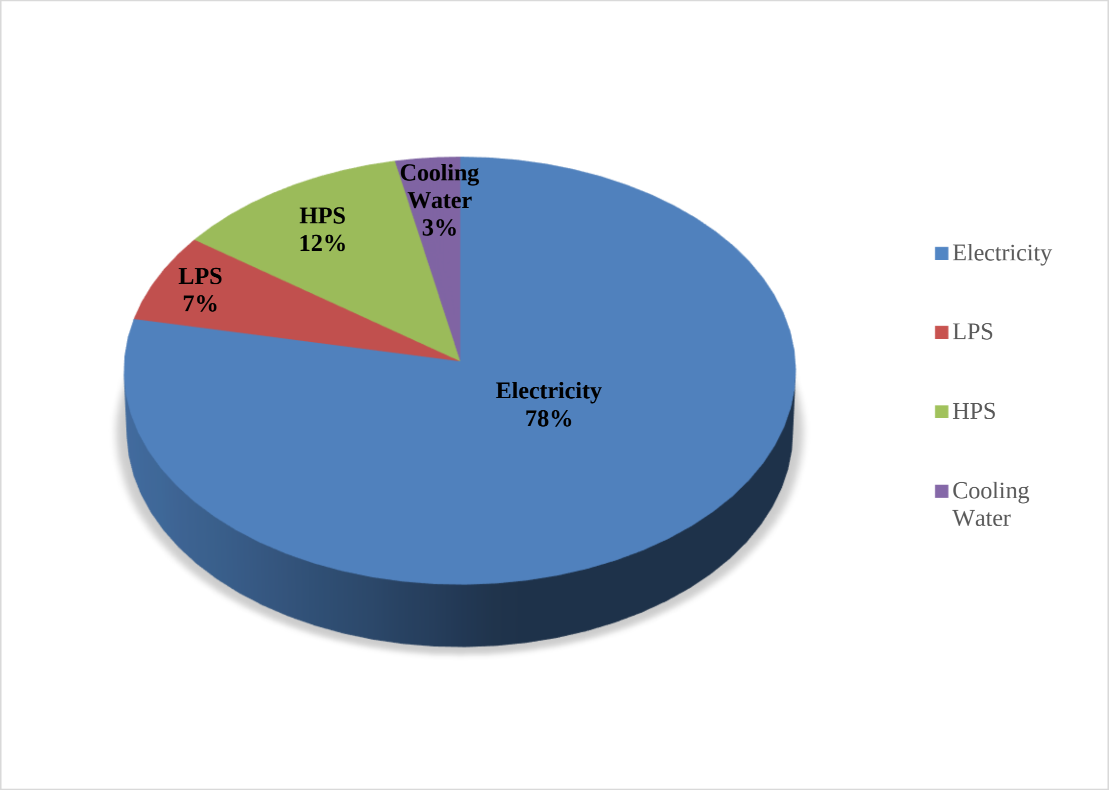


Figure 3.2 Distribution of cost of utilities.

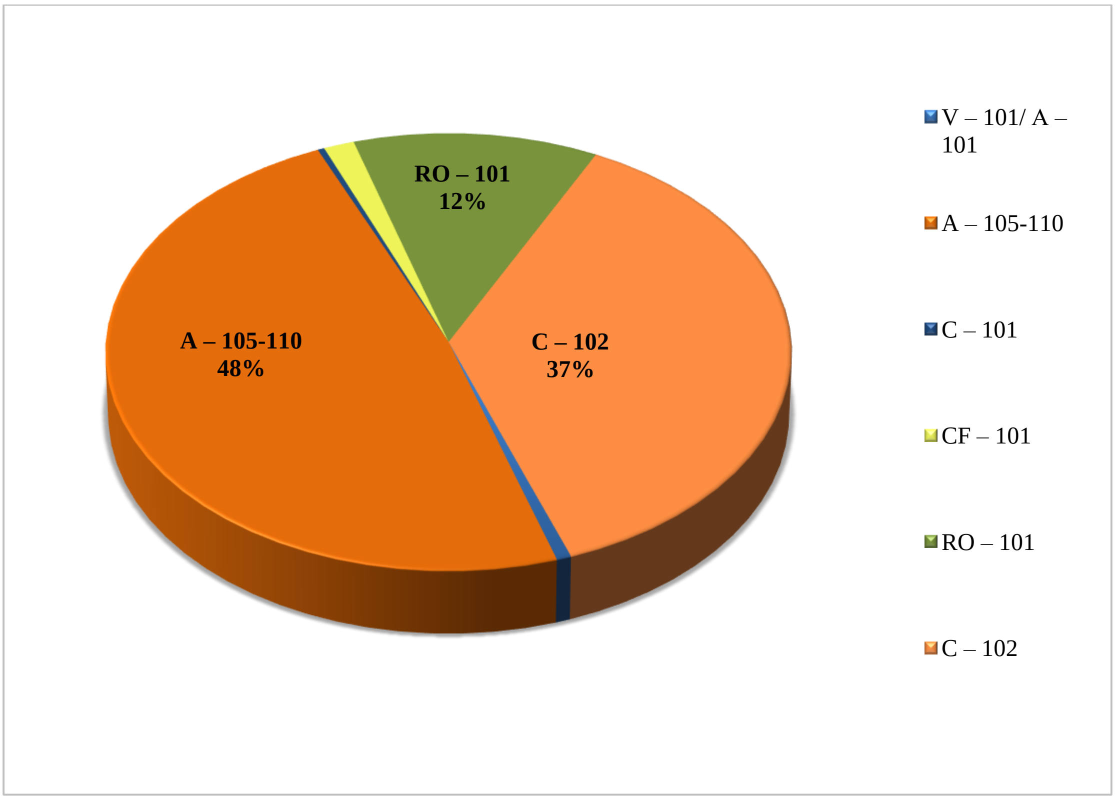


Figure 3.3 Distribution of electricity use among equipment.

3.2 PBS production process (polymerization)

Table 3.3 presents the characteristic size of the equipment employed in Figure 2.2 as well as their purchased cost. These results are representative for capacity of raw materials 80 $kt\cdot y^{-1}$ (40 $kt\cdot y^{-1}$ of succinic acid and 40 $kt\cdot y^{-1}$ of 1,4 – BDO). Given that the yield of the product is 0.73 $kg_{PBS} \cdot kg^{-1}{}_{\text{raw materials}}$, the annual capacity of PBS is 58.4 $kt\cdot y^{-1}$. The cost of polymerization reactor (R – 202) and the cost of the compressor constitute the main percentage of the purchased cost of equipment and therefore increase the FCI (Figure 3.4).

To calculate the overall cost involved in polymerization, the cost of utilities C_{UT} and the cost of labor C_{OL} are estimated. The consumption of utilities, their annual costs as well as the labor requirements per equipment are summarized in Table 3.4. It is obvious that the main cost of utilities is that of heating the reactors during esterification and polymerization, in order for the temperature to maintain constant and the next one is the agitation of this process (Figures 3.5 and 3.6). Therefore, High Pressure Steam (HPS) is the most important utility of the process with percentage 87%. The total cost of utilities (C_{UT}) is 2.55 $M\$\cdot y^{-1}$.

Concerning the cost of raw materials, firstly, the evaluation of the production process of PBS without considering succinic acid and 1,4 – BDO as raw materials is carried out. As a result, only the cost of catalyst employed in the polycondensation reactor should be estimated. The required quantity per reaction for the selected capacity of PBS is approximately 114 kg. By changing it three times a year and with price 14,600 $\$\cdot kg^{-1}$, the final cost of catalyst is 4,997,747 $\$\cdot y^{-1}$. Finally, the total COM for the polymerization stage is determined 15.35 $M\$\cdot y^{-1}$.

Table 3.3 Summary of equipment specifications, purchased cost and FCI for PBS production (polymerization).

Unit	Specifications	Characteristic size	M$@2017
V – 201/ A – 201	T = 80 °C, LPS	V = 10.24 m^3 Q = 9.11 kW	0.045
E – 201	U = 1 $kW\cdot m^{-2}K^{-1}$	A = 23.21 m^2	0.024
R – 201/ A – 202	T = 230 °C, P = 1 bar, t = 3 h	V = 30.74 m^3	0.076
E – 202	Condenser U = 1 $kW\cdot m^{-2}K^{-1}$	A = 10.89 m^2	0.020
T – 201	N=8 Tray Spacing = 0.61 m	H = 5.12 m D = 0.67 m	0.068
E – 203	Reboiler U = 1 $kW\cdot m^{-2}K^{-1}$	A = 8.16 m^2	0.020
R – 202/ A – 203	T = 240 °C, P = 2 torr, t = 16.5 h 6 units	V = 31.75 m^3 Q = 169.31 kW	0.465
E – 206	U = 1 $kW\cdot m^{-2}K^{-1}$	A = 1 m^2	0.026
C – 201	P = 0.05 bar, 2 units	Q = 224.74 kW	0.158
E – 207	U = 1 $kW\cdot m^{-2}K^{-1}$	A = 9.18 m^2	0.020
P – 201	P = 1 bar	Q = 0.045 kW	0.004
E – 204	Condenser U = 1 $kW\cdot m^{-2}K^{-1}$	A = 11.76 m^2	0.020
T – 202	N=8 Tray Spacing = 0.61 m	H = 5.12 m D = 0.697 m	0.068
E – 205	Reboiler U = 1 $kW\cdot m^{-2}K^{-1}$	A = 7.95 m^2	0.019
E – 208	U = 1 $kW\cdot m^{-2}K^{-1V}$	A = 22.94 m^2	0.024
		Total	**1.06**
		FCI	**5.30**

Table 3.4 Summary of the utilities cost and the labor requirements for PBS production (polymerization).

Unit	**Worker/shift**	**Electrical Energy ($kWh \cdot y^{-1}$)**	**Low Pressure Steam (LPS) ($t \cdot y^{-1}$)**	**High Pressure Steam (HPS) ($t \cdot y^{-1}$)**	**Cooling Water ($t \cdot y^{-1}$)**
V – 201/ A – 201	0.5	76,220	5,300		
E – 201	0.1				
R – 201/ A – 202	0.5	228,659		19,629	
E – 202	0.1				640,246
T – 201	0.5				
E – 203	0.1			5,845	
R – 202/ A – 203	0.5	1,407,135		199,045	
E – 206	0.1				76,964
C – 201	0.1	1,864,454			
E – 207	0.1				627,817
P – 201	0.1	373.16			
E – 204	0.1				691,238
T – 202	0.5				
E – 205	0.1			5,845	
E – 208	0.1				1,225,843
Total	9.5	3,576,842	5,300	230,366	3,262,109
Unitary Cost ($/unit)		0.0674	9.45	9.61	0.0157
Cost ($M\$ \cdot y^{-1}$)	**1.87**	**0.24**	**0.05**	**2.21**	**0.05**

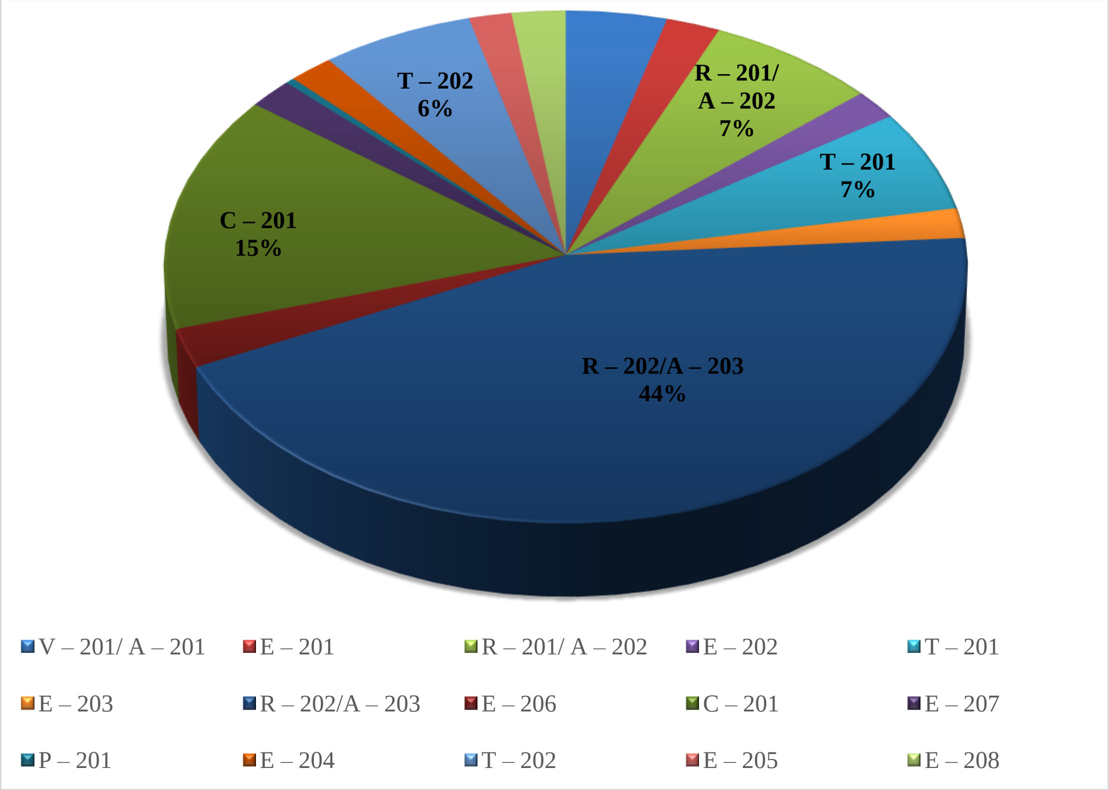


Figure 3.4 Distribution of purchase cost of equipment for 1,4 – BDO production.

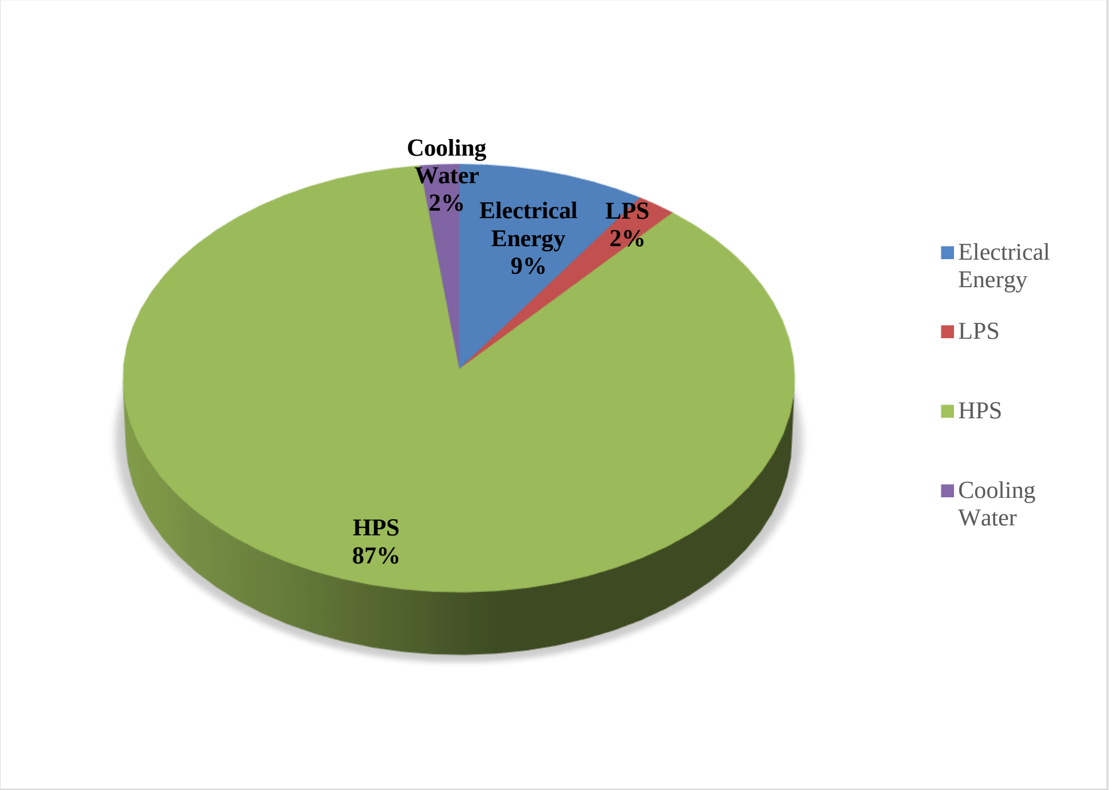


Figure 3.5 Distribution of cost of utilities.

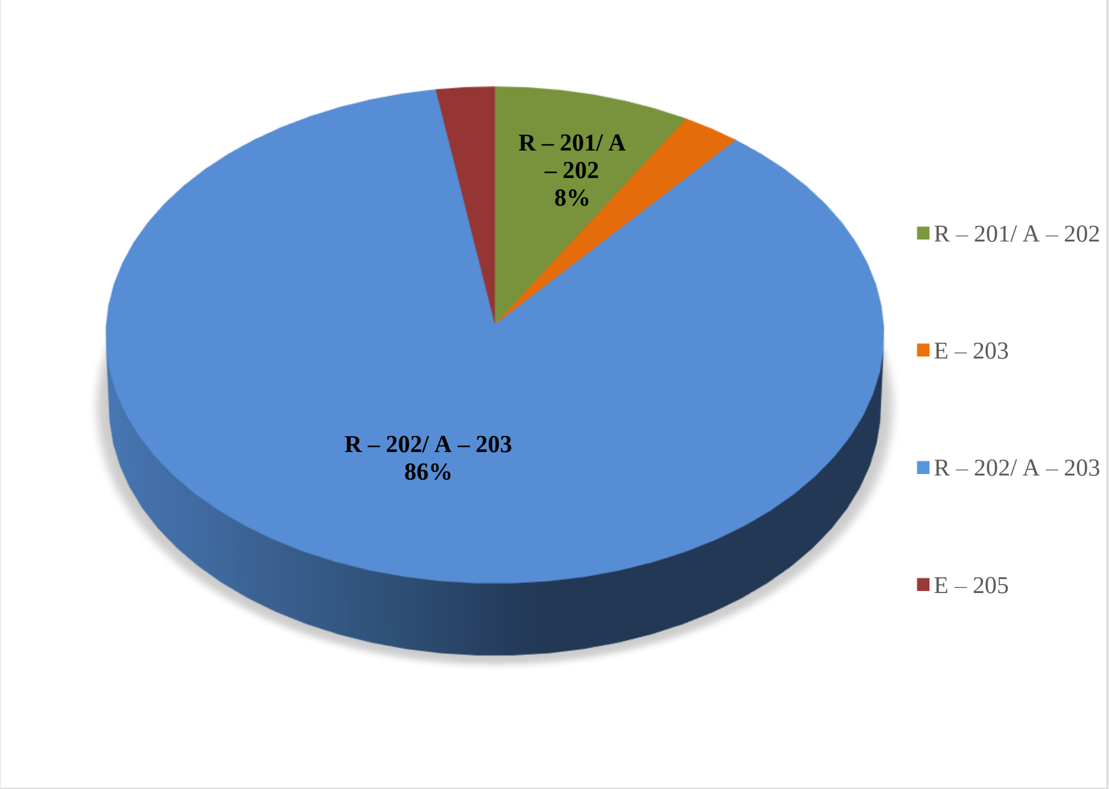


Figure 3.6 Distribution of HPS use among equipment.

3.3 Estimation of the total production cost of the processes

In this chapter, the estimation of the production cost of 1,4 – BDO production and the whole production process of PBS is estimated for the selected capacity. Regarding the whole production of PBS, the production cost is calculated by adding the individual costs of each product (Table 3.5). The economics of the production process of succinic acid are derived from Ladakis (2018). The total production cost is calculated for various annuals capacities and illustrated in Figure 3.7. Both processes utilize as raw materials pure glucose.

Table 3.5 Summary of individual costs of each product.

	Succinic Acid	**1,4 – Butanediol**	**PBS (polymerization)**	**Total**
FCI (M$)	89.02	36.08	5.30	130.41
CUT (M$)	5.38	2.27	2.55	10.21
COL (M$)	2.62	1.62	1.87	6.11
CRM (M$)	29.91	31.11	4.99	66.01
COM (M$)	66.59	51.99	15.35	133.91

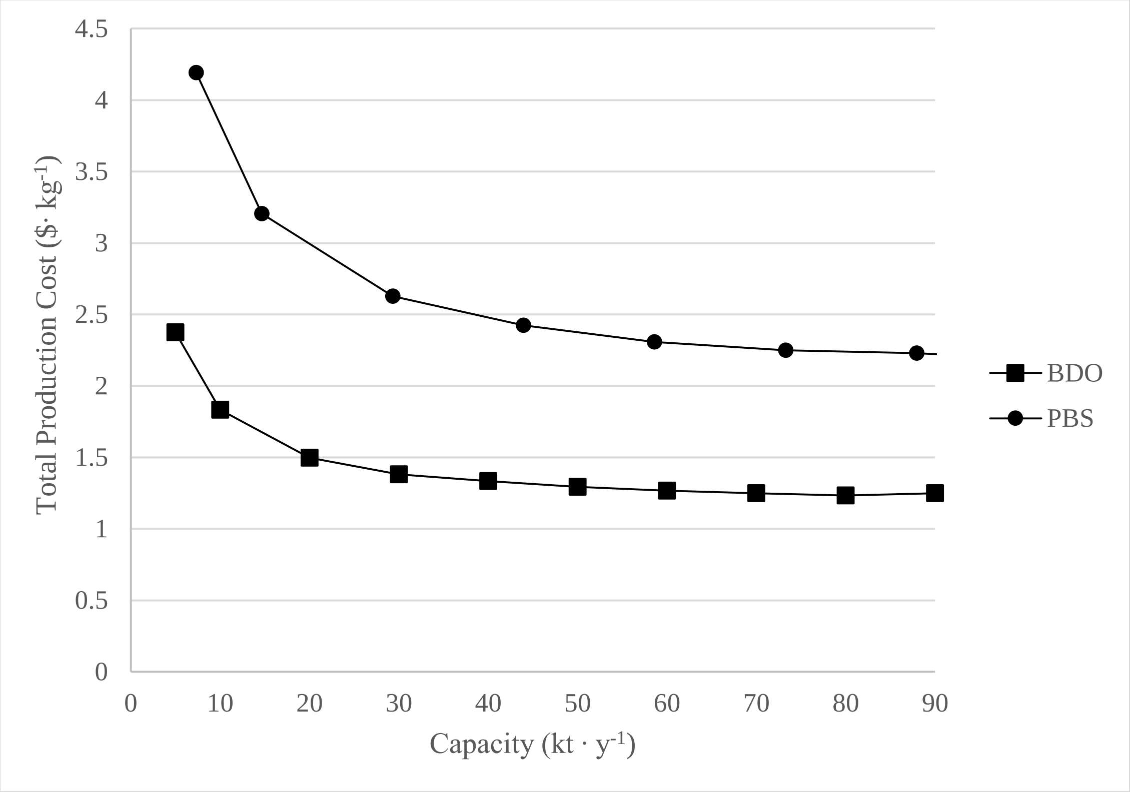


Figure 3.7 Total cost of manufacturing.

3.4 Results of Economic Analysis

The techno – economic evaluation of both the 1,4 – BDO and the PBS production process is carried out and the total production cost is calculated for various annuals capacities. Next, a discounted cash flow (DCF) analysis is performed and the minimum selling price of the products is determined. The assumptions for performing the DCF analysis are based on the 2011 NREL bioethanol production report and are summarized in Table 3.8. NPV is calculated by using the present selling price of 1,4 – BDO and PBS, approximately 3 $\$\cdot kg^{-1}$ and 4 $\$\cdot kg^{-1}$, respectively.

As Figure 3.8 presents, net present value is positive for all annual capacities and for both the processes, thus they can be feasible and profitable. As Figure 3.9 illustrates, MSP has a constant value after annual capacity of 40,000 t for 1,4 – BDO and approximately 55,000 t for PBS. The minimum selling prices are equal to approximately 1.3 $\$\cdot kg^{-1}$ and 2.5 $\$\cdot kg^{-1}$, respectively.

Table 3.6 Assumptions for the DCF analysis.

Internal rate of return	10 %
Interest rate	8 %
Plant lifetime	30 y
Equity financing	100 %
Depreciation	7 year MACRS
Tax rate	35 %
Construction time	3 y
% of project cost in the 1st, 2nd and 3rd year of construction	8 % / 60% / 32 %
Working capital	5 %
Salvage value	0
Land cost	0

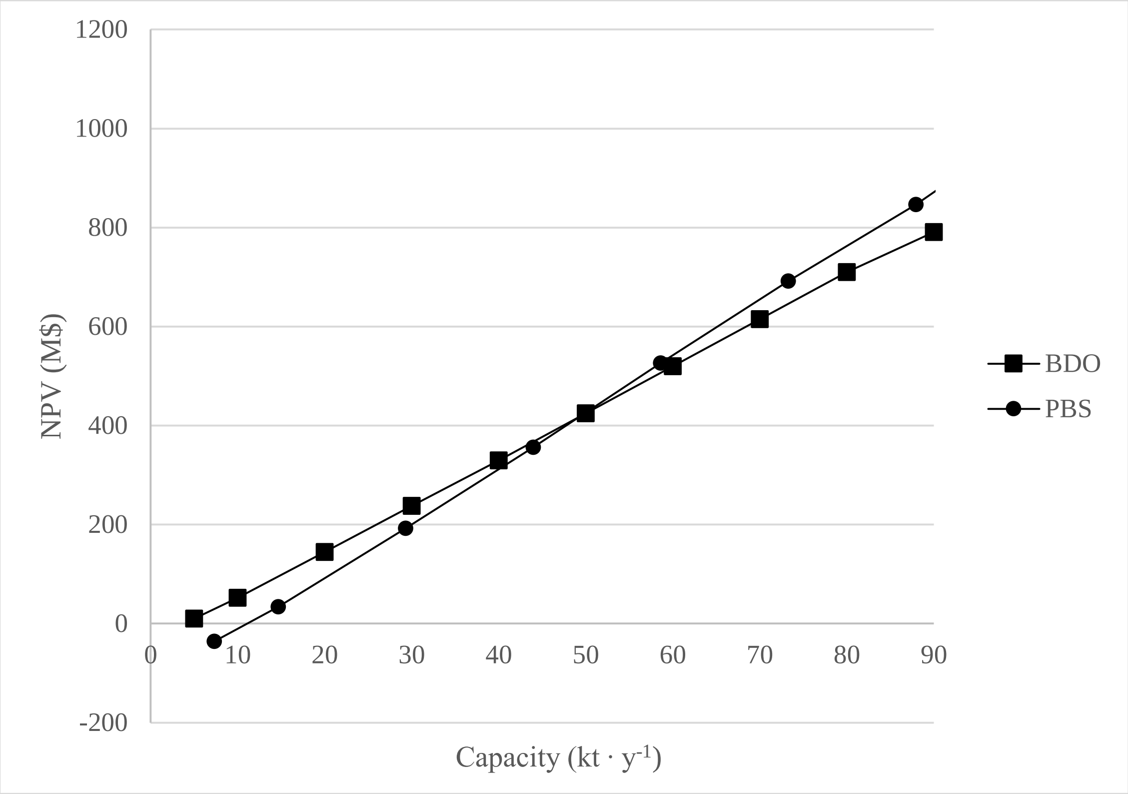


Figure 3.8 Net Present Value (NPV).

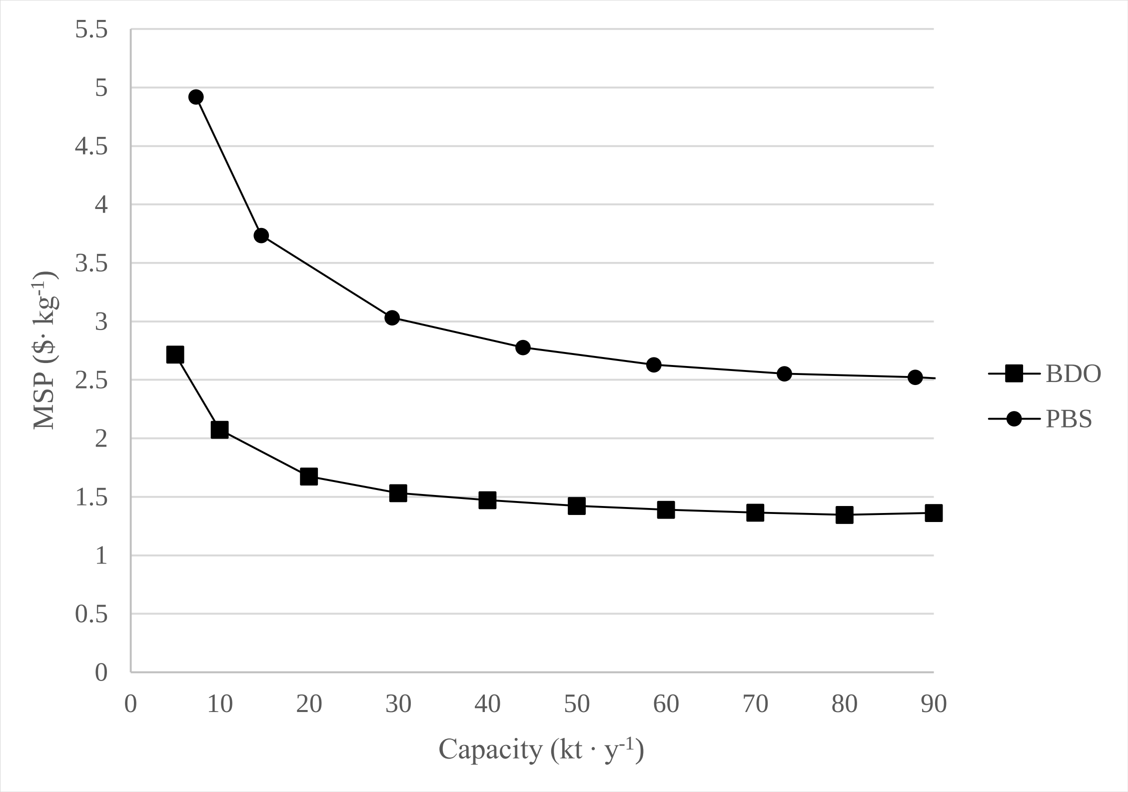


Figure 3.9 Minimum Selling Price (MSP).

3.5 Pretreatment of corn stover

As already mentioned, corn stover can be used as renewable feedstock from which the required sugars for the fermentation can be extracted. After the simplified design of the pretreatment process, mass balances are calculated so as the initial quantity of feedstock, as well as quantities of the rest utilities and materials to be determined.

Table 3.6 presents data concerning the NREL analysis for the pretreatment of corn stover. The correlation between materials and utilities with corn stover occurs by dividing their quantities. Consequently, the yields of this process are derived. (Table 3.7).

Table 3.7 NREL data.

Corn stover ($t \cdot y^{-1}$)	876,044
Process Water ($t \cdot y^{-1}$)	2,780,823
Sulfuric Acid ($t \cdot y^{-1}$)	15,491
Ammonia ($t \cdot y^{-1}$)	8,839
Enzyme ($t \cdot y^{-1}$)	5,214
HPS ($t \cdot y^{-1}$)	235,682
Electricity ($kWh \cdot y^{-1}$)	66,559,442
Cooling Water ($t \cdot y^{-1}$)	7,427
Total sugars ($t \cdot y^{-1}$)	422,013
Glucose ($t \cdot y^{-1}$)	249,693
Xylose ($t \cdot y^{-1}$)	138,597
Other sugars ($t \cdot y^{-1}$)	33,724

Table 3.8 Yields of sugars, other materials and utilities per kg of corn stover.

$Y_{glucose/corn\ stover}$ ($t \cdot t^{-1}$)	0.285
$Y_{xylose/corn\ stover}$ ($t \cdot t^{-1}$)	0.158
$Y_{other\ sugars/corn\ stover}$ ($t \cdot t^{-1}$)	0.039
$Y_{total\ sugars/corn\ stover}$ ($t \cdot t^{-1}$)	0.482
Process Water ($t \cdot t^{-1}$)	3.17
Sulfuric Acid ($t \cdot t^{-1}$)	0.02
Ammonia ($t \cdot t^{-1}$)	0.01
Enzyme ($t \cdot t^{-1}$)	0.01
HPS ($kg \cdot t^{-1}$)	269.03
Electricity ($kWh \cdot t^{-1}$)	75.98
Cooling Water ($kg \cdot t^{-1}$)	8.48

After the material balances determination, the techno – economic evaluation of the pretreatment process is carried out in order for the sugars price deriving from corn stover to be determined. Similarly to the previous production processes and by using data from NREL report, Fixed Capital Investment, Cost of raw materials, Cost of utilities and Cost of labor are calculated (Table 3.9). Cost of labor is considered as 0.8% of the FCI cost. The related calculations are presented in Appendix C. The calculated cost of manufacturing is divided by the quantity of the produced total sugars (422.013 kt $\cdot$ y^{-1}) and therefore the unitary price of glucose is determined.

After the determination of the price of glucose that is derived from corn stover, the new cost of raw materials for the production process of 1,4 – BDO is 1.035 \$ $\cdot$ kg_{BDO}^{-1}, which is higher than the previous one (0.777 \$ $\cdot$ kg_{BDO}^{-1}). As a result, the new minimum selling price (MSP) of 1,4 – BDO is calculated 1.746 \$ $\cdot$ kg_{BDO}^{-1}. This price is higher than the one calculated with the pure glucose price (1.3 \$$\cdot$$kg_{BDO}^{-1}$), but nevertheless still approximate. If the corn stover pretreatment could be integrated in the production process of 1,4 – BDO and the parallel streams could be exploited, then it is highly probable that the final 1,4 – BDO price would be much lower.

Table 3.9 Estimation of sugars price.

	Corn Stover Pretreatment
FCI (M\$)	241.01
CUT (M\$)	6.75
COL (M\$)	1.87
CRM (M\$)	68.65
COM (M\$)	136.37
Sugars Price (\$ $\cdot$ kg^{-1})	0.323

3.6 Life Cycle Assessment

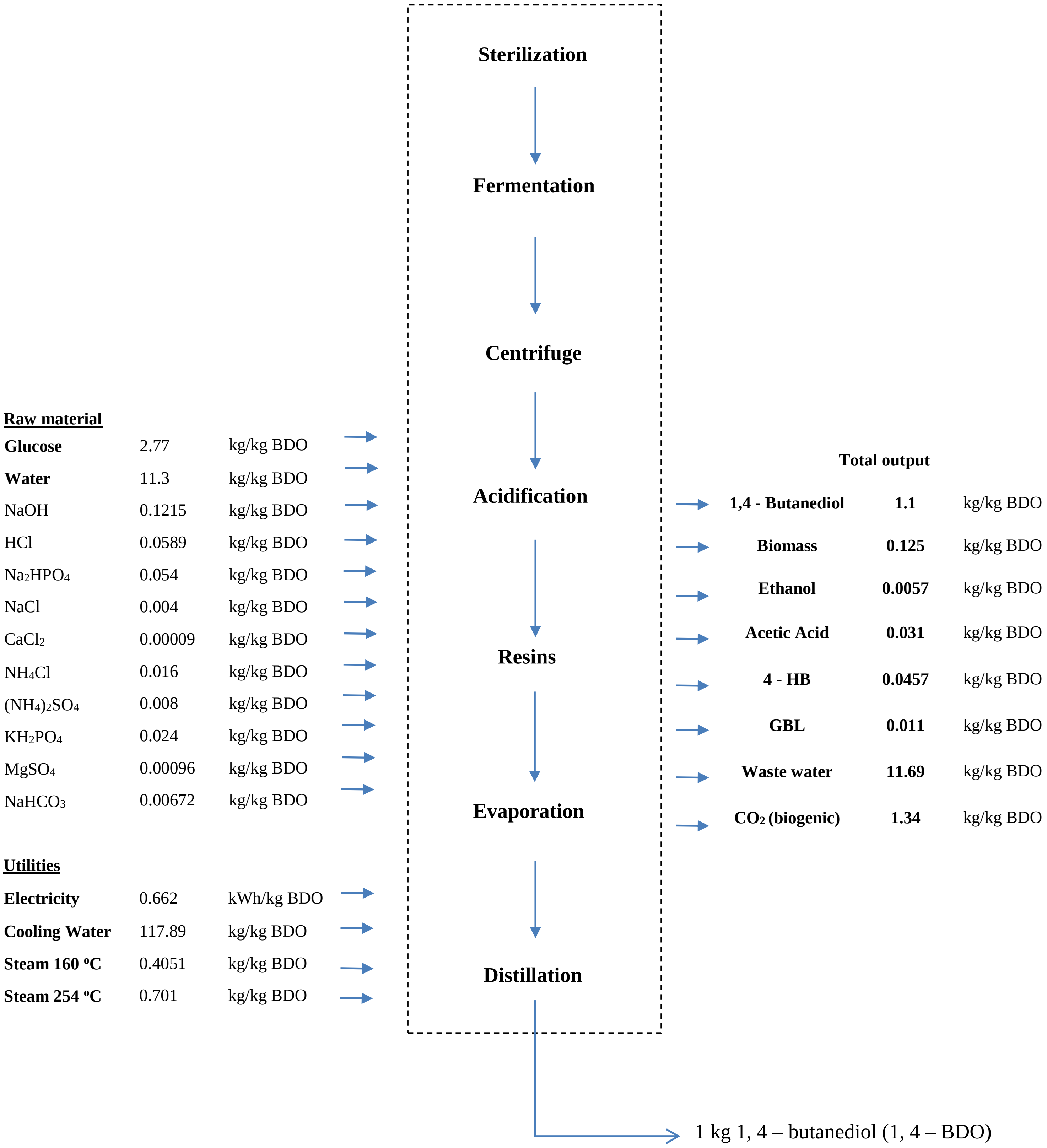
As it has already been mentioned, Life Cycle Assessment (LCA) has become one of the most systematic techniques for the evaluation of a process with respect to its life cycle environmental performance. In this study, the inventory analysis for the fermentative production of 1,4 – BDO and the production of PBS is performed and the results are compared with those from the petrochemical production.

3.6.1 Inputs and Outputs of the process

The design of a biotechnological production process demands different series of inputs, outputs, each of which has impacts on the environment. In order to conduct the inventory analysis, it is necessary to account for all the inputs and outputs throughout the life cycle of the process (cradle to gate process) and allocate them to 1 kg of final product. The quantities of raw materials and utilities per kilogram of the product are presented in Figures 3.10 and 3.11.

3.6.2 Data for nutrients and utilities

All materials used in the inventory list have been converted to their equivalent life-cycle energy content. The lifecycle energy of a material is defined as the total nonrenewable energy embedded and incurred during extraction, processing, and transport of that material. (Pradhan et al., 2011). Energy Consumption Factors (ECFs) and Carbon Emission Factors (CEFs) of materials and utilities used in the production processes of 1,4 – BDO and PBS derived from literature and presented in Table 3.10.



Raw material

Glucose	2.77	kg/kg BDO
Water	11.3	kg/kg BDO
NaOH	0.1215	kg/kg BDO
HCl	0.0589	kg/kg BDO
Na_2HPO_4	0.054	kg/kg BDO
NaCl	0.004	kg/kg BDO
$CaCl_2$	0.00009	kg/kg BDO
NH_4Cl	0.016	kg/kg BDO
$(NH_4)_2SO_4$	0.008	kg/kg BDO
KH_2PO_4	0.024	kg/kg BDO
$MgSO_4$	0.00096	kg/kg BDO
$NaHCO_3$	0.00672	kg/kg BDO

Utilities

Electricity	0.662	kWh/kg BDO
Cooling Water	117.89	kg/kg BDO
Steam 160 °C	0.4051	kg/kg BDO
Steam 254 °C	0.701	kg/kg BDO

Total output

1,4 - Butanediol	**1.1**	kg/kg BDO
Biomass	**0.125**	kg/kg BDO
Ethanol	**0.0057**	kg/kg BDO
Acetic Acid	**0.031**	kg/kg BDO
4 - HB	**0.0457**	kg/kg BDO
GBL	**0.011**	kg/kg BDO
Waste water	**11.69**	kg/kg BDO
CO_2 (biogenic)	**1.34**	kg/kg BDO

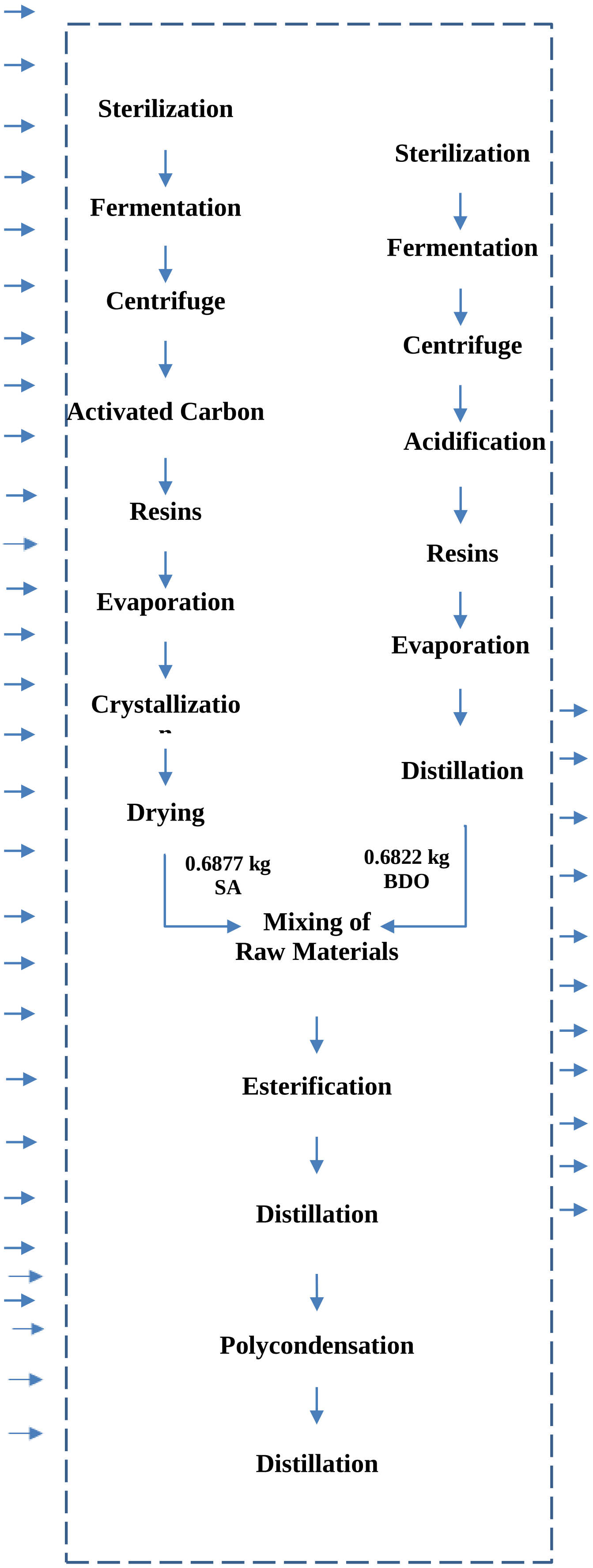
Figure 3.10 Inputs and Outputs of the 1,4 – BDO production process.

Raw Materials

Glucose	2.7700	kg/kg_{PBS}
Water	24.6813	kg/kg_{PBS}
CO_2	0.1788	kg/kg_{PBS}
NaOH	0.9081	kg/kg_{PBS}
HCl	0.8654	kg/kg_{PBS}
Na_2HPO_4	0.0573	kg/kg_{PBS}
$CaCl_2$	0.0001	kg/kg_{PBS}
$MgSO_4$	0.0075	kg/kg_{PBS}
KH_2PO_4	0.0708	kg/kg_{PBS}
NaCl	0.0027	kg/kg_{PBS}
NH_4Cl	0.0123	kg/kg_{PBS}
$(NH_4)_2SO_4$	0.0108	kg/kg_{PBS}
Citric acid	0.0204	kg/kg_{PBS}
$(NH_4)2HPO_4$	0.0545	kg/kg_{PBS}
$NaHCO_3$	0.0046	kg/kg_{PBS}
$ZnSO_47H_2O$	3.4041E-06	kg/kg_{PBS}
$CuCl_22H_2O$	2.0425E-06	kg/kg_{PBS}
$MnSO_4H_2O$	1.6986E-05	kg/kg_{PBS}
$CoCl_26H_2O$	1.2241E-05	kg/kg_{PBS}
H_3BO_3	6.8082E-07	kg/kg_{PBS}
$Al_2(SO_4)_3xH_2O$	1.2241E-05	kg/kg_{PBS}
$Na_2MoO_42H_2O$	3.4041E-06	kg/kg_{PBS}
Fe(III) citrate	1.1003E-04	kg/kg_{PBS}
thiamineHl	1.3754E-04	kg/kg_{PBS}
Biotin	1.3616E-05	kg/kg_{PBS}

Utilities

Electricity	1.3000	kWh/kg_{PBS}
Cooling Water	213.4033	kg/kg_{PBS}
Steam 160 °C	0.9171	kg/kg_{PBS}
Steam 254 °C	4.4072	kg/kg_{PBS}



Total output

Succinic acid	0	kg/kg_{PBS}
1,4 – BDO	0.159	kg/kg_{PBS}
Biomass	0.305	kg/kg_{PBS}
Acetic acid	0.036	kg/kg_{PBS}
Ethanol	0.004	kg/kg_{PBS}
4 – HB	0.031	kg/kg_{PBS}
GBL	0.008	kg/kg_{PBS}
Waste water	25.296	kg/kg_{PBS}
NaCl	1.31	kg/kg_{PBS}
PBS	1	kg/kg_{PBS}
CO2 (biogenic)	0.914	kg/kg_{PBS}

Figure 3.11 Inputs and Outputs of the total PBS production process.

Table 3.10 CEF and ECF of materials and utilities of the processes.

Material	CEF	Unit	Reference	ECF	Unit	Reference
Glucose	0.1	$kg_{CO2-eq} \cdot kg^{-1}$	35	-7	$MJ \cdot kg^{-1}$	35
Water	0.001	$kg_{CO2-eq} \cdot kg^{-1}$	1	0.0016	$MJ \cdot kg^{-1}$	1
NaOH	1.2	$kg_{CO2-eq} \cdot kg^{-1}$	7	33.13	$MJ \cdot kg^{-1}$	7
HCl	0.58	$kg_{CO2-eq} \cdot kg^{-1}$	33	1.7	$MJ \cdot kg^{-1}$	33
Na_2HPO_4	3.94	$kg_{CO2-eq} \cdot kg^{-1}$	39	20	$MJ \cdot kg^{-1}$	LCI database
$CaCl_2$	3.34	$kg_{CO2-eq} \cdot kg^{-1}$	39	-	$MJ \cdot kg^{-1}$	LCI database
$MgSO_4$	1.43	$kg_{CO2-eq} \cdot kg^{-1}$	39	1.4	$MJ \cdot kg^{-1}$	LCI database
KH_2PO_4	3.05	$kg_{CO2-eq} \cdot kg^{-1}$	39	20	$MJ \cdot kg^{-1}$	LCI database
NaCl	0.11	$kg_{CO2-eq} \cdot kg^{-1}$	39	33.19	$MJ \cdot kg^{-1}$	LCI database
NH_4Cl	0.92	$kg_{CO2-eq} \cdot kg^{-1}$	39	-	$MJ \cdot kg^{-1}$	LCI database
$(NH_4)_2SO_4$	0.68	$kg_{CO2-eq} \cdot kg^{-1}$	LCI database	12	$MJ \cdot kg^{-1}$	LCI database
Citric acid	0.9	$kg_{CO2-eq} \cdot kg^{-1}$	LCI database	37	$MJ \cdot kg^{-1}$	LCI database
$(NH_4)2HPO_4$	0.894	$kg_{CO2-eq} \cdot kg^{-1}$	46	16.5	$MJ \cdot kg^{-1}$	LCI database
$NaHCO_3$	0.00159	$kg_{CO2-eq} \cdot kg^{-1}$	LCI database	5.9	$MJ \cdot kg^{-1}$	LCI database
Electricity	0.55	$kg_{CO2-eq} \cdot kWh^{-1}$	1	9.42	$MJ \cdot kWh^{-1}$	1
Cooling Water	0.0001	$kg_{CO2-eq} \cdot kg^{-1}$	1	0.0016	$MJ \cdot kg^{-1}$	1
Steam 160 ºC	0.25	$kg_{CO2-eq} \cdot kg^{-1}$	1	3.33	$MJ \cdot kg^{-1}$	1
Steam 254 ºC	0.25	$kg_{CO2-eq} \cdot kg^{-1}$	1	3.33	$MJ \cdot kg^{-1}$	1

3.6.3 LCI for the production processes of 1,4 – BDO and PBS

Given that the inputs, outputs of the processes (Figures 3.10 and 3.11), as well as their environmental impacts (Table 3.10) are known, the total environmental impacts of the processes are estimated. Table 3.11 presents the total environmental impact of the processes, as well as the allocated result derived from both the allocation methods. The allocation factor regarding the mass allocation is 82 % for 1,4 – BDO and 65 % for PBS, while the allocation factor regarding the energy allocation is 86 % for 1,4 – BDO (calculations in Appendix D).

Table 3.11 Environmental impacts of the production processes of the study.

	1,4 - Butanediol	PBS
CEF ($kg_{CO2-eq} \cdot kg^{-1}$)	2.77	5.23
ECF ($MJ \cdot kg^{-1}$)	-3.31	46.99
After Mass Allocation		
CEF ($kg_{CO2-eq} \cdot kg^{-1}$)	2.27	3.40
ECF ($MJ \cdot kg^{-1}$)	-2.71	30.54
After Energy Allocation		
CEF ($kg_{CO2-eq} \cdot kg^{-1}$)	2.38	
ECF ($MJ \cdot kg^{-1}$)	-2.84	

As Figure 3.12 presents, regarding the materials employed in the 1,4 –BDO production, glucose is mostly responsible for the greenhouse emissions, while regarding the utilities, electricity is mostly responsible, divided equally into the upstream and downstream section. As regards the energy consumption, sodium hydroxide contributes the most. As Figure 3.13 illustrates, glucose has a negative impact on energy consumption. That is because the factor for glucose is derived from sugarcane and after its pretreatment, surplus energy is available from the bagasse. If glucose deriving from another crop was employed, its energy factor would be positive. Electricity is also the utility that mostly increases the energy consumption.

As for the total PBS production process, sodium hydroxide is mostly responsible concerning greenhouse emissions, and more specifically the sodium hydroxide used in the fermentation of succinic acid. HPS that is employed for the polymerization of PBS, and more specifically for the heating of reactors, contributes the most concerning the carbon emissions. Finally, the energy consumption for the total PBS production presents the same behavior to that of 1,4 – BDO production with the difference that HPS for the polymerization of PBS has a higher impact (Figures 3.14 and 3.15).

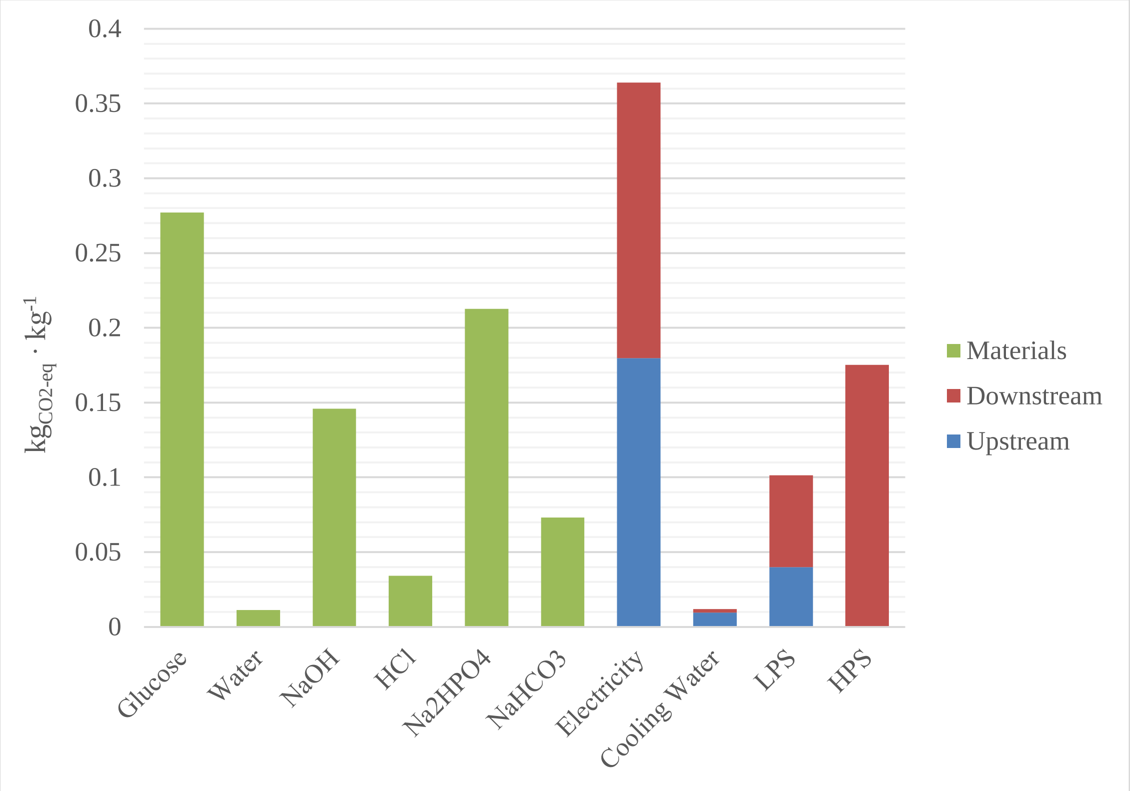


Figure 3.12 Greenhouse emissions for the production of 1 kg 1,4 – BDO regarding the most important inputs of the process.

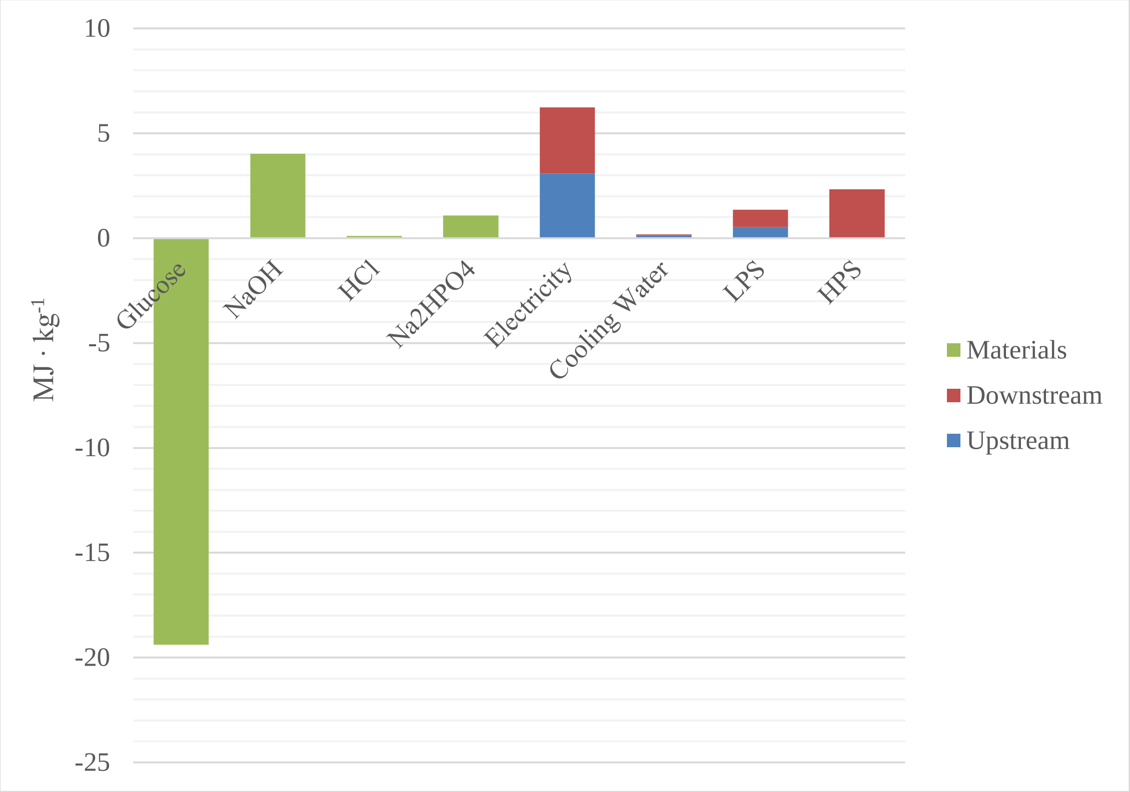


Figure 3.13 Energy consumption for the production of 1 kg 1,4 – BDO regarding the most important inputs of the process.

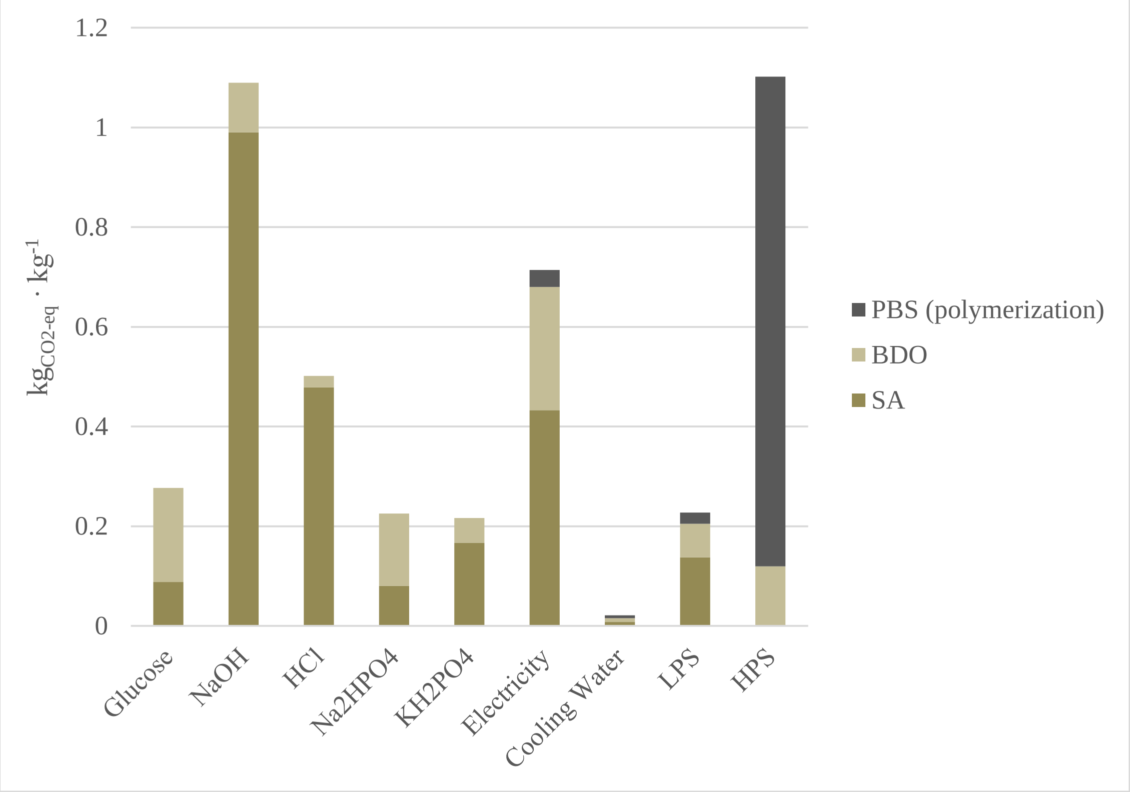


Figure 3.14 Greenhouse emissions for the total production of 1 kg PBS regarding the most important inputs of the process.

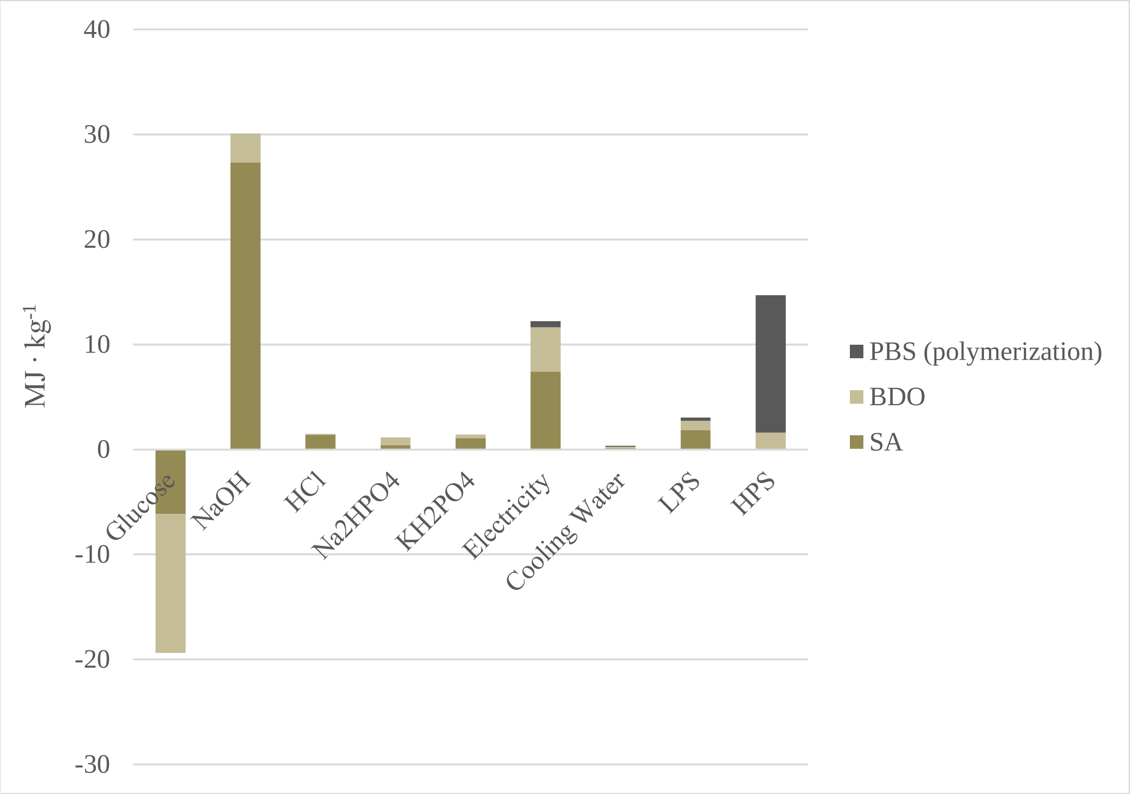


Figure 3.15 Energy consumption for the total production of 1 kg PBS regarding the most important inputs of the process.

3.6.4 Comparison with petrochemical production

Table 3.11 presents a LCIA comparison between the two different methods used for the production of the products: petrochemical and biotechnological. The LCI analysis for the 1,4 – BDO petrochemical process has been performed by Argonne National Laboratory (Dunn et. al, 2015), while the same analysis for PBS has been performed by Moussa et. al (2012). It should be mentioned that this comparison is possible because all the analyses have the same boundaries: cradle – to – gate. It is obvious that the processes chosen for the biotechnological production of 1,4 – BDO and the production process of PBS under study are at an advantage compared to the petrochemical process for both environmental impacts (Figures 3.16 - 3.19).

Table 3.12 Comparison between petrochemical and biotechnological production.

	1,4 - Butanediol			**PBS**		
	Petro - based	**Bio - based**	**Percent Deviation**	**Petro - based**	**Bio - based**	**Percent Deviation**
Greenhouse Gas Emissions ($kg_{CO2\text{-}eq} \cdot kg^{-1}$)	3.44	2.27	-34.01 %	6.6	3.40	-48.48 %
Energy Consumption ($MJ \cdot kg^{-1}$)	72	-2.71	-103.76 %	140	30.54	-78.18 %

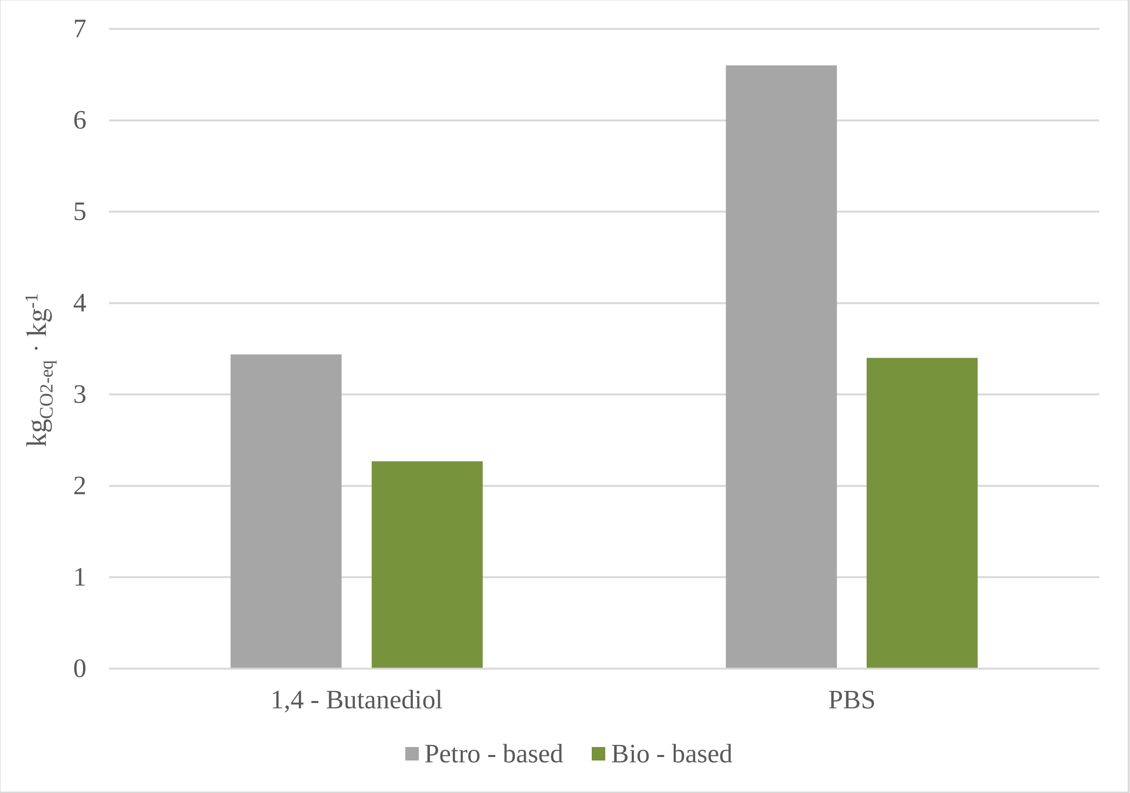


Figure 3.16 Comparison between the petrochemical process and the studied process for the production of 1,4 – BDO and PBS regarding greenhouse emissions.

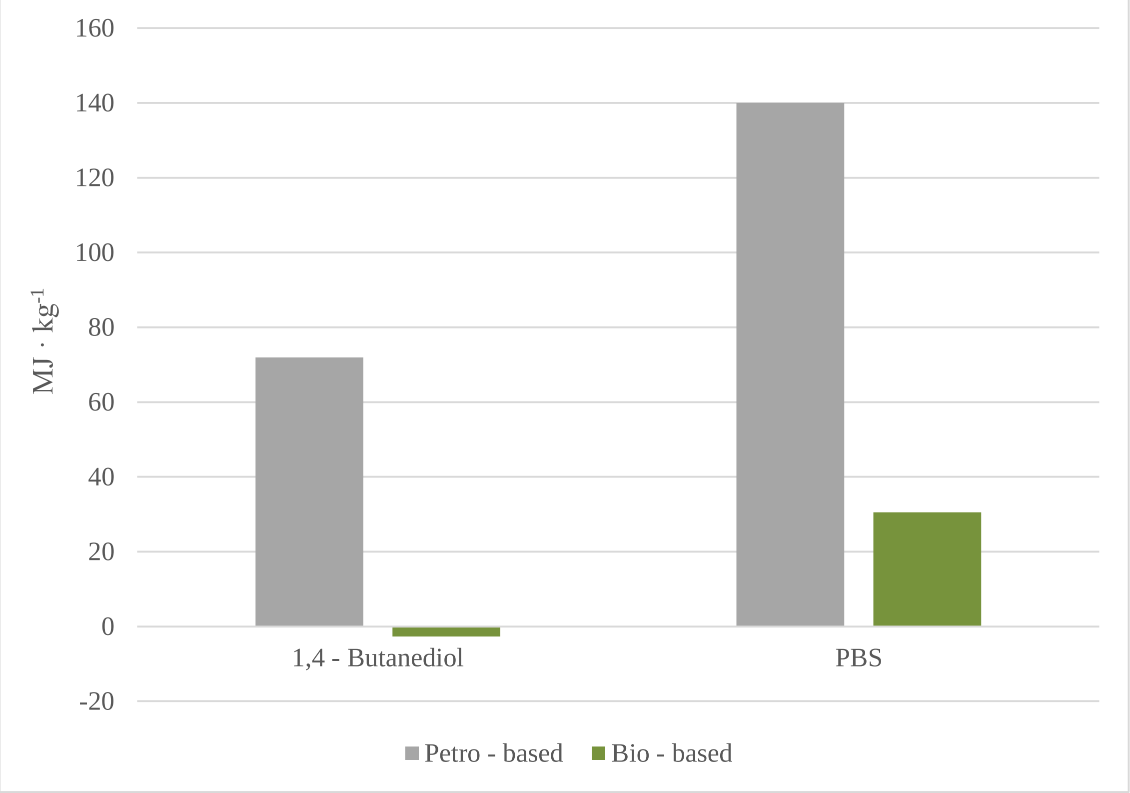


Figure 3.17 Comparison between the petrochemical process and the studied process for the production of 1,4 – BDO and PBS regarding energy consumption.

4 Conclusions

This study examined the techno-economic and environmental evaluation of the biotechnological production of 1,4 – butanediol and the production of PBS from biobased raw materials. Moreover, the pretreatment of corn stover was evaluated in order for sugars to be extracted and employed in biotechnological processes. After that, the following conclusions have been drawn.

As regards the 1,4 – BDO production, the cost of upstream section of the process is higher than that of the downstream product recovery area, because of the use of the fermentors. The utility mostly employed is electricity since it is used in both sections, thus it highly affects the final cost of utilities. Cost of raw materials is a large part of the total cost of manufacturing for the production of 1,4 – BDO. By conducting the DCF analysis, the process under study can be a feasible and profitable possibility for biotechnological production. The minimum selling price calculated is 1.3 $\$\cdot kg^{-1}$ and remains fixed after annual capacity of 40,000 t. Finally, the results of the Life Cycle Assessment depict that the biotechnological production shows a better environmental impact than the petrochemical one.

PBS from biobased raw materials seems to be a good alternative for the replacement of the conventional plastics. The yield of the polymerization process is 0.73 $kg_{PBS} \cdot kg^{-1}{}_{raw\ materials}$. The most serious cost regarding the equipment is that of the main polycondensation reactor, while High Pressure Steam that is used for the heating of the reactors is the utility mostly employed. If the production process of PBS is evaluated as a whole along with the production of the biobased raw materials (1,4-butanediol and succinic acid), the final economic assessment proves that it is a profitable investment with a constant minimum selling price 2.5 $\$\cdot kg^{-1}$ after annual capacity of 55,000 t. The environmental impact of the process as a whole is better than the impact of the petrochemical production. However, by examining the various impacts that are derived from the production of raw materials separately, the total impact may be further reduced.

Finally, as regards the utilization of corn stover as renewable feedstock, the final price of sugars obtained from its pretreatment is higher than the price of commercial glucose. However, the use of corn stover as raw material could be more cost effective, if the co – products after pretreatment were exploited and energy that could be used in the next processes was produced.

5 Literature

1. Akiyama, M., Tsuge, T., Doi, Y., 2003. Environmental life cycle comparison of polyhydroxyalkanoates produced from renewable carbon resources by bacterial fermentation. Polymer Degradation and Stability.80, 183–194.
2. Barton, N.R., Burgard, A.P, Burk, M.J., Crater,J.S., Osterhout, R.E, Pharkya, P., Steer, B.A., Sun, J., Trawick, J.D., Van Dien, S.J., Yang, T.H., Yim, H., 2014. An integrated biotechnology platform for developing sustainable chemical processes. J Ind Microbiol Biotechnol. DOI 10.1007/s10295-014-1541-1.
3. Burgard, A., Burk, M.J., Osterhout, R., Van Dien, S., Yim, H., 2016. Development of a commercial scale process for production of 1,4 – butanediol from sugar. Current Opinion in Biotechnology. 42, 118–125.
4. Chen, G.Q., Steinbüchel, A., 2010. Plastics from Bacteria: Natural Functions and Applications. Volume 14.
5. Cheng, K., Wang, G.Y., Zeng, J., Zhang, J.A., 2013. Improved Succinate Production by Metabolic Engineering. BioMed Research International 2013.
6. Cho, C., Choi, S. Y., Luo, Z. W., Lee, S. Y., 2014. Recent advantages in microbial production of fuels and chemicals using tools and strategies of systems metabolic engineering. Biotechnol. Adv. 33, 1455-1466.
7. De Souza, S.P., Pacca, S., De Avila, M.T., Borges, J.L.B., 2010. Greenhouse gas emissions and energy balance of palm oil biofuel. Renewable Energy. 35, 2552 – 2561.
8. Dheskali, E., Michailidi, K., Machado de Castro,A., Koutinas, A., Kookos, I., 2017. Optimal design of upstream processes in biotransformation technologies. Bioresource Technology. 224, 509–514.
9. Dunn, J.B., Adom, F., Sather, N., Han, J., Snyder, S., 2015. Life-cycle Analysis of Bioproducts and Their Conventional Counterparts in GREET. Energy Systems Division, Argonne National Laboratory, 24 – 26
10. E4tech, RE-CORD and WUR, 2015. From the Sugar Platform to biofuels and biochemicals. Final report for the European Commission, contract No ENER/C2/423 2012/SI2.673791.
11. Environmental Protection Agency. 1993. Life Cycle Assessment: Inventory Guidelines and Principles.
12. European Commission, 2005. Techno-economic Feasibility of Large-scale Production of Bio-based Polymers in Europe. Technical report series.
13. Fava, J.A., Denison, R., Jones, B., Curran, M., Vigon, B., Selke, S., & Barnum, J, 1991. A Technical Framework for Life-Cycle Assessment. Society of Environmental Toxicology and Chemistry.
14. Fujimaki, 1997. Processability and properties of aliphatic polyesters, “BIONOLLE”, synthesized by polycondensation reaction. Polymer Degradation and Stability 59, 209 – 214.
15. Guidotti, G., Soccio, M., Siracusa, V., Gazzano, M., Salatelli, E., Munari, A., Lotti, N., 2017. Novel Random PBS-Based Copolymers Containing Aliphatic Side Chains for Sustainable Flexible Food Packaging. Polymers 9, 724.
16. Gumede, T.P., Luyt, A.S., Mueller, A.J., 2018. Review on PCL, PBS and PCL/PBS blends containing carbon nanotubes. Express Polymer Letters Vol. 12, No.6, 505 – 529.
17. Hocking, M.B., 1991. Paper versus polystyrene: a complex choice. Science. 251.4993, 504-505.
18. Huo, H., M. Wang, C. Bloyd, and V. Putsche. 2008. Life-cycle assessment of energy and greenhouse gas effects of soybeanderived biodiesel and renewable fuels. Argonne National Laboratory.
19. Institute for Bioplastics and Biocomposites, 2017.Biopolymers facts and statistics.

20. Jang, Y. S., Kim, B., Shin, J. H., Choi, Y. J., Choi, S., Song, C. W., Lee, J., Park, H. G., Lee, S. Y., 2012. Bio-based production of C2-C6 platform chemicals, Biotechnol. Bioeng. 109, 2437-2459.
21. Kamikawa, M., Matsuo, T., Oka, K., Kondo, T., Sase, Y., Tanto, M., 2012. Device and Methods for producing Polybutylene Succinate. United States Patent
22. Kamm, B., Kamm, M., 2004. Principles of biorefineries. Appl. Micribiol. Biotechnol. 64,137-145.
23. Kookos, I.K., 2007. Introduction to plant Design, Tziola publishing (in Greek), Thessaloniki
24. Koutinas, A. A., Vlysidis, A., Pleissner, D., Kopsahelis, N., Lopez Garcia, Kookos, I.K., Papanikolaou, S, Kwan, T. H., Lin, C. S., 2014. Valorization of industrial waste and by-product streams via fermentation for the production of chemicals and biopolymers. Chem Soc Rev 43, 2587-2627.
25. Krevelen, D.W., Nijenhuis, K., 2009. Properties of polymers: their correlation with chemical structure : their numerical estimation and prediction from additive group contributions, 4th ed.
26. Ladakis D., 2018. Bioprocess development and design for the production of succinic acid via continous fermentation of spent sulphate liquor. PhD study.
27. Liguori, R., Amore, A. & Faraco, V., 2013. Waste valorization by biotechnological conversion into added value products. Appl Microbiol Biotechnol 97, 6129–6147.
28. Matthews, H. S., Hendrickson, C.T., Matthews, D.H., 2015. Life Cycle Assessment: Quantitative Approaches for Decisions That Matter. http://www.lcatextbook.com/
29. Moussa, H.I., Young, S.B., Gerand, Y., 2012. Polybutylene Succinate Life Cycle Assessment Variations and Variables.
30. National Renewable Energy Laboratory, 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. Technical report.
31. Pateraki, C., Patsalou, M., Vlysidis A., Kopsahelis, N., Webb, C., Koutinas, A., Koutinas, M., 2016. Actinobacillus succinogenes: Advances on succinic acid production and prospects for development of integrated biorefineries. Biochemical Engineering Journal 112, 285 – 303.
32. Peters, M.S., Timmerhaus, K.D., West, R.E., 2003. Plant Design and Economics for Chemical Engineers, McGraw Hill, NY.
33. Pradhan, A., Shrestha, D.S., McAloon, A., Yee, W., Haas, M., Duffield, J.A., 2011. Energy Life-Cycle Assessment of soybean biodiesel revisited. Transactions of the ASABE. 54(3), 1031-1039
34. Puchalski M., Szparaga, G., Biela, T., Gutowska, A., Sztajnowski, S., Krucinska, I., 2018. Molecular and Supramolecular Changes in Polybutylene Succinate (PBS) and Polybutylene Succinate Adipate (PBSA) Copolymer during Degradation in Various Environmental Conditions. Polymers 10, 251.
35. Renouf, M.A., Wegener, M.K., Nielsen, L.K., 2008. An environmental life cycle assessment comparing Australian sugarcane with US corn and UK sugar beet as producers of sugars for fermentation. Biomass and Bioenergy 32, 1144-1155.
36. Samuelov, N.S., Lamed, R., Lowe, S., Zeikus, J.G., 1991. Influence of CO2-HCO3- levels and pH on growth, succinate production, and enzyme activities of Anaerobiospirillum succiniciproducens. Appl Environ Microbiol. 57, 3013–3019.
37. Song, J.H., Murphy, R.J., Narayan, R., Davies, G.B.H., 2009. Biodegradable and compostable alternatives to conventional plastics. Philosophical Transactions of the Royal Society B 364, 2127 - 2139.
38. Succinity. Biobased Polybutylene Succinate (PBS) – An attractive polymer for biopolymer compounds.
39. Sun, X.Z., Minowa, T., Yamaguchi, K., Genchi, Y., 2015. Evaluation of energy consumption and greenhouse gas emissions from poly(phenyllactic acid) production using sweet sorghum. Journal of Cleaner Production. 87, 208-215

40. The French Network of Food Technology Institutes,2014. Development of active, intelligent and sustainable food packaging using Polybutylenesuccinate. Project Succipack.
41. Turton, R., Bailie, R. C., Whiting, W. B., and Shaeiwitz, J. A., 2008. Analysis, synthesis and design of chemical processes. Pearson Education.
42. United States Environmental Protection Agency, EPA, 2006. Life Cycle Assessment: Principles and Practice.
43. Werpy, T., Petersen, G., 2004. Top Value Added Chemicals From Biomass, Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas. U.S. Department of Energy. (http://www1.eere.energy.gov/biomass/pdfs/35523.pdf).
44. Xu, J., Guo, B.H., 2010. Poly(butylene succinate) and its copolymers: Research, development and industrialization. Biotechnol. J. 5, 1149-1163.
45. Yim, H., Haselbeck, R., Niu, W., Pujol-Baxley C., Burgard, A., Boldt, J., Khandurina, J., Trawick, J.D., Osterhout, R.E., Stephen, R., Estadilla, J., Teisan, S., Schreyer, H.B., Andrae, S., Yang, T.H., Lee, S.Y., Burk, M.J., Van Dien, S., 2011. Metabolic engineering of Escherichia coli for direct production of 1,4-butanediol. Nat Chem Biol. 7, 445-452.
46. Zhang, X., Yan, S., Tyagi, R.D., Surampalli, R.Y., 2013. Energy balance and greenhouse gas emissions of biodiesel production from oil derived from wastewater and wastewater sludge. Renewable Energy 55, 392-403.

Appendix A. 1,4 – BDO process

Mass Balance

E. coli that produces 1,4 – BDO is a genetically engineered microorganism, thus specific modifications result to better yields and productivities.

The first case study is based on data published by Yim et. al (2001). Having known the concentration of all products, the total mass of carbon of components is calculated (Table A.1). After that, the distribution of the carbon among by-products is determined (Figure A.1).

The second case study considers the change of yield due to the better modification of the microorganism. Based on the percentage of by-products and biomass given by Burgard et. al (2016) for production of 1,4 – BDO with concentration 99 g · L^{-1}, the new concentration of glucose is calculated, the total mass of carbon is distributed among 1,4 – BDO, biomass, by-products and CO_2 and finally, the concentration of by – products is determined based on Figure A.1 (Table A.2).

The final case study is the best reported concentration of 1,4 – BDO, 125 g · L^{-1}. For this case study, the concentration of by – products is reduced by a factor of 3 (Burgard et. al, 2016), while the biomass has the same percentage of mass carbon as the previous case study (Table A.3).

In order for the mass balance of the bioreactor to be calculated, the total formation reaction of 1,4 – BDO is determined. The total reaction is divided into two different reactions, the formation of biomass and the production of the desired product

$$\mathrm{a\,C_6H_{12}O_6 + b\,O_2 + c\,NH_3 \rightarrow\ d\,CH_{1.77}O_{0.49}N_{0.24} + e\ \ H_2O\ \ + f\,CO_2}$$

$$\mathrm{a'C_6H_{12}O_6 + b'O_2 \rightarrow c'C_4H_{10}O_2 + d'C_2H_6O + e'C_4H_6O_2 +\ f'\,C_2H_4O_2\ +\ \ g'\,C_4H_8O_3 + h'\,H_2O\ \ + i'CO_2}$$

Stoichiometry of glucose ($C_6H_{12}O_6$), biomass ($CH_{1.77}O_{0.49}N_{0.24}$), by – products and CO_2 is calculated from the mass of components (g) per one liter of the broth for the production of 125 g · L^{-1} 1,4 – BDO. In order to divide the total mass of glucose into the two reactions, it is assumed that the theoretical stoichiometric amount of CO_2 is used in the second reaction and the excess one is used for the production of biomass (Table A.4 and A.5). The stoichiometry of O_2, NH_3 and H_2O is calculated by component mass balance in its reaction.

Finally, the stoichiometry reaction according to the calculations is:

$$\mathrm{0.2759\,C_6H_{12}O_6 + 1.0195\,O_2 + 0.15\,NH_3 \rightarrow\ 0.625\,CH_{1.77}O_{0.49}N_{0.24} + 1.3273\ \ H_2O\ \ + 1.03\,CO_2}$$

$$\mathrm{1.4602\,C_6H_{12}O_6 + 0.6434\,O_2 \rightarrow 1.387\,C_4H_{10}O_2 + 0.0154\,C_2H_6O + 0.0154\,C_4H_6O_2 + 0.0636\,C_2H_4O_2\ +\ \ 0.0548\,C_4H_8O_3 + 1.3874\,H_2O\ \ + 2.7744\,CO_2}$$

and the total reaction is:

$$\begin{aligned}&\mathrm{1.7361\,C_6H_{12}O_6 + 1.6629\,O_2 + 0.15\,NH_3 \rightarrow}\\&\mathrm{0.625\,CH_{1.77}O_{0.49}N_{0.24} + 1.387\,C_4H_{10}O_2 + 0.0154\,C_2H_6O + 0.0154\,C_4H_6O_2}\\&\qquad\mathrm{+\ 0.0636\,C_2H_4O_2\ +\ \ 0.0548\,C_4H_8O_3 + 2.715\,H_2O\ \ + 3.805\,CO_2}\end{aligned}$$

Table A.1 Data for case study 1 (18 g · L^{-1} 1,4 – BDO).

	Concentration (g · L^{-1})	**MW (g · mol^{-1})**	**Carbon Mass (g)**
Biomass ($CH_{1.77}O_{0.49}N_{0.24}$)	2.76	24.97	1.33
1,4 – Butanediol ($C_4H_{10}O_2$)	18	90.12	9.59
Ethanol (C_2H_6O)	1.15	46.07	0.6
GBL ($C_4H_6O_2$)	2.15	86.09	1.20
Acetic Acid ($C_2H_4O_2$)	6	60.05	2.40
4 – HB ($C_4H_8O_3$)	9.11	104.1	4.20
		Total carbon mass of by – products (g)	8.40
Carbon Dioxide (CO_2)		44	0.15
Glucose ($C_6H_{12}O_6$)	48.65	180	19.46

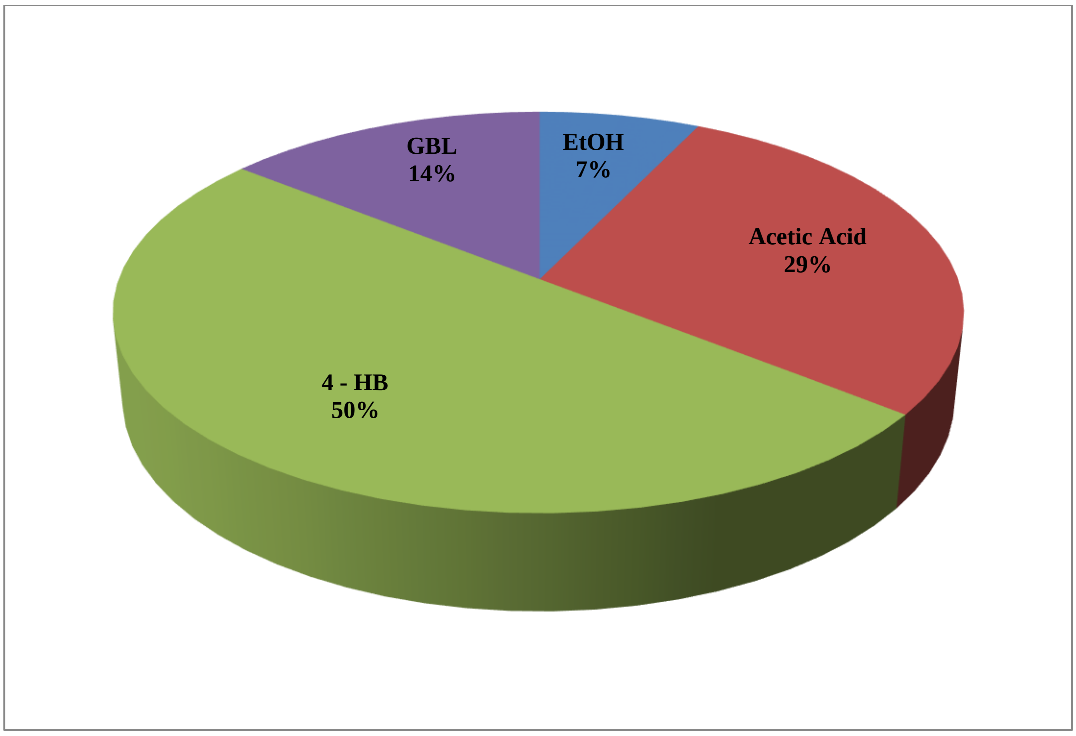


Figure A.1. Distribution of carbon among by – products (Case study 1).

Table A.2 Data for case study 2 (99 g · L^{-1} 1,4 – BDO).

	Concentration (g · L^{-1})	**MW (g · mol^{-1})**	**Carbon Mass (g)**
Biomass ($CH_{1.77}O_{0.49}N_{0.24}$)	14.09	24.97	6.77
1,4 – Butanediol ($C_4H_{10}O_2$)	99	90.12	52.73
Ethanol (C_2H_6O)	2.12	46.07	1.11
GBL ($C_4H_6O_2$)	3.97	86.09	2.21
Acetic Acid ($C_2H_4O_2$)	11.46	60.05	4.58
4 – HB ($C_4H_8O_3$)	17.13	104.1	7.90
Total carbon mass of by – products (g)			15.79
Carbon Dioxide (CO_2)		44	37.53
Glucose ($C_6H_{12}O_6$)	282.05	180	112.82

Table A.3 Data for case study 3 (125 g · L^{-1} 1,4 – BDO).

	Concentration (g · L^{-1})	**MW (g · mol^{-1})**	**Carbon Mass (g)**
Biomass ($CH_{1.77}O_{0.49}N_{0.24}$)	15.61	24.97	7.5
1,4 – Butanediol ($C_4H_{10}O_2$)	125	90.12	66.58
Ethanol (C_2H_6O)	0.71	46.07	0.37
GBL ($C_4H_6O_2$)	1.32	86.09	0.74
Acetic Acid ($C_2H_4O_2$)	3.82	60.05	1.53
4 – HB ($C_4H_8O_3$)	5.71	104.1	2.63
Total carbon mass of by – products (g)			5.26
Carbon Dioxide (CO_2)		44	45.66
Glucose ($C_6H_{12}O_6$)	312.5	180	125

Table A.4 Data used for the reaction of biomass formation.

	Concentration (g · L^{-1})	**MW (g · mol^{-1})**	**n (mol)**
Glucose ($C_6H_{12}O_6$)	49.67	180	0.276
Biomass ($CH_{1.77}O_{0.49}N_{0.24}$)	15.61	24.97	0.625
Carbon Dioxide (CO_2)	12.37	44	1.03

Table A.5 Data used for the reaction of 1,4 – BDO production.

	Concentration (g · L^{-1})	**MW (g · mol^{-1})**	**n (mol)**
Glucose ($C_6H_{12}O_6$)	262.83	180	1.46
1,4 – Butanediol ($C_4H_{10}O_2$)	125	90.12	1.387
Ethanol (C_2H_6O)	0.71	46.07	0.0154
GBL ($C_4H_6O_2$)	1.32	86.09	0.0154
Acetic Acid ($C_2H_4O_2$)	3.82	60.05	0.0636
4 – HB ($C_4H_8O_3$)	5.71	104.1	0.0548
Carbon Dioxide (CO_2)	33.29	44	2.774

Table A.6 Flow summary table for 1,4 - BDO production.

Stream	**101**	**102**	**103**	**104**	**105**	**106**	**107**	**108**	**109**	**110**	**111**	**112**	**113**	**114**	**115**	**116**
Temperature (°C)	20	130	140	37	25	37	37	37	37	37	37	100	56	100	100	227
Pressure (bar)	1	1	1	1	1	1.17	1	1	1	1	1	1	1.6	1	1	1
Mass Flow ($kg \cdot h^{-1}$)	52,807.08	52,807.08	52,807.08	52,807.08	3,094	3,094	47,704.91	46,439.14	1,268	1,907.12	44,532.02	44,532.02	38,187.97	6,344.02	1,508.83	4,834
Mass Flow of Components ($kg \cdot h^{-1}$)																
Glucose ($C_6H_{12}O_6$)	13,350	13,350	13,350	13,350	0	0	0	0	0	0	0	0	0	0	0	0
Oxygen (O_2)	0	0	0	0	3,094	3,094	0	0	0	0	0	0	0	0	0	0
Ammonia (NH_3)	110	110	110	110	0	0	0	0	0	0	0	0	0	0	0	0
Minerals	703.61	703.61	703.61	703.61	0	0	703.61	703.61	0	703.61	0	0	0	0	0	0
Biomass ($CH_{1.77}O_{0.49}N_{0.2}$)	0	0	0	0	0	0	663.03	0	663.03	0	0	0	0	0	0	0
1,4 – butanediol ($C_4H_{10}O_2$)	0	0	0	0	0	0	5,335.26	5,335.26	0	0	5,335.26	5,335.26	514.63	4,820.62	0.92	4,819
Ethanol (C_2H_6O)	0	0	0	0	0	0	28.29	28.29	0	0	28.29	28.29	27.914	0.37	0.37	0
GBL ($C_4H_6O_2$)	0	0	0	0	0	0	56.58	56.58	0	0	56.58	56.58	20.57	36.01	20.54	15.46
Acetic Acid ($C_2H_4O_2$)	0	0	0	0	0	0	161.81	161.81	0	161.81	0	0	0	0	0	0
4 – HB ($C_4H_8O_3$)	0	0	0	0	0	0	243.50	243.50	0	243.50	0	0	0	0	0	0
Water (H_2O)	38,643	38,643	38,643	38,643	0	0	40,512.84	39,910.09	602.75	798.20	39,111.89	39,111.89	37,624.86	1,487.02	1,487.00	0

Cost of raw materials

Table A.7 Calculation of cost of raw materials.

Raw Material	**Unitary prices 2017 ($ · t_{rm}^{-1})**	**Quantity ($t_{rm} \cdot t_{1,4-BDO}^{-1}$)**	**C_{RM} ($\$ \cdot t_{1,4-BDO}^{-1}$)**
Glucose	230	2.77000	637.10
Na_2HPO_4	900	0.05424	48.82
NaCl	35	0.00400	0.14
$CaCl_2$	275	0.00009	0.02
NH_4Cl	200	0.01600	3.20
$(NH_4)_2SO_4$	150	0.00800	1.20
KH_2PO_4	1150	0.02400	27.60
$MgSO_4$	360	0.00096	0.35
$NaHCO_3$	270	0.00672	1.81
NaOH	400	0.12153	48.61
resins	2600	0.0002034	0.52884
HCL	61	0.05898	3.59778
Water	0.4346	11.3	4.91
		Total cost of raw materials ($\$ \cdot t_{1,4-BDO}^{-1}$)	**777.89**
		Total cost of raw materials ($\$ \cdot y^{-1}$)	**31.11**

Appendix B. PBS process

Table B.1 Flow summary table for PBS production.

Streams	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217
Temperature (oC)	25	25	80	180	230	230	99.67	226.2	240	240	80	329.4	30	30.02	99.63	210.3	30
Pressure (bar)	1	1	1	1	1	1	1	1	0.0026	0.0026	0.0026	0.05	0.05	1	1	1	1
Mass Flow (kg·h^{-1})	3,314.4	3,287.9	6,602.3	6,602.3	5,707.4	894.8	489.3	405.4	888.3	4,819.2	888.3	888.3	888.3	888.3	523.3	364.9	4,819.2
Mass Flow of Components (kg·h^{-1})																	
Succinic Acid ($C_4H_6O_4$)	3,314.4	0	3,314.4	3,314.4	0	0	0	0	0	0	0	0	0	0	0	0	0
1,4 – butanediol ($C_4H_{10}O_2$)	0	3,287.9	3,287.9	3,287.9	363.5	394.9	3.8	391.1	363.5	0	363.5	363.5	363.5	363.5	0	363.5	0
Monomer	0	0	0	0	5,324.0	14.2	0	14.2	0	0	0	0	0	0	0	0	0
Water (H_2O)	0	0	0	0	19.9	485.7	485.5	0.2	524.7	0	524.7	524.7	524.7	524.7	523.3	1.4	0
PBS	0	0	0	0	0	0	0	0	0	4,819.2	0	0	0	0	0	0	4,819.2

Appendix C. Corn Stover pretreatment

Table C.1 Flow summary table for initial corn stover pretreatment.

Streams	**301**	**302**	**303**	**304**	**305**	**306**	**307**
Temperature (ºC)	25	158	130	130	97	101	78
Pressure (atm)	1	5.7	9.6	2.6	1	1	4.3
Mass Flow (kg · h^{-1})	104,167	311,842	292,060	19,782	278,194	13,866	429,554
Mass Flow of Components (kg · h^{-1})							
Water	20,833	224,002	204,469	19,533	190,754	13,715	341,063
Glucose	0	3,550	3,550	0	3,550	0	3,550
Xylose	0	16,643	16,643	0	16,643	0	16,476
Other Sugars	642	3,720	3,720	0	3,720	0	3,682
Sugar Oligomers	0	566	566	0	566	0	566
Organic Soluble Solids	12,208	12,866	12,866	0	12,866	0	14,727
Inorganic Soluble Solids	0	0	0	0	0	0	2,482
Ethanol	0	18	10	8	6	4	6
Acetic Acid	0	1,508	1,473	36	1,450	23	0
Sulfuric Acid	0	1,842	1,842	0	1,842	0	0
Furfurals	0	1,034	829	205	705	124	705
Cellulose	29,205	26,138	26,138	0	26,138	0	26,138
Xylan	16,273	423	423	0	423	0	423
Other Struct. Carbohydr.	3,675	96	96	0	96	0	96
Acetate	1,508	0	0	0	0	0	0
Lignin	13,132	12,475	12,475	0	12,475	0	12,475
Protein	2,583	2,583	2,583	0	2,583	0	2,583
Other Insoluble Solids	4,108	4,377	4,377	0	4,377	0	4,581

Table C.2 Flow summary table for the enzymatic hydrolysis of corn stover.

Streams	**308**	**309**	**310**	**311**	**312**
Temperature (ºC)	49	48	32	32	32
Pressure (atm)	2.5	5.1	1	1	1
Mass Flow (kg · h^{-1})	429,554	443,376	443,389	29,531	413,858
Mass Flow of Components (kg · h^{-1})					
Water	341,063	354,117	351,490	12,475	339,015
Glucose	3,550	3,550	29,690	0	29,690
Xylose	16,476	16,476	16,480	0	16,480
Other Sugars	3,682	3,682	4,010	0	4,010
Sugar Oligomers	566	566	1,610	0	1,610
Organic Soluble Solids	14,727	14,768	14,770	0	14,770
Inorganic Soluble Solids	2,482	2,482	2,480	0	2,480
Ethanol	6	6	10	0	10
Acetic Acid	0	0	0	0	0
Sulfuric Acid	0	0	0	0	0
Furfurals	705	705	710	0	710
Cellulose	26,138	26,138	1,250	0	1,250
Xylan	423	423	420	0	420
Other Struct. Carbohydr.	96	96	100	0	100
Acetate	0	0	0	0	0
Lignin	12,475	12,475	12,475	12,475	0
Protein	2,583	3,203	3,203	0	3,203
Cell Mass	0	108	110	0	110
Other Insoluble Solids	4,581	4,581	4,581	4,581	0

Estimation of the unitary price of sugars

Table C.3 Calculation of cost of utility and raw materials (extraction of 422 kt · y^{-1} total sugars).

Raw Material	**Unitary prices 2017 ($ · t_{rm}^{-1})**	**Quantity (t_{rm} · y^{-1})**	**C_{RM} (M$ · y^{-1})**
Corn stover (dry)	58.5	700,838	40.999
Water	0.4346	2,780,824	1.208
Sulfuric Acid	80	15,491	1.240
Ammonia	350	8,839	3.093
Enzyme	4,240	5,214	22.108
Total cost of raw materials ($ · y^{-1})			68.65
Utility	**Unitary prices ($ · t^{-1})**	**Quantity (unit · y^{-1})**	**C_{RM} (M$ · y^{-1})**
HPS (t)	9.61	235,682	2.265
Electricity (kWh)	0.0674	66,559,442	4.486
Cooling Water (t)	0.0157	7,427	0.0001
Total cost of utilities ($ · y^{-1})			**6.75**

Appendix D. Life Cycle Assessment

Figures 3.10 and 3.11 present the mass of the products produced from the production processes of 1,4 – butanediol and PBS. Moreover, the enthalpy of combustion of the products is used, so as the energy allocation method to be carried out. (Table D.1)

Mass allocation factor

BDO $$\mathrm{f_m} = \frac{1\ \mathrm{kg}}{(1+0.125+0.0057+0.031+0.0457+0.011)\ \mathrm{kg}} = 0.82$$

PBS $$\mathrm{f_m} = \frac{1\ \mathrm{kg}}{(1+0.159+0.305+0.036+0.004+0.031+0.008)\ \mathrm{kg}} = 0.65$$

Energy allocation factor

$$\mathrm{f_e} = \frac{\dfrac{1000\ \mathrm{g} \cdot 2{,}499.9\ \mathrm{kJ \cdot mol^{-1}}}{90.12\ \ \mathrm{g \cdot mol^{-1}}}}{\mathrm{D}} = \ 0.86$$

$$\begin{aligned}\mathrm{D} = {} & \frac{1000\ \mathrm{g} \cdot 2{,}499.9\ \mathrm{kJ \cdot mol^{-1}}}{90.12\ \ \mathrm{g \cdot mol^{-1}}} + \frac{125\ \mathrm{g} \cdot 552\ \mathrm{kJ \cdot mol^{-1}}}{24.97\ \ \mathrm{g \cdot mol^{-1}}} + \frac{5.7\ \mathrm{g} \cdot 1{,}336.8\ \mathrm{kJ \cdot mol^{-1}}}{46.07\ \ \mathrm{g \cdot mol^{-1}}} \\ & + \frac{31\ \mathrm{g} \cdot 872.4\ \mathrm{kJ \cdot mol^{-1}}}{60.05\ \ \mathrm{g \cdot mol^{-1}}} + \frac{45.7\ \mathrm{g} \cdot 2{,}007.36\ \mathrm{kJ \cdot mol^{-1}}}{104.1\ \ \mathrm{g \cdot mol^{-1}}} \\ & + \frac{11\ \mathrm{g} \cdot 2{,}000.4\ \mathrm{kJ \cdot mol^{-1}}}{86.09\ \ \mathrm{g \cdot mol^{-1}}}\end{aligned}$$

Table D.1. Enthalpies of combustions.

	Enthalpy of Combustion ($\mathbf{kJ \cdot mol^{-1}}$)	**MW ($\mathbf{g \cdot mol^{-1}}$)**
1,4 – Butanediol ($C_4H_{10}O_2$)	2,499.9	90.12
Biomass ($CH_{1.8}O_{0.5}N_{0.2}$)	552	24.97
Acetic Acid ($\mathrm{C_2H_4O_2}$)	872.4	60.05
Ethanol (C_2H_6O)	1,366.8	46.07
4 – HB ($\mathrm{C_4H_8O_3}$)	2,007.36	104.1
GBL ($\mathrm{C_4H_6O_2}$)	2,000.4	86.09