AGRICULTURAL UNIVERSITY OF ATHENS
DEPARTMENT OF FOOD SCIENCE & HUMAN NUTRITION
LABORATORY OF FOOD PROCESS ENGINEERING

PhD Thesis

Process design, techno-economic and environmental impact assessment of novel biorefineries for the sustainable production of bio-based and biodegradable products

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Σχεδιασμός καινοτόμων βιοδιυλιστηρίων και ανάλυση οικονομικής και περιβαλλοντικής βιωσιμότητας για την παραγωγή βιογενών και βιοαποικοδομήσιμων προϊόντων

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ABSTRACT

The restructuring of conventional industrial processes into sustainable entities is urgent given the limited fossil-resources and the continuously increasing environmental concerns. That transition towards a sustainable bio-based economy and the substitution of emission-intensive and non-renewable resources with renewable resources has resulted in numerous scientific studies evaluating the production of bio-based products. Sustainable production of chemicals and biopolymers should depend on renewable feedstock utilisation within novel biorefinery concepts.

This PhD thesis presents novel research on sustainability assessment of biorefineries using various waste and by-product streams for the production of bio-based chemicals and polymers. A computational methodology, including process design, techno-economic evaluation, life cycle assessment, profitability risk assessment, social assessment and life cycle costing, was employed to evaluate alternative processes for the production of succinic acid and poly(butylene succinate) (PBS) from different renewable resources.

The sustainable production of PBS from corn glucose syrup, corn stover and sugar beet pulp (SBP) has been assessed via process design, preliminary techno-economic evaluation, life cycle assessment and life cycle costing. The techno-economic and environmental impact of PBS production has been compared to its fossil counterpart, namely General Purpose Polystyrene (GPPS). Cost-competitive PBS production can be achieved in a SBP-based biorefinery, including separation of crude pectin-rich extract as co-product, leading to minimum selling price of \$1.37/kg_{PBS} at 50,000 t annual biopolymer production capacity. The Acidification Potential, Eutrophication Potential and Human Toxicity Potential are lower when SBP is used. The life cycle costing of PBS (\$1.72/kg_{PBS}) production from SBP is lower than general purpose polystyrene (GPPS, \$2.04/kg) at pectin-rich extract market price of \$4/kg. Techno-economic risk assessment via Monte-Carlo simulations showed that PBS could be produced from SBP at the market price of GPPS (\$1.72/kg) with 100% probability to achieve a positive Net Present Value at pectin-rich extract market prices of \$4/kg. As a result, SBP-based biorefinery development ensures sustainable production of PBS as compared to fossil-derived counterparts and single product bioprocesses using glucose syrup and corn stover.

The techno-economic and environmental performance of succinic acid (SA) production by an engineering *Yarrowia lipolytica* strain has been evaluated in a process using the organic fraction of municipal solid waste (OFMSW) as feedstock and an electrochemical membrane bioreactor (EMB) for simultaneous SA production and extraction. The minimum selling price (MSP) of SA ($2.70-3.71/kg) considering 50,000 t_{SA}/year production capacity using the EMB-based process was slightly lower than the conventional bioprocess depending on OFMSW management fees ($0-35/$t_{OFMSW}$). Profitability risk assessment indicated that the probability to achieve positive Net Present Value (NPV) is over 90% when the current SA market price ($2.94/kg) is considered at $70/$t_{OFMSW}$ management fees. Life Cycle Assessment was carried out for the EMB-based bioprocess and the conventional bioprocess considering either conventional electricity production mix (grid) or renewable electricity production from photovoltaics. The use of renewable electricity in the EMB-based bioprocess led to lower Global Warming Potential (0.81 CO_2-eq/kg_{SA}), Abiotic Depletion Potential (15.73 CO_2-eq/kg_{SA}), Eutrophication Potential (1.87 g SO_2-eq/kg_{SA}) and Acidification Potential (0.25 g PO_4-eq/kg_{SA}) than the current bioprocess when renewable electricity was used, while higher Human Toxicity Potential (0.29 kg DCB-eq/kg_{SA}) was observed due to the raw materials (e.g. heavy metals) and utilities (e.g. electricity) used in photovoltaics production.

OFMSW was used for the assessment of biorefinery development, within a circular bioeconomy context, towards extraction of lipids and proteins as well as succinic acid production via fermentation using *Actinobacillus succinogenes*. The MSP_{SA} ($1.13-2.39/kg) considering 60,000 t_{SA}/year production capacity varied depending on co-product market prices and OFMSW management fees. The biorefinery using 1000 kg OFMSW contributes 35% lower CO_2 emissions than conventional processes for the production of 105 kg vegetable oil, 87 kg vegetable protein and 206.4 kg fossil-derived SA, considering also the CO_2 emissions due to OFMSW landfilling. The proposed OFMSW biorefinery leads to cost-competitive SA production with lower CO_2 emissions for OFMSW treatment.

OFMSW was also considered as feedstock for the evaluation of four biorefinery concepts resulting in the production of biosurfactants together with lactic acid (LA), succinic acid (SA), hot melt adhesives (HMAs) or polyurethane urea dispersions (PUDs). LA and SA were produced via fermentation using sugar-rich OFMSW enzymatic hydrolysates, while biosurfactants were produced from OFMSW-derived lipids and proteins and bacterial biomass remaining after the end of fermentation. OFMSW-derived SA replaces fossil-based SA and adipic acid in PUDs production. HMAs and PUDs production could be profitable when biosurfactants are produced as co-product in OFMSW-based biorefineries, leading to MSP of $2.92/$kg_{HMAs}$ and $1.95/$kg_{PUDs}$

when biosurfactants market price of \$4.1/kg, OFMSW management fees of \$0.035/kg and production capacities of SA and LA at economies of scale are considered. If LA or SA are considered as final products together with biosurfactants, then the corresponding MSPs are $\$1.58/\mathrm{kg}_{\mathrm{LA}}$ and $\$2.14/\mathrm{kg}_{\mathrm{SA}}$. Five environmental indicators were estimated considering either conventional electricity production mix (grid) or renewable electricity usage from photovoltaics. The proposed biorefineries lead to 25-35% greenhouse gas emission savings per kg main product (or 0.95-2.06 kg CO_2-eq per kg dry OFMSW) when compared to conventional production of end-products and two OFMSW management practices based on either landfilling alone or combined composting (37.45%) and landfilling (62.55%). The results demonstrate that OFMSW-based biorefineries could lead to profitable and sustainable production of bio-based products and OFMSW utilisation as feedstock.

Finally, the techno-economic and environmental performance of a novel biorefinery using the three main waste streams generated by wineries was evaluated for the production of SA, crude phenolic-rich extract, grape-seed oil, calcium tartrate and crude tannin-rich extract. The $\mathrm{MSP}_{\mathrm{SA}}$ within a winery waste biorefinery varies ($\$1.23\text{-}2.76/\mathrm{kg}_{\mathrm{SA}}$) depending on the market price and the potential end-uses of the extracted fractions. The Global Warming Potential and the Abiotic Depletion Potential of winery waste valorisation through the proposed biorefinery are 1.47 kg CO_2-eq per kg dry waste and 25.2 MJ per kg dry waste, respectively. Biorefining of winery waste could lead to the development of a sustainable and novel bioeconomy business model with new market opportunities and efficient waste management. Profitability risk assessment proved that the proposed winery wastes biorefinery could be profitable in all different cases and even at the worst case scenarios of the values of process variables.

Scientific area: Sustainable biorefinery devepoment

Keywords: Industrial side streams, Biorefinery, Succinic acid, Biopolymers, Process design, Techno-economic assessment, Life cycle assessment, Life cycle costing, Profitability risk assessment.

Σχεδιασμός καινοτόμων βιοδιυλιστηρίων και ανάλυση οικονομικής και περιβαλλοντικής βιωσιμότητας για την παραγωγή βιογενών και βιοαποικοδομήσιμων προϊόντων

Τμήμα Επιστήμης Τροφίμων & Διατροφής του Ανθρώπου
Εργαστήριο Μηχανικής & Επεξεργασίας Τροφίμων

ΠΕΡΙΛΗΨΗ

Η αναδιάρθρωση των συμβατικών βιομηχανικών διεργασιών σε καινοτόμες και βιώσιμες βιοδιεργασίες είναι ιδιαίτερα επιτακτική, δεδομένης της περιβαλλοντικής επιβάρυνσης που προκαλεί η χρήση ορυκτών πόρων. Η ανάγκη μετάβασης στην εποχή της κυκλικής βιο-οικονομίας όπως και της αντικατάστασης των ορυκτών πόρων από ανανεώσιμες πρώτες ύλες έχει οδηγήσει, τόσο την επιστημονική κοινότητα όσο και τη βιομηχανία, σε πολυάριθμες μελέτες αξιολόγησης των διεργασιών παραγωγής βιογενών προϊόντων. Η βιώσιμη παραγωγή χημικών ουσιών και βιοπολυμερών θα πρέπει να στηρίζεται στην αξιοποίηση ανανεώσιμων πρώτων υλών, στο πλαίσιο ανάπτυξης καινοτόμων βιοδιυλιστηρίων.

Η παρούσα διδακτορική διατριβή παρουσιάζει καινοτόμα αποτελέσματα όσον αφορά στην αξιολόγηση ανάπτυξης βιώσιμων βιοδιυλιστηρίων αξιοποιώντας διαφορετικά απόβλητα και παράπλευρα ρεύματα για την παραγωγή βιογενών προϊόντων και πολυμερών. Συγκεκριμένα, πραγματοποιήθηκε αξιολόγηση της αειφορίας διαφορετικών βιοδιεργασιών και βιοδιυλιστηρίων παραγωγής ηλεκτρικού οξέος και πολυ(ηλεκτρικού βουτυλεστέρα) (PBS) από ανανεώσιμες πρώτες ύλες μέσω σχεδιασμού διεργασιών, τεχνο-οικονομικής μελέτης, περιβαλλοντικής αποτίμησης κύκλου ζωής, εκτίμησης και ποσοτικοποίησης κινδύνου επενδύσεων, κοινωνικής αξιολόγησης και οικονομικής αποτίμησης κύκλου ζωής.

Αρχικά, αξιολογήθηκε η βιώσιμη παραγωγή του PBS από σιρόπι γλυκόζης από καλαμπόκι, σπάδικες καλαμποκιού και πούλπα ζαχαρότευτλου (SBP) μέσω σχεδιασμού της διεργασίας, τεχνο-οικονομικής αξιολόγησης, περιβαλλοντικής και οικονομικής αποτίμησης κύκλου ζωής. Τα αποτελέσματα της αξιολόγησης παραγωγής του PBS συγκρίθηκαν με τα αντίστοιχα του πολυστυρενίου (GPPS), δηλαδή του συμβατικού πλαστικού που δύναται να αντικαταστήσει. Η παραγωγή PBS στο πλαίσιο ανάπτυξης βιοδιυλιστηρίου, χρησιμοποιώντας το SBP ως πρώτη ύλη και λαμβάνοντας υπόψη την ταυτόχρονη ανάκτηση των πηκτινών, μπορεί να οδηγήσει σε ένα ιδιαίτερα ανταγωνιστικό κόστος παραγωγής, επιτυγχάνοντας ελάχιστη τιμή πώλησης $1.37/kg$_{PBS}$ για ετήσια παραγωγή 50,000 t βιοπολυμερούς. Αναφορικά με την περιβαλλοντική αξιολόγηση, οι δείκτες “Δυναμικό Οξίνισης”, “Δυναμικό Ευτροφισμού” και “Δυναμικό Τοξικότητας στον Άνθρωπο” είναι χαμηλότεροι όταν χρησιμοποιείται το SBP ως πρώτη ύλη. Το συνολικό κόστος

που προέκυψε για την παραγωγή PBS από την οικονομική αποτίμηση κύκλου ζωής (\$1.72/kg_{PBS}) είναι μικρότερο από το αντίστοιχο του GPPS (\$2.04/kg), θεωρώντας τιμή πώλησης της πηκτίνης \$4/kg. Η εκτίμηση κινδύνου επενδύσεων μέσω της μεθοδολογίας Monte-Carlo έδειξε ότι το PBS μπορεί να παραχθεί χρησιμοποιώντας το SBP ως πρώτη ύλη και να επιτευχθεί τιμή πώλησης ίση με αυτή του GPPS (\$1.72/kg) με πιθανότητα κερδοφορίας 100%, θεωρώντας τιμή πώλησης της πηκτίνης \$4/kg.

Στη συνέχεια πραγματοποιήθηκε τεχνο-οικονομική και περιβαλλοντική αξιολόγηση της διεργασίας παραγωγής ηλεκτρικού οξέος (SA), χρησιμοποιώντας ένα γενετικά τροποποιημένο στέλεχος της ζύμης *Yarrowia lipolytica* και την καινοτόμο τεχνολογία που βασίζεται στη χρήση ενός ηλεκτροχημικού βιοαντιδραστήρα για ταυτόχρονη παραγωγή και διαχωρισμό του SA. Ως πρώτη ύλη για την παραγωγή SA χρησιμοποιήθηκε το οργανικό κλάσμα των αστικών στερεών αποβλήτων (OFMSW) ως ανανεώσιμη πρώτη ύλη. Η ελάχιστη τιμή πώλησης του SA (MSP_{SA}, \$2.70-3.71/kg) για ετήσια παραγωγή 50,000 t χρησιμοποιώντας τον ηλεκτροχημικό βιοαντιδραστήρα ήταν λίγο μικρότερη από την αντίστοιχη MSP_{SA} που μπορεί να επιτευχθεί με την συμβατική βιοδιεργασία, ανάλογα με το ύψος του τέλους διαχείρισης του OFMSW (\$0-35/t_{OFMSW}). Η εκτίμηση κινδύνου επενδύσεων έδειξε ότι η πιθανότητα κερδοφορίας είναι πάνω από 90% όταν θεωρηθεί τιμή πώλησης SA ίση με την αντίστοιχη σημερινή τιμή (\$2.94/kg) και αντίστοιχα τέλος διαχείρισης του OFMSW \$70/t_{OFMSW}. Η περιβαλλοντική αποτίμηση κύκλου ζωής πραγματοποιήθηκε για την διεργασία παραγωγής SA με τη χρήση ηλεκτροχημικού βιοαντιδραστήρα, θεωρώντας τη χρήση ηλεκτρικής ενέργειας που προέρχεται είτε από το δίκτυο είτε από ανανεώσιμες πηγές ενέργειας (φωτοβολταϊκά), και συγκρίθηκε με τη συμβατική βιοδιεργασία. Η χρήση ανανεώσιμης πηγής ενέργειας όταν εφαρμόζεται η τεχνολογία του ηλεκτροχημικού βιοαντιδραστήρα οδήγησε σε χαμηλότερες τιμές των δεικτών "Δυναμικό θέρμανσης του πλανήτη" (0.81 CO_2-eq/kg_{SA}), "Δυναμικό εξάντλησης των αβιοτικών πόρων" (15.73 CO_2-eq/kg_{SA}), "Δυναμικό Οξίνισης" (0.25 g PO_4-eq/kg_{SA}) και "Δυναμικό Ευτροφισμού" (1.87 g SO_2-eq/kg_{SA}) συγκριτικά με τη συμβατική βιοδιεργασία. Ωστόσο, ο δείκτης "Δυναμικό Τοξικότητας στον Άνθρωπο" (0.29 kg DCB-eq/kg_{SA}) ήταν υψηλότερος λόγω των πρώτων υλών (π.χ. βαρέα μέταλλα) και των βοηθητικών παροχών (π.χ. ηλεκτρική ενέργεια) που χρησιμοποιούνται στην παραγωγή των φωτοβολταϊκών.

Ακολούθως αξιολογήθηκε η βιωσιμότητα ενός βιοδιυλιστηρίου με βάση το OFMSW με σκοπό την ανάκτηση λιπιδίων και πρωτεϊνών και στη συνέχεια τη βιοτεχνολογική παραγωγή SA μέσω ζύμωσης με τη χρήση του βακτηρίου *Actinobacillus succinogenes*. Οι τιμές πώλησης των προϊόντων προστιθέμενης αξίας που παράγονται από το βιοδιυλιστήριο καθώς και το ύψος του τέλους διαχείρισης του OFMSW επηρέασαν ιδιαίτερα το εύρος του MSP_{SA} ($1.13-2.39/kg) για ετήσια παραγωγή 60,000 t_{SA}. Στην περίπτωση του βιοδιυλιστηρίου, όταν χρησιμοποιούνται 1000 kg OFMSW επιτυγχάνεται 35% μείωση των εκμπομπών διοξειδίου του άνθρακα αν συγκριθεί με συμβατικές διεργασίες για την παραγωγή 105 kg φυτικού ελαίου, 87 kg φυτικής πρωτεΐνης και 206.4 kg πετροχημικού ηλεκτρικού οξέος, λαμβάνοντας ταύτοχρονα υπόψη και τις εκπομπές διοξειδίου του άνθρακα που προκύπτουν από χώρους υγειονομικής ταφής του OFMSW.

Αξιολογήθηκαν επίσης τέσσερα βιοδιυλιστήρια τα οποία αξιοποιούν το OFMSW για την ταυτόχρονη παραγωγή βιογενών επιφανειοδραστικών ουσιών και ενός από τα παρακάτω βιογενή προϊόντα, ήτοι γαλακτικό οξύ (LA), ηλεκτρικό οξύ (SA), συγκολλητικές ουσίες (HMAs) ή πολυουρεθάνες (PUDs). Τα LA και SA παρήχθησαν μέσω μικροβιακών ζυμώσεων χρησιμοποίωντας υδρόλυματα πλούσια σε σάκχαρα και θρεπτικά συστατικά μετά την ενζυμική υδρόλυση του OFMSW, ενώ οι βιογενείς επιφανειοδραστικές ουσίες παρήχθησαν από τα λιπίδια και τις πρωτεΐνες που περιέχονται στο υπολείπομενο στερεό του OFMSW μετά την ενζυμική υδρόλυση. Το βιογενές SA αντικατέστησε το πετροχημικό SA και το αδιπικό οξύ στην παραγωγή των PUDs. Η παραγωγή των HMAs και PUDs μπορεί να είναι κερδοφόρα όταν οι βιογενείς επιφανειοδραστικές ουσίες πωλούνται ως προϊον συμπαραγωγής στο προτεινόμενο βιοδιυλιστήριο με τιμή πώλησης $4.1/kg, οδηγώντας σε MSP ίση με $2.92/$kg_{HMAs}$ και $1.95/$kg_{PUDs}$, θεωρώντας τέλη διαχείρισης OFMSW $35/t και ετήσιες παραγωγές SA και LA στις οποίες έχει επιτευχθεί οικονομία κλίμακος. Θεωρώντας τα LA και SA ως τελικά προϊόντα με ταυτόχρονη παραγωγή βιογενών επιφανειοδραστικών ουσιών με τιμή πώλησης $4.1/kg, τα MSP είναι $1.58/$kg_{LA}$ και $2.14/$kg_{SA}$. Κατά την περιβαλλοντική αξιολόγηση εκτιμήθηκαν πέντε διαφορετικοί δείκτες θεωρώντας τη χρήση ηλεκτρικής ενέργειας που προέρχεται είτε από το δίκτυο είτε από ανανεώσιμες πηγές ενέργειας (φωτοβολταϊκά). Τα προτεινόμενα βιοδιυλιστήρια οδήγησαν σε 25-35% εξοικονόμηση των εκμπομπών διοξειδίου του άνθρακα ανά κιλό βασικού προϊόντος (ή 0.95-2.06 kg CO_2-eq/$kg_{dry\ OFMSW}$) κατά τη σύγκριση τους με συμβατικές διεργασίες παραγωγής των τελικών προϊόντων και τους διαφορετικούς τρόπους διαχείρησης του OFMSW (υγειονομική ταφή και κομποστοποίηση).

Τέλος, πραγματοποιήθηκε τεχνο-οικονομική και περιβαλλοντική αξιολόγηση ενός καινοτόμου βιοδιυλιστηρίου, που αξιοποιεί τα τρία παράπλευρα ρεύματα που παράγονται κατά την διεργασία οινοποίησης, για την παραγωγή ηλεκτρικού οξέος με ταυτόχρονη παραγωγή γιγαρτέλαιου, φαινολικού εκχυλίσματος, άλατος τρυγικού οξέος και εκχυλίσματος πηκτινών. Οι τιμές πώλησης των προϊόντων προστιθέμενης αξίας που παράγονταν από το βιοδιυλιστήριο, ανάλογα με τις τελικές εφαρμογές τους, επηρέασαν σημαντικά το εύρος του MSP_{SA} ($1.23-2.76/$kg_{SA}$) για ετήσια

παραγωγή 60,000 t_{SA}. Οι τιμές των δεικτών “Δυναμικό θέρμανσης του πλανήτη” και “Δυναμικό εξάντλησης των αβιοτικών πόρων” κατά την αξιολόγηση της ανάπτυξης του βιοδιυλιστηρίου ήταν 1.47 kg CO_2-eq και 25.2 MJ ανά κιλό ξηρής πρώτης ύλης (OFMSW), αντίστοιχα. Η εκτίμηση κινδύνου επενδύσεων έδειξε ότι το προτεινόμενο βιοδιυλιστήριο μπορεί να είναι κερδοφόρο σε όλα τα διαφορετικά σενάρια που μελετήθηκαν.

Επιστημονική περιοχή: Ανάπτυξη βιώσιμων βιοδιυλιστηρίων

Λέξεις κλειδιά: Παράπλευρα ρεύματα βιομηχανίας, Βιοδιυλιστήριο, Ηλεκτρικό οξύ, Βιοπολυμερή, Σχεδιασμός διεργασιών, Τεχνο-οικονομική αξιολόγηση, Περιβαλλοντική Αποτίμηση Κύκλου Ζωής, Οικονομική Αποτίμηση Κύκλου Ζωής, Εκτίμηση Κινδύνου Επενδύσεων

“Process design, techno-economic and environmental impact assessment of novel biorefineries for the sustainable production of bio-based and biodegradable products”

Με την άδειά μου, η παρούσα εργασία ελέγχθηκε από την Εξεταστική Επιτροπή μέσα από λογισμικό ανίχνευσης λογοκλοπής που διαθέτει το Γ.Π,Α και διασταυρώθηκε η εγκυρότητα και η πρωτοτυπία της.

DISSEMINATION ACTIVITIES

Journal Publications & Book Chapters

1. Ladakis, D., Stylianou, E., **Ioannidou, S.M.**, Koutinas, A., & Pateraki, C. (2022). Biorefinery development, techno-economic evaluation and environmental impact analysis for the conversion of the organic fraction of municipal solid waste into succinic acid and value-added fractions. *Bioresource Technology*, 354, 127172.
2. **Ioannidou, S.M.**, Filippi, K., Kookos, I.K., Koutinas, A., Ladakis, D. (2022). Techno-economic evaluation and life cycle assessment of a biorefinery using winery waste streams for the production of succinic acid and value-added co-products. *Bioresource Technology*, 348, 126295.
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Chapter 1 Introduction

Sustainability has emerged as a global objective in industrial processes and products due to the growing environmental and social concerns as well as the realization that fossil resources are limited. In the industrial sector, reporting the sustainability performance of individual products and processes is anticipated to become standard practice as suggested by international initiatives (Sacramento-Rivero, 2012). Sustainable development can be defined as the movement of fulfilling the needs of current generations without compromising the needs of future generations, while ensuring a balance among economic growth, environmental beingness and social well-being. Sustainability is the intersection of the three pillars, namely economic, environmental and social (Wellisch et al., 2010). To gain an in-depth understanding of sustainability and its implications, Europe introduced the Sustainable Development Goals and the 2030 Agenda. The 2030 Agenda is the successor to the Millennium Development Goals and is structured through the so-called Sustainable Development Goals (SDGs), amounting to a total of 17 goals (D'Adamo et al., 2021).

Biotechnology offers an alternative, innovative and sustainable approach to chemical manufacture that leverages inherent strengths associated with biological processes. Microorganisms have evolved, through white biotechnology, into the microbial platform for bio-based chemical and polymer production through the consumption of various carbon sources, such as carbohydrates, glycerol, carboxylic acids and oils. A single fermentation step can result in the direct synthesis of the desired product, since most or all of the processes needed to transform a raw material into the desired product can take place inside the microbial cell (Burk and Van Dien, 2016). Bioprocesses could be designed towards the reduction of greenhouse gas emissions and the production of lower waste stream quantities that result in lower disposal costs.

Bioprocesses could be integrated in biorefineries using crude renewable resources for the production of numerous marketable products. The term "biorefinery" describes the combination of physical, biological and/or chemical processes leading to the conversion of biomass into fuels, chemicals, polymers, materials, food, feed and value-added products that can be exploited within a commercial context (Koutinas et al., 2014). Biorefineries can be developed in different regions depending on the demand for certain products, the availability of specific or multiple biomass feedstock, the capital investment required and the policies that encourage the shift to a more sustainable bio-economy (Wellisch et al., 2010). The efficient utilization of renewable feedstocks to satisfy both marketable products and energy demands is imperative for the sustainable development of novel biorefineries.

Renewable feedstocks can be classified as first (1G), second (2G) or third (3G) generation. This is an important issue in order to understand how feedstock supply and conversion can affect the overall performance of the biorefinery (Moncada et al., 2016). Industrial and food supply chain side streams (IFSS) are 2G type of feedstocks that could be valorised due to their wide availability in different countries and regions and their composition that offers the potential for biorefineries development. Sugar beet pulp (SBP) is the main solid by-product of the European sugar production industry. An integrated wet SBP-based biorefinery aims at valorizing this by-product stream for sustainable production of many bio-based chemicals and polymers and at the same time eliminate the energy requirements for drying the SBP when it is used as animal feed (ca. 35% of the total energy requirements at the sugar mill according to Mujumdar (2014). Another example of 2G feedstock type is the organic fraction of the municipal solid waste (OFMSW) that corresponds to approximately 30% of the total municipal solid waste. The OFMSW contains mainly food and green waste. It constitutes a cheap and abundant feedstock in which the high carbohydrate content could be relatively easily hydrolysed for biotechnological production of chemicals and polymers, while the extraction of the remaining components (e.g. lipids, proteins etc.) could improve the sustainability performance of an OFMSW-based biorefinery (Ladakis et al., 2022). Another 2G feedstock type is the winery wastes, namely pomace, stalks and wine lees, that contain many value-added fractions, namely lignocellulosics, crude phenolic-rich extract, grape-seed oil, calcium tartrate and crude tannin-rich extract. There are many literature-cited studies which focus on biorefinery development using individual winery waste streams, but the simultaneous utilisation of all major winery waste streams for the production of multiple end-products (Filippi et al., 2022) could be the way to achieve their sustainable valorisation that cannot be achieved by single-step conventional bioprocesses.

The bio-based chemicals market size is projected to reach $141,881.66 million by 2028 with a Compound Annual Growth Rate (CAGR) of 10.1% during the forecast period 2021-2030 (Bio-based Chemicals Market Size, 2021). Bio-based chemicals can be produced from renewable resources, such as agro-industrial residues, forestry residues and aquatic biomass among others. Succinic acid is considered as one of the most important platform chemicals in the circular bioeconomy era with a global production capacity in 2021 in the range of 16,000-30,000 t ($161.3 million) (Global Succinic Acid Market Analysis, 2021). The increasing demand for sustainable chemicals is the primary driver for succinic acid growth in the chemical industry (E4tech et al., 2015). Accordingly, biopolymers can be also derived from renewable resources by producing either the structural monomers via fermentation or through direct polymerisation of the biopolymer by microbial cells during fermentation. Poly(butylene succinate) is a biodegradable aliphatic polyester produced by the polycondensation of succinic acid and 1,4-butanediol. The two monomers can be produced via microbial fermentation followed by their polycondensation into poly(butylene succinate). The global poly(butylene succinate) market production capacity was 86,500 t ($276.51 million) in 2021 and it is expected to expand at a CAGR of 19.7% during the forecast period 2022-2030 (Global Polybutylene Succinate Market Size, 2021). The rise in demand for poly(butylene succinate) from end-use industries such as food packaging, pharmaceutical, agriculture, and consumer goods, among others, is estimated to contribute to further growth of poly(butylene succinate) production.

The implementation of biorefinery concepts depend on process efficiency and sustainability, including techno-economic, environmental and social impact assessment following circular bioeconomy principles. Circularity will be achieved by choosing the optimal combination of End-of-Life recirculation scenarios, such as material or chemical recycling. The development of specific frameworks and indicators that allow for the assessment of process performance and the comparison of various technologies are key aspects for the evaluation of biorefinery sustainability potential. Within this concept, this PhD thesis has focussed on the sustainability assessment of different biorefinery and bioprocessing concepts for the production of major bio-based chemicals, biopolymers and materials.

Chapter 2 State of the art

The production of bio-based chemicals and polymers depends on the utilisation of renewable resources, such as agricultural crops and associated residues, forestry residues, marine biomass resources, industrial side streams and food supply chain side streams. According to Pleissner et al. (2016), around 3.7×10^9 t of agricultural residues and 1.3×10^9 t of food residues occur annually worldwide. Mohammed et al. (2018) mentioned that the USA agriculture can probably support up to 155 million t of residues for producing bioenergy in 2030, without the need for additional land requirement since these residues are derived from major crops. Forestry residues are mainly used for heat and electricity production (Gonçalves et al., 2018) as well as for the production of bio-based products (Frankó et al., 2016). According to the Food and Agriculture Organisation (FAO) food losses refers to "the decrease in edible food mass throughout the part of the supply chain that specifically leads to edible food for human consumption" (Gustavsson et al., 2013). Global estimates of waste production at different stages of the food supply chain, including (i) production, (ii) postharvest, (iii) handling and storage, (iv) processing and packaging, (v) distribution and retail, (vi) consumer losses, are provided in the 2011 FAO report. Approximately 1.3 billion t per year of food losses, corresponding to the one third of global food production (Gustavsson et al., 2013), is lost or wasted. The carbon footprint of these specific losses is estimated at 3.3 billion t of CO_2 equivalent of greenhouses gasses (GHG) released into the atmosphere and a direct economic loss (excluding fish and seafood) of $750 billion annually (Food and Agriculture Organization of the United Nations, 2013). Current Sustainable Development Goals aim for the reduction of global quantities of food waste per capita, in half at the retail and consumer levels and for the reduction of food supply chain waste (including post-harvest losses) by 2030 (UNFAO, 2019). The notion of food waste biorefinery has been gaining prominence in recent years and technologies for the valorisation of food waste has been developed (Cristóbal et al., 2018). These developments are critical in promoting the implementation of EU policies such as the Bioeconomy Strategy and the Circular Economy Plan (Caldeira et al., 2020).

The goal within the biorefinery concept is to start with a biomass feedstock to produce multiple products by a technology-mix in a systematic and technologically feasible way so as to improve techno-economic 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). According to De Jong et al., (2020), biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials and chemicals) and energy (fuels, power, heat).

Many authors use the analogy between a biorefinery and the current oil refineries, which produce multiple fuels and chemicals from petroleum. However, there are two aspects that make oil refineries and biorefineries different. The first is the raw material, because those employed in biorefineries have not undergone the biodegradation of crude oil over millions of years. The second is the complexity that results from the use of different existing and emerging technologies in order to obtain bioproducts integrally and simultaneously. Furthermore, a biorefinery involves assessing and using a wide range of technologies to separate biomass into its principal constituents (carbohydrates, protein, triglycerides, etc.), which can subsequently be transformed into added-value products (Moncada et al., 2016).

As the raw material plays a vital role for biorefinery development, it is important to consider also the feedstock classification. This is an important issue in order to understand how feedstock generation can affect the overall performance of the biorefinery. First generation feedstocks (1G) include edible crops (e.g. edible vegetables oils, cane, rice, wheat). This type poses social, economic and environmental challenges, as their use can raise food prices and put pressure on land use, which makes it unlikely to be completely sustainable. Second generation feedstocks (2G) can address the challenges of 1G feedstocks, as they are non-edible, biodegradable and can grow on marginal land. 2G feedstocks overcome the fuel vs. food dilemma (e.g. wood, wood waste, non-food crops, waste cooking oil, forestry residues, and biomass resources). However, they may compete with feed and in some cases with direct filed fertilization. Third generation feedstocks (3G), are mainly microalgae and have some remarkable advantages such as being cultured at low-cost, high energy, eco-friendly and entirely renewable (Moncada et al., 2016).

Koutinas et al. (2014) presented potential bio-based chemicals and polymers that could be produced via bioprocessing as well as various industrial and food supply chain side streams (IFSS) that could be used as feedstock for biorefinery development. However, it is critical to quantify feedstock availability and consider the geographic distribution of relevant IFSS feedstocks in order to assess the fermentative production of bio-based chemicals and polymers within a biorefinery concept. Moreover, the knowledge of (bio)products properties and applications, processing routes through biorefinery development and novel technologies is also an important aspect for achieving the desired target of sustainability. It is nowadays common knowledge that conventional fermentation processes are less cost-competitive than petrochemical processes. For this reason, biomass refining should be optimized taking also into consideration the assessment of techno-economic, environmental and social impacts in comparison to relevant benchmarks (e.g. relevant petrochemical products). Biorefinery development should also include circular bioeconomy principles involving a suitable combination of End-of-Life (EoL) scenarios (e.g. mechanical, chemical, energy, nutrient recycling) in order to enhance process sustainability.

This chapter presents the geographic distribution and availability of representative IFSS in EU countries, while the most important bio-based chemicals and polymers are discussed. Criteria and indicators for sustainability aspects are, finally, presented as an integrated part for a sustainable biorefinery development.

2.1 Resource efficiency and biorefinery development using industrial and food supply chain side streams

Biorefinery development should be employed for the production of value-added bio-based products from different renewable resources (Moncada et al., 2016), such as agricultural residues, forestry residues, algal biomass and IFSS. The first two residues are characterized as lignocellulosic biomass. The construction of industrial plants in the optimal location is directly associated with crop residue-related parameters (e.g. quantity, accessibility, weather conditions, etc.). Monforti et al. (2013) estimated the potential for bioenergy production from agricultural residues by evaluating the geographic distribution of eight agricultural crops and the possible optimal location of the power plants. The estimated crop residues in EU could support around 850 plants, which are expected to produce annually about 150×10^{10} MJ of bioenergy.

Previous studies have focused on the evaluation of agricultural and forestry residues and algal biomass for the production of biofuels, energy, food, feed and bio-based chemicals and polymers. The following sections present the biorefinery development potential of IFSS in EU-28. The Eurostat has been used in order to estimate the production capacities of representative side streams in EU-28 in 2016 derived from different industrial sectors (e.g. juice processing, breweries, wineries, sugar production from sugar beet, pulp and paper industry) and municipal solid waste. The side streams derived from the industrial processes were estimated from relevant process flow sheets. Representative literature-cited compositions of all IFSS were used in order to calculate the protein, lipids, pectin and carbohydrates that could be separated from these side streams (Table 2.1). The geographic distribution was based on the fermentable sugar content of IFSS considering as the limiting factor the fermentative production capacity of around 50,000 t of a platform chemical where it is expected that economies of scale have been reached. Considering an overall sugar to fermentation product conversion yield of around 0.5 g/g, then a carbohydrate availability of around 100,000 t will be required to enable the development of such a biorefinery.

Table 2.1 Composition (% on a dry basis) of the evaluated IFSS

	Grape Pomace	**Grape stalks**	**Wine lees**	**Brewer's Spent Grains**	**Sugar Beet Pulp**	**Orange peels**	**Apple pomace**	**Spent Coffee Grounds**	**OFMSW**	**Spent liquors [2]**
Moisture (%)	75	50	63[1]	75	7	80	80	65	75	-
Soluble sugars	2.7-12.3	-	-	-	7.1	22.9	10.8 – 15.0	-	0.7–7.4	9.0-20.0
Cellulose	14.5-20.8	25.3-36.3	-	16.8 - 26.0	23.0	22.0	7.2 – 43.6	8.6-13.3	8.5–15.4	-
Hemicellulose	10.3-12.5	13.9-35.3	-	19.2 - 41.9	19.5	11.2	4.3 – 24.4	30.0-40.0	4.2-11.5	-
Lignin	17.2-22.4	17.4-40.6	-	11.9- 27.8	2.6	2.2	15.3 – 23.5	25.0-33.0	5.6-12.1	30.0-45.0
Pectin	5.4-6.2	-	-	-	30.3	25.0	3.5 – 14.3	-	-	-
Starch	-	-	-	-	-	-	-	-	14.2-22.1	-
Phenolics	-	-	2.5	1.0-2.0	1.0	-	-	2.5	-	1.0-2.0 (dry solids)
Tannins	13.8-26.8	6.4-15.9	-	-	-	-	-	-	-	-
Proteins	11.6-18.8	-	10.4	15.3 - 24.7	9.6	6.1	2.9 – 5.7	6.7-13.6	7.0-11.8	-
Fat/Lipids	6.9-13.5	-	1.2	3.0 – 13.0	-	-	1.2 – 3.9	10.0-20.0	1.5-11.5	-
Acetic acid	-	-	-	-	-	-	-	-	-	0.3-0.7
Ash	5.5-9.2	3.9-7.7	5.8	1.1 - 4.6	-	3.7	2.0 – 3.0	-	5.7-25.0	-
Tartrate salts	-	-	20.7	-	-	-	-	-	-	-
Limonene	-	-	-	-	-	3.8	-	-	-	-
References	(Galanakis, 2017)	(Galanakis, 2017)	(Kopsahelis et al., 2018)	(Lynch et al., 2016; Mussatto, 2014)	(Alexandri et al., 2019a)	(Pourbafrani et al., 2010)	(Dhillon et al., 2013)	(Obruca et al., 2015)	(Stylianou et al., 2020)	(Koutinas et al., 2014)

[1] 63% water and 5.7% ethanol content in 100 g wine lees; [2] generic composition of spent liquors produced by the pulp and paper industry

2.1.1 Fruit and vegetable processing

Around 132.96 million t of fruit and vegetables were produced in EU in 2016 according to FAOSTAT. In 2016, juice production in EU was 11.38 million t according to Eurostat data. Based on the AWARENET report (2004), the solid side streams produced from the juice production process of fruit and vegetables represents 30-50% of the initial raw material. Considering an average percentage of 40% and juice production data from Eurostat (11.38 million t), approximately 7.58 million t of solid side streams were produced in 2016 in EU-28 from the juice production industries.

The composition of solid side streams varies depending on the fruit used as raw material. Assuming that 60% of the produced juice comes from oranges (35%) and apples (25%), the potential fermentable sugar availability has been estimated considering their content in soluble sugars (22.9% and 10.8-15.0%), cellulose (22% and 7.2-43.6%) and hemicellulose (11.2% and 4.3-24.4%) as presented in Table 2.1. Fermentable sugars from orange peels and apple pomace at quantities higher than 100,000 t will be available in 2 countries, in particular Germany (ca. 150×10^3 t/year) and Spain (ca. 105×10^3 t/year). Hydrolysates from fruit and vegetables processing have been used for the production of D-lactic acid (de la Torre et al., 2019).

Figure 2.1 presents the potential fermentable sugars and value-added fractions (e.g. D-limonene, pectins) that can be extracted from orange peels within a biorefinery concept. For instance, the fungal strain *Trichoderma reesei* QM6a Δgar1 udh has been used for the production of galactaric (mucic) acid from D-galacturonic acid derived via pectin hydrolysis (Paasikallio et al., 2017).

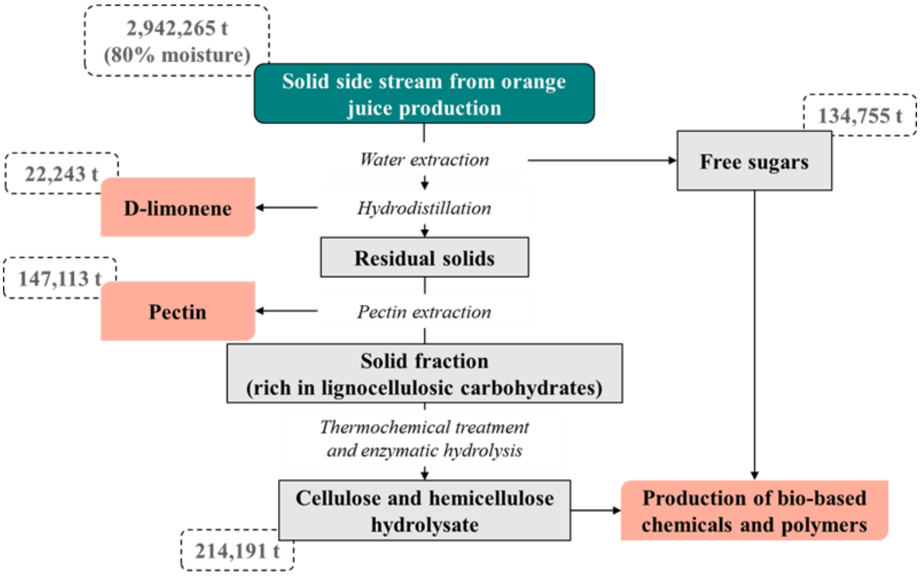


Figure 2.1 Biorefinery development for the extraction of value-added fractions and the production of fermentable sugars from orange peels. The quantities have been estimated using average contents based on the composition range presented in Table 2.1. The total orange peel quantity is presented in wet basis and the components in dry basis.

Similar to juice production, more than 27 million t of processed and preservation products from fruit and vegetables were produced in EU-28 in 2016. According to the AWARENET report (2004), the percentage of the solid side streams produced from preservation processes ranges from 5% to 30% depending on the fruit or vegetable that is used as raw material. Thus, around 5.73 million t of solid side streams were produced in 2016 in EU-28 from fruit & vegetables preservation processes.

2.1.2 Breweries

Around 39.9 million t of beer were produced in EU-28 in 2016 with Germany (8.68 million t) and UK (5.15 million t) being the main producers (Eurostat, 2016). Brewer's spent grain (BSG) and spent yeast are the main by-products derived from breweries. BSG corresponds to around 30% (w/w) of the starting material and accounts to 85% of the total by-product generation in breweries (Tang et al., 2009). Approximately, 270 kg of solid wastes are produced from the production of 1 cubic meter of beer. The overall BSG generated by breweries in EU-28 in 2016 was around 10.8 million t. BSG has a high polysaccharide content (cellulose and hemicellulose content 36.0-67.9%, db, Table 2.1) and a significant protein content (15.3-24.7%, db, Table 2.1). BSG is currently mainly used as animal feed (Lynch et al., 2016). Mussatto et al. (2013) has developed a biorefinery concept using BSG for the production of xylitol, lactic acid, activated carbon and phenolic acids. Initially, the hemicellulose fraction is hydrolyzed, while the cellulose and lignin fractions are treated via soda pulping. The black liquor derived from lignin processing is processed in a phenolic acid and activated carbon plant. Chemical pre-treatment and enzymatic hydrolysis of BSG has been employed for the production of a hydrolysate that was subsequently used in fermentations carried out by *Lactobacillus delbrueckii* for the production of 35.5 g/L lactic acid with a productivity of 0.59 g/L/h (Mussatto et al., 2008).

Figure 2.2 presents the potential fermentable sugars and other value-added fractions (e.g. lipids, phenolics, protein isolate) that could be derived from BSG in EU-28 countries. The geographic distribution of BSG could be regarded as poor, considering platform chemical production via fermentation, because BSG is only available in four EU-28 countries at quantities higher than 100,000 t per annum, including Germany (ca. 327×10^3 t/year) and UK (ca. 194×10^3 t/year) as the predominant ones (Figure 2.3).

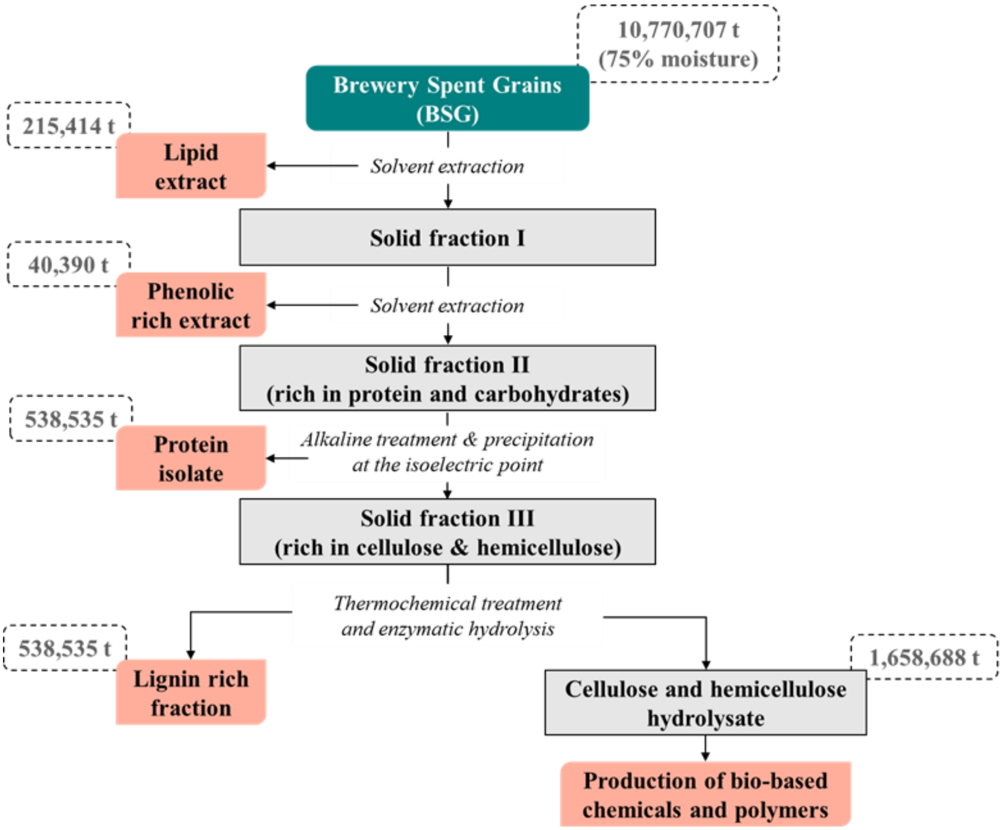


Figure 2.2 Biorefinery development for the extraction of value-added fractions and the production of fermentable sugars from BSG. The quantities have been estimated using average contents based on the composition range presented in Table 2.1. The total BSG quantity is presented in wet basis and the components in dry basis.

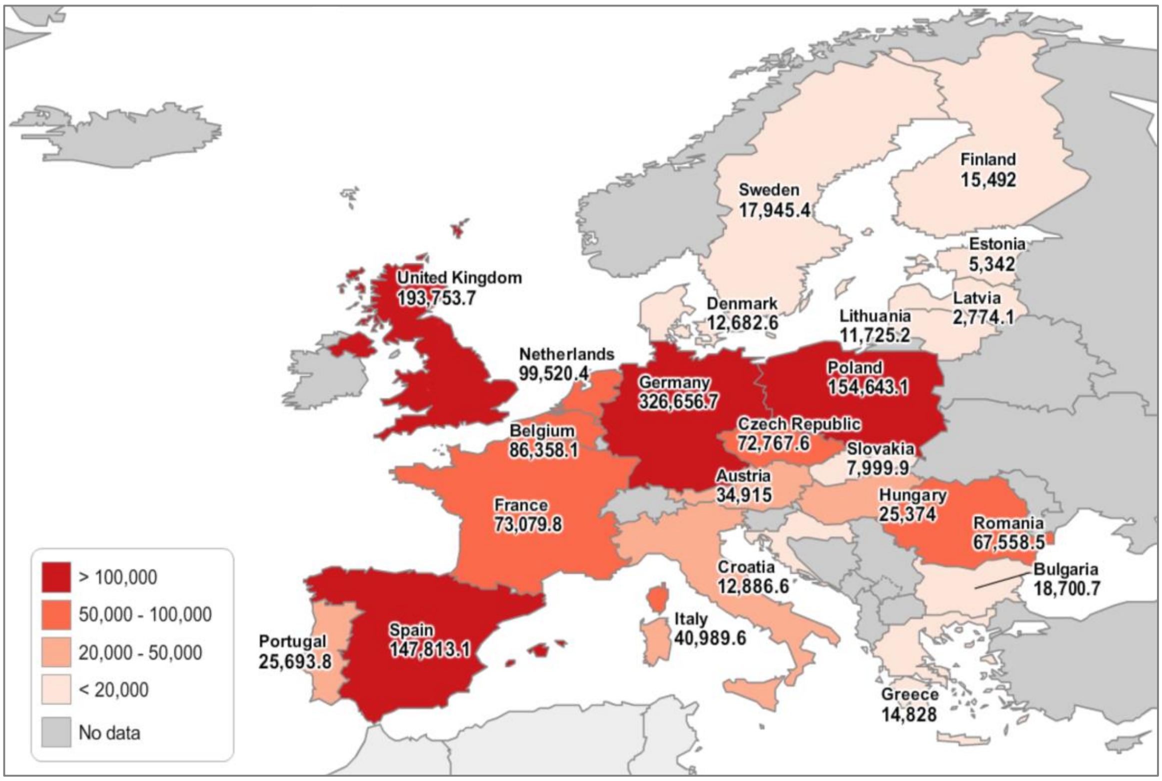


Figure 2.3 Geographic distribution in EU-28 in 2016 of potential fermentable sugar availability derived from BSG

2.1.3 Wineries

Wine production in EU was estimated at more than 16.16 million t of red and white wine in 2016. The main producers are Spain (4.22 million t), Italy (3.78 million t) and France (3.47 million t) producing more than 75% of the wine in EU-28 (Eurostat, 2019a). The main side streams from wine making processes are wine lees, grape pomace, grape seeds and stalks. According to the AWARENET report (2004), the total solid side streams of wine production processes (red or white) are 20-30% of incoming grapes. Based on the data for wine production and by taking into consideration the average side stream generation (25%), 5.4 million t of side streams were produced in 2016 in EU-28 from both red wine and white wine making processes. More than 4 million t of side streams are available in Spain, Italy and France.

Winery side streams may provide around 659×10^3 t of fermentable sugars per year, based on the average content of the composition range presented in Table 2.1 (Figure 2.4). Winery waste refining may also lead to the production of various value-added fractions (Figure 2.4). Grape pomace contains residual sugars that can be extracted and used as carbon source for fermentative production of bio-based chemicals and polymers. Furthermore, grape seed oil could be also extracted as a value-added co-product. The remaining solids from grape pomace and grape stalks could be thermochemically and enzymatically treated to produce a hydrolysate rich in fermentable sugars. Wine lees represent 2-6% of wine production and they are rich in phenolic compounds, residual ethanol and tartrate salts that could be extracted as co-products (Dimou et al., 2016). The remaining fraction of wine lees is rich in yeast biomass and could be converted into a nutrient-rich hydrolysate. The sugar-rich and the nutrient-rich hydrolysates constitute a fermentation feedstock for the production of various bio-based chemicals and polymers.

The geographic distribution of winery waste could be regarded as poor, considering platform chemical production via fermentation, because winery waste is only available in three EU-28 countries at quantities higher than 100,000 t per annum, including Spain (ca. 184×10^3 t/year), Italy (ca. 164×10^3 t/year) and France (ca. 151×10^3 t/year) (Figure 2.5).

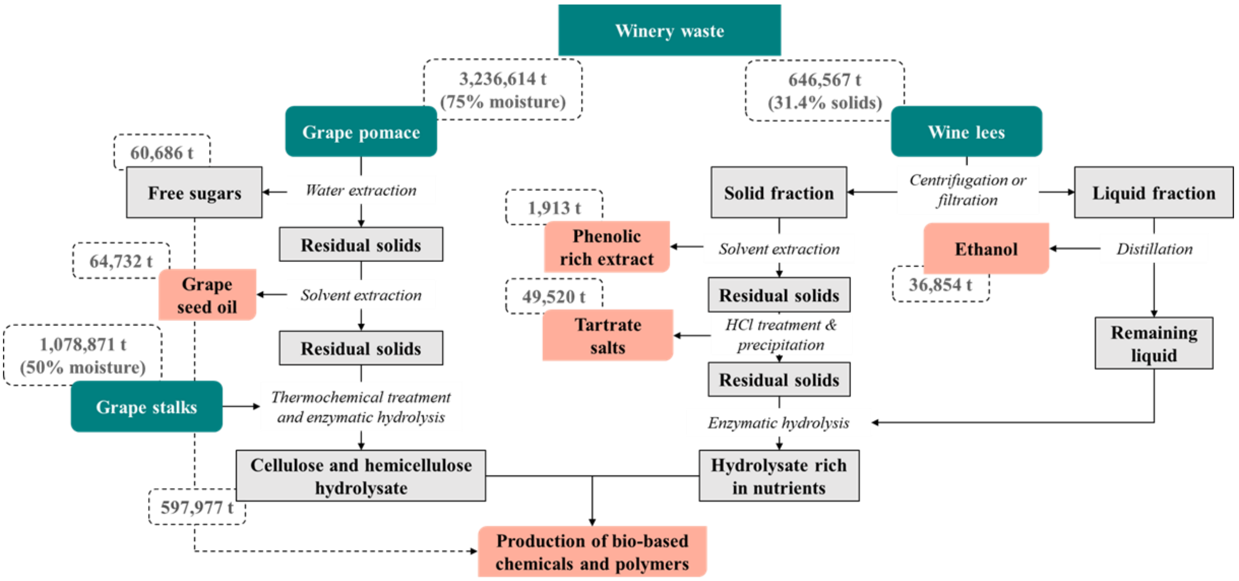


Figure 2.4 Biorefinery development for the extraction of value-added fractions and the production of fermentable sugars from grape pomace, stalks and wine lees. The quantities have been estimated using average contents based on the composition range presented in Table 2.1. The winery waste quantities are presented in wet basis and the components in dry basis.

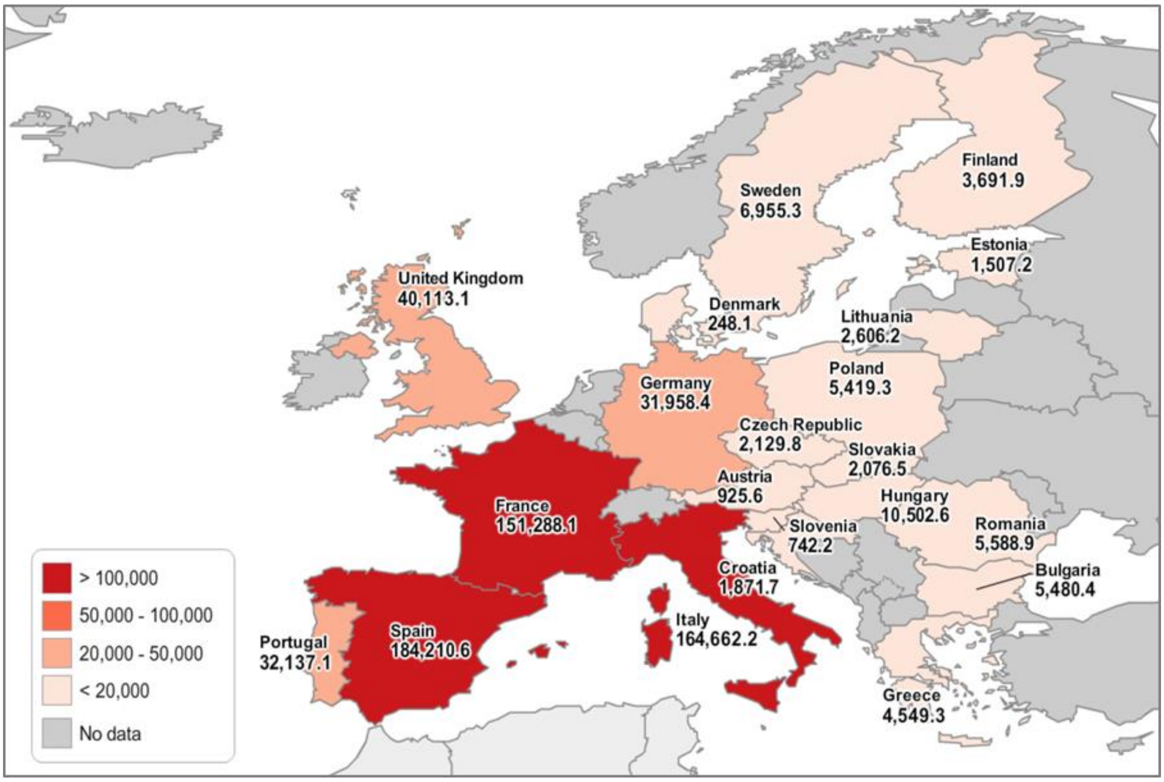


Figure 2.5 Geographic distribution in EU-28 in 2016 of potential fermentable sugar availability derived from winery waste

2.1.4 Sugar beet processing

Sugar beet pulp (SBP) is the main solid by-product of the European sugar production industry. According to FAOSTAT, the total amount of SBP that was generated in 2016 in EU-28 is ca. 10.35 million t/y. The fermentable sugars that can potentially be produced from this stream in EU-28 is 5.2 million t/y, if we take into consideration the composition of the SBP (7.1% free sugars, cellulose and hemicellulose 42.5%, db, Table 2.1).

SBP is mainly used as animal feed. The fermentable sugar availability derived from SBP is higher than 100,000 t in seven EU-28 countries, including France (ca. 1,035×10^3 t/year), Germany (ca. 810×10^3 t/year), Poland (ca. 405×10^3 t/year) and UK (ca. 170×10^3 t/year) as the major producing countries (Figure 2.6). Figure 2.7 presents the potential fermentable sugars and value-added fractions that could be derived from SBP in EU-28 based on the process developed by Alexandri et al. (2019). Alexandri et al. (2019) presented a biorefinery concept for the separation of a phenolic rich extract and pectin followed by chemical and enzymatic hydrolysis of the carbohydrates for the production of bio-based chemicals and polymers. SBP has been also used in the production of fermentation products such as bioethanol and succinic acid (Alexandri et al., 2019a; Zheng et al., 2013).

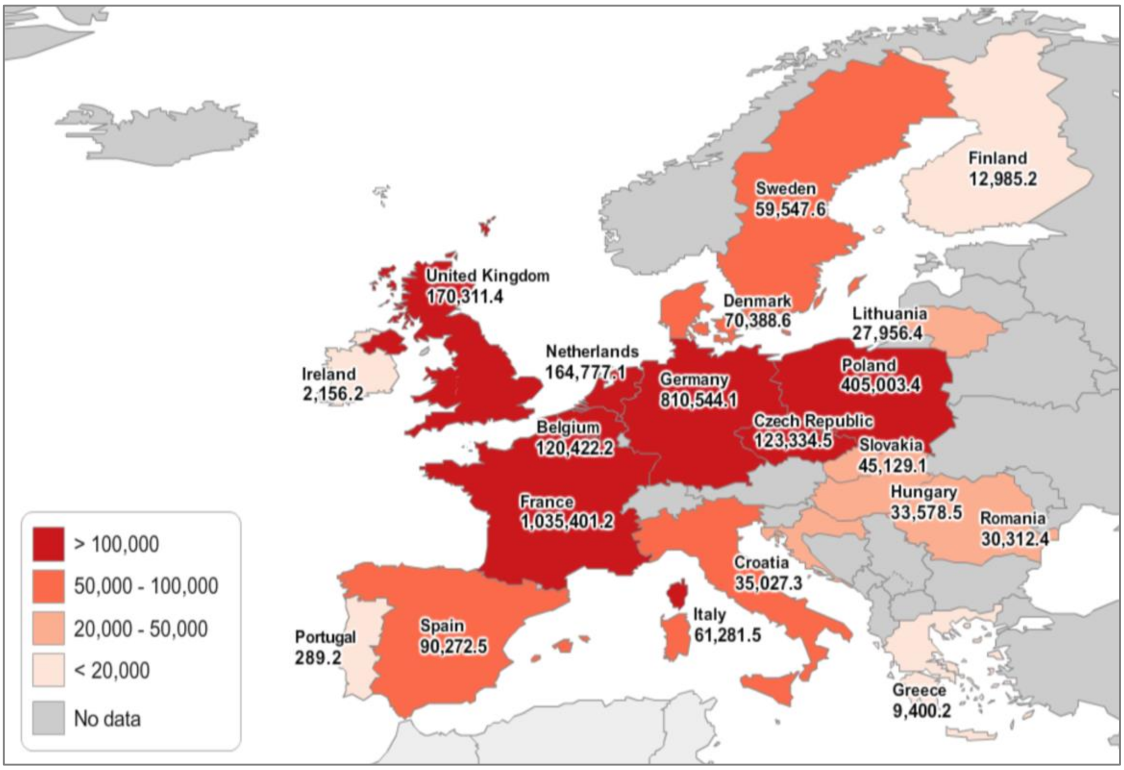


Figure 2.6 Geographic distribution in EU-28 in 2016 of potential fermentable sugar availability derived from SBP

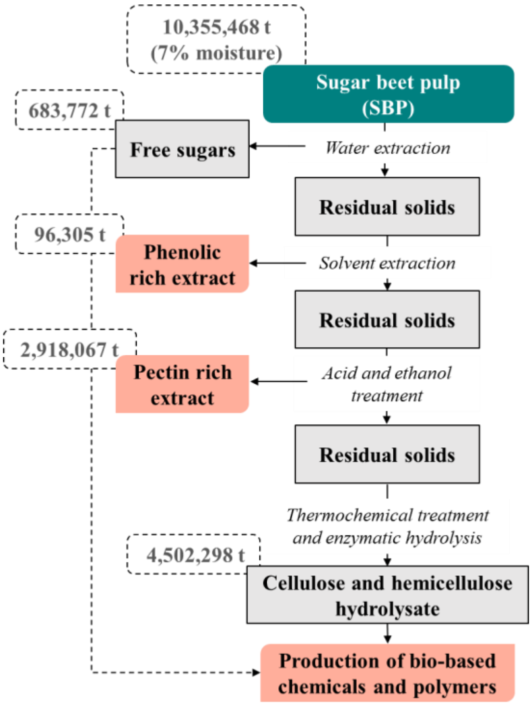


Figure 2.7 Biorefinery development for the extraction of value-added fractions and the production of fermentable sugars from SBP. The quantities have been estimated using average contents based on the composition range presented in Table 2.1. The total SBP quantity is presented in wet basis and the components in dry basis.

2.1.5 Spent coffee grounds

Wet processing of coffee cherries involves the removal of husks, peel and pulp followed by roasting, while the coffee extract represents around 5-10 % of the cherry mass and 45-50 % of the cherry mass is finally disposed as spent coffee ground (SCG) (Campos-Vega et al., 2015). Roasted coffee contains 27.5 % of water-soluble compounds and 72.5 % of water insoluble compounds (Van Dam and Harmsen, 2010). Thus, around 725 kg of SCG are generated from 1 t of coffee. The SCG production in EU-28 is calculated based on the coffee consumption per country and the water insoluble compounds of coffee.

In 2016, more than 1.8 million t of SCG were generated from the consumption of 2.5 million t coffee in EU-28. Germany (387×10^3 t/y), Italy (248×10^3 t/y) and France (244×10^3 t/y) produced more than 48 % of the total SCG produced in EU-28. SCG has poor geographic distribution regarding platform chemical production via fermentation as only three counties, including Germany (ca. 188×10^3 t/y), Italy (ca. 120×10^3 t/y) and France (118×10^3 t/y), are able to provide more than 100,000 t of fermentable sugars per annum. SCG has been considered as feedstock for the production of chlorogenic acid, bioethanol, polyhydroxyalkanoates and carotenoids (Burniol-Figols et al., 2016; Obruca et al., 2015; Petrik et al., 2014).

2.6. Crude glycerol

Crude glycerol is the main by-product of the biodiesel industry that contains 77-90% glycerol, 5.3-14.2% water, up to 1.7% methanol and either 4.2-5.5% NaCl or 0.8–6.6% K_2SO_4 based on the catalyst used (Koutinas et al., 2014). According to EU Biofuels Annual Report (2019), the biodiesel production accounts for 9.8 million t. Around 1 kg of glycerol is produced per 10 kg biodiesel (Quispe et al., 2013), thus around 0.98 million t per year of glycerol are available in EU-28. Crude glycerol has been evaluated as feedstock for the production of various bio-based chemicals and polymers (e.g. succinic acid, poly(3-hydroxybutyrate), microbial oil, butanol, 1,3-propanediol) via fermentation (Casali et al., 2012; Krasňan et al., 2018; Salakkam and Webb, 2018a; Vlysidis et al., 2011; Xu et al., 2012).

2.1.6 Spent liquor from the pulp and paper industry

The thick liquor generated from the pulp and paper industry accounts for approximately 26.4 million t per year in EU-28. For the production of 1 t of pulp with sulphite pulping process, 8-9 m^3 liquid wastes are generated, while the sulphate pulping process generates 7 t of liquid wastes. The generic composition of spent liquors is presented in Table 2.1. Both liquors have 10-20 % solid content and they are processed through multiple evaporation steps to increase their solid content to 60-75%. Spent liquors from the pulp and paper industry are rich in C5 and C6 sugars. The thick liquor contains around 90-200 g/L sugar monomers (Koutinas et al., 2014). It is estimated that the fermentable sugars derived from the spent liquors will be higher than 100,000 t in 8 countries, especially in Sweden (ca. 897×10^3 t/y), Finland (ca. 815×10^3 t/y) and Portugal (ca. 303×10^3 t/y).

Spent liquors from the pulp and paper industry have been evaluated for the production of bioethanol, antioxidant-rich extract, lignosulphonates and succinic acid (Alexandri et al., 2016; Pateraki et al., 2016; Sebastião et al., 2016). Ladakis et al. (2018) has evaluated spent sulphite liquor for the development of continuous cultures for succinic acid production using *Actinobacillus succinogenes* and *Basfia succiniciproducens*.

2.1.7 Organic fraction of municipal solid wastes

The organic fraction of the municipal solid waste (OFMSW) has been estimated considering around 30% content in the MSW. The fermentable sugars in OFMSW have been estimated considering 75% moisture content and 45.8% fermentable sugar content in OFMSW (Table 2.1) based on Stylianou et al. (2020). Thus, the OFMSW is estimated at around 74.4 million t in 2016 in EU-28

(Eurostat, 2019a). This amount corresponds to 8.5 million t of potential fermentable sugars. This is the highest fermentable sugar content that can be generated among all the IFSS. OFMSW has high geographic distribution regarding platform chemical production via fermentation as 16 countries, including Germany (ca. 1,786×10^3 t/y), France (ca. 1,192×10^3 t/y), UK (ca. 1,084×10^3 t/y) and Italy (ca. 1,035×10^3 t/y), will be able to provide more than 100,000 t of fermentable sugars per year (Figure 2.8). Even if half of the estimated quantities are considered as raw material for biogas and compost production, the remaining quantities are still sufficient for the development of many industrial biorefinery plants for bio-based chemical production via fermentation. Figure 2.9 presents a potential biorefinery concept that focuses on the valorization of the OFMSW for the production of ethanol, lactic acid and/or succinic acid from the sugar-rich hydrolysate of OFMSW, while the fermentation products and the remaining OFMSW fractions (e.g. protein, lipids/fats) are subsequently used for the production of various end-products (e.g. poly(lactic acid), ethyl lactate, biosurfactants, polyester polyols and polyurethanes).

OFMSW hydrolysates have been used for the production of succinic acid and lactic acid (Babaei et al., 2019; López-Gómez et al., 2019). Individual food supply chain side streams collected at source could be also used for the production of bio-based chemicals and polymers, such as succinic acid production from waste bread (Leung et al., 2012).

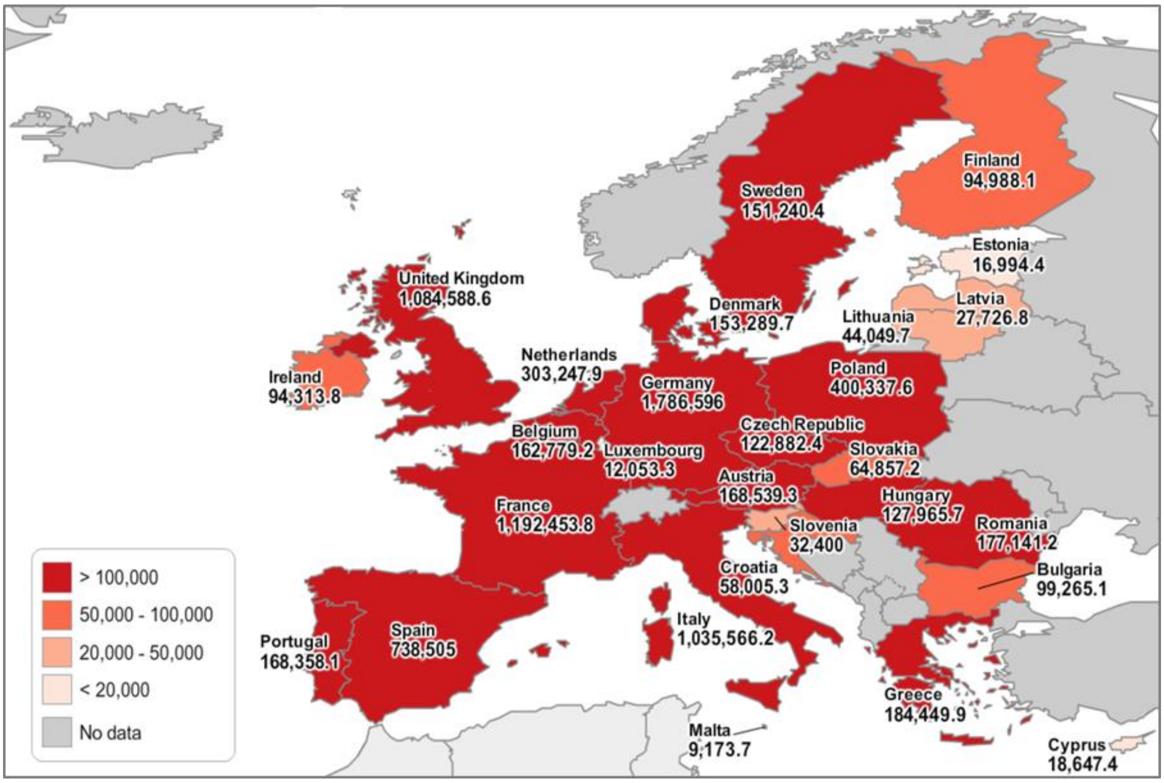


Figure 2.8 Geographic distribution in EU-28 in 2016 of potential fermentable sugar availability derived from OFMSW

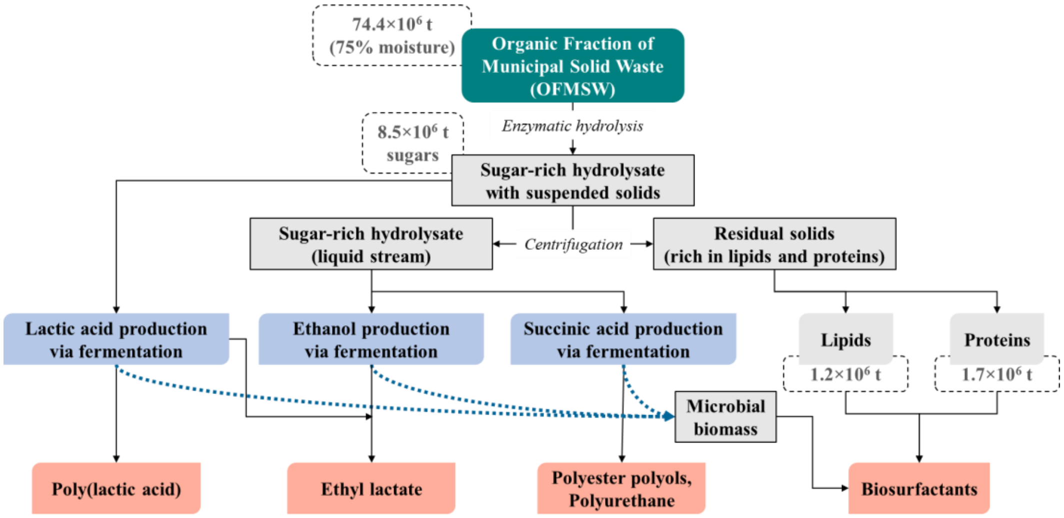


Figure 2.9 Biorefinery development for the production of bio-based products from OFMSW. The quantities have been estimated using average contents based on the composition range presented in Table 2.1. The total OFMSW quantity is presented in wet basis and the components in dry basis.

2.2 Bio-based chemicals and polymers

The global issue of climate change and the desire to reduce greenhouse gas emissions, an overdependence of many countries on fossil fuel imports and the expectation that fossil resources (e.g. oil, gas etc.) extraction will reach a peak in the not-too-distant future are all driving forces for the transition to a bio-based economy (De Jong et al., 2020). According to the USDA, bio-based products are commercial or industrial products, other than food and feed, which consist, in whole or in significant part, of biological products, including renewable domestic agricultural materials, renewable chemicals, and forestry materials. Their production can provide an alternative to conventional petroleum derived products and include a diverse range of final goods such as lubricants, detergents, inks, fertilizers, and bioplastics (USDA, 2021). The final targets should have high economic and environmental performance, good recyclability and biodegradable properties, where applicable, to underpin transition towards more sustainable manufacturing.

There is a wide array of potential combinations of feedstock, pretreatment options, sugars, conversion technologies and downstream processes that can be followed as potential pathways to produce bio-based biochemicals and polymers and develop bio-based value chains. After the screening of the possible feedstocks (section 2.1) to be valorised for bioconversion, some of the most important bio-based chemicals and polymers are discussed in the following subsections, based on their level of industry activity (De Jong et al., 2020; E4tech et al., 2015), potential market growth and sustainability performance. Lactic acid, succinic acid, 1-4 butanediol, poly(lactic acid), poly(3-hydroxybutyrate) and poly(butylene succinate) are among the 10 case studies developed and assessed by the European Commission (E4tech et al., 2015), while biosurfactants have been selected due to their potential chemical production from biowaste and their rapid market growth.

2.2.1 Lactic acid and poly(lactic acid)

Lactic acid (LA) is an important, naturally occurring, organic acid. It is white and water soluble in its solid form, and colourless in its liquid form. It is an alpha-hydroxyl acid that has both a hydroxyl and a carboxyl group, making it suitable for a wide range of uses. LA has two optical isomeric forms, L−(+)−LA (or (S)−LA) and D−(−)−LA (or (R)−LA), with the most common form being L−lactic acid. It is naturally produced from pyruvate in the metabolism of microorganisms. LA can be produced either by fermentation or by chemical synthesis, while approximately 90% of industrial lactic acid production is derived via fermentation. One of the highest LA concentrations reported in the literature is 182.3 g/L (Ou et al., 2011), while the yield and productivity that could be achieved during LA fermentation are up to 0.97 g/g and 4.37 g/(L h) (Qin et al., 2009).

Worldwide production capacity of LA in 2019 was more than 600,000 t. Its market size exceeded $1.25 billion in 2019 and it is estimated to grow at over 11.5% CAGR from 2020 to 2026 (Global Market Insights, 2021). Some of its main applications are related to the food and beverage industries as a preservative and pH adjusting agent. Moreover, it can be utilized as solvent and starting material in the manufacture of lactate ester in the pharmaceutical and chemical industries. Because of its moisturizing, pH-regulating, and skin-lightening qualities, lactic acid is frequently utilized as a standard or active component in personal care products (De Jong et al., 2020). Other applications include tanning and textile finishing operations as well as pharmaceuticals. Lactic acid is generally recognized as safe (GRAS) by the U.S. Food and Drug Administration (FDA) (Biddy et al., 2016). The Dutch company Corbion is the world leader in lactic acid production and is actively exploiting their technology base through its joint-venture Total-Corbion. The company recently announced the opening of their 75,000 t/year plant in Thailand (Renewable Carbon News, 2019).

The expected high LA growth rates are due to its application in bio-based polymers manufacturing. LA polymerisation results in the bio-based polymer poly(lactic acid) (PLA). PLA is a thermoplastic that is classified under the family of aliphatic polyesters. PLA is mainly derived from renewable resources, particularly sucrose and starch. Based on the stereochemistry of the polymer backbone, PLA can be semicrystalline or amorphous. Due to its relatively low price and availability, PLA is considered to be one of the most important bio-based polyesters for packaging and medical applications as well as mulching films and garbage bags. PLA could be also used as fiber that may be utilized in garments, carpets and industrial applications. Moreover, it can be considered as the main component for hot melt adhesives (HMAs) production. Although HMAs compositions have historically been based on petroleum-derived polymers, HMAs based on PLA are claimed to have excellent hot tack strength along with long open time and moderate setting time. It can be used as a high performance sealant for heat sealing packaging (up to 80°C) (Viljanmaa et al., 2002). PLA annual worldwide production capacity is 394,500 t, while European demand is now 25,000 t/year (De Jong et al., 2020). According to Byun and Kim (2013), PLA has similar properties to biaxial oriented polypropylene (BOPP) and oriented polyethylene, while its price is the lowest of all biobased polymers ($1.91-2.64/kg) (Naser et al., 2021; Plastic Insight, 2018).

The global leader in PLA production is NatureWorks based in Blair Nebraska, USA. NatureWorks polymer products span multiple industries and categories, including rigid and flexible packaging solutions, food service ware, health and personal care, durable products in home, appliance, electronic categories and 3D printing filament. Other companies active in PLA include Galactic, Henan Jindan and BBCA in China.

2.2.2 Succinic acid

Succinic acid (SA) is a naturally occurring C4-dicarboxylic acid, solid at room temperature and soluble in water, alcohol, acetone and ether (Pateraki et al., 2016). Due to its physical and chemical properties, SA has a broad range of applications, from high-value niche applications such as personal care products, pharmaceuticals and food additives (used in the food and beverage industry as an acidity regulator and flavouring agent), to large volume applications such as bio-polymers (for example PBS and polyester polyols), plasticizers, polyurethanes, resins and coatings (Ioannidou et al., 2020; Patel et al., 2011), or precursor for establishing a sustainable chemical industry and produce many important chemicals such as adipic acid, N-methyl pyrrolidinone, 1,4-butanediol, tetrahydrofuran and γ-butyrolactone among others (Pateraki et al., 2016). Common industrial routes of its fossil synthesis include partial hydrogenation of maleic acid and carbonylation of ethylene glycol. 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). The physical properties of bio-based succinic acid 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. The highest concentration of succinic acid (105.8 g/L) with a yield and productivity of 0.82 g/g and 1.36 g/(L·h), respectively, was achieved by (Guettler et al., 1996) in anaerobic batch fermentation.

SA has been considered as one of the most important platform chemicals in the circular bioeconomy era and listed by the US Department of Energy among the top ten chemical building blocks that could be produced from renewable resources (Chandel and Segato, 2021). Its global production capacity in 2021 was 16,000-30,000 t ($161.3 million) with the major manufacturing companies being BASF, Myriant and Corbion among others, and it is projected to reach $226.29 million by 2026 at a CAGR of 7% (Global Market Estimates, 2021). Despite the high commercial prospects of industrial SA production and the significant investments that started around 2009, the commercialization of SA did not meet the expectations mainly due to the limited use of this intermediate into final products (Bettenhausen, 2021). The higher market price of bio-based succinic acid ($2.9/kg) as compared to the combined bio- and fossil-based succinic acid ($2.5/kg) (Stylianou et al., 2021), is one of the issues that impedes bio-based succinic acid market growth.

Minimizing manufacturing costs is crucial for bio-based SA to compete with petro-based SA production. The cost of downstream separation and purification (DSP) of SA accounts for around 60% of the total production costs. The main DSP processes for industrial SA recovery are crystallization (Reverdia), Mg-based process (BASF and Corbion), precipitation (Myriant) and electrodialysis (used in the past by BioAmber) (Jansen and van Gulik, 2014). SA production can be achieved either by bacterial cultures at neutral pH or by yeast cultures at low pH during fermentation where the acidification step is no longer required. Although the conventional industrial DSP technologies offer many advantages, including few unit operations, low technological barriers and mature commercialization level, the high energy and chemical requirements increase the succinic acid production cost. The evaluation of five different DSP to identify the most promising separation and purification process from crude fermentation broths was examined by Alexandri et al. (2019b). Calcium precipitation method, reactive extraction, salting-out method and direct crystallisation using acidification or cation-exchange resins have been investigated in fermentation broths derived from SSL-based medium. The highest succinic acid yield recovery of 79% resulted from applying direct crystallisation using cation-exchange membrane. In comparison, the highest succinic acid purity (97.2%) was achieved by reactive extraction using back-extraction with pH-swing (Alexandri et al., 2019b). Novel DSP technologies should be developed to minimise utility and chemical requirements and integrate fermentative SA production (preferably at low pH) with SA extraction and purification.

Membrane electrolysis is an electrochemical extraction technique demonstrated for carboxylate recovery. During ion exchange membrane electrolysis, ions are transported, across ion-exchange membranes from one solution to another, under the influence of an electrical potential. When an electric current is applied, water splitting electrolysis protons (H^+) are formed at the anode compartment of the electrochemical cell, while simultaneously hydroxide ions (OH^-) are formed at the cathode compartment (Andersen et al., 2014; Kocks et al., 2019). By applying a constant current between the cathode and the anode chambers (e^- from the anode to the cathode), an equal flux of anions must be transferred through the anion exchange membrane (AEM) (Desloover et al., 2012).

A key benefit of using membrane electrolysis to extract carboxylic acids, such as succinic acid, from fermentation broths is pH balancing. The in situ production of OH^- positively affects the bioreactor operating conditions by reducing the automatic application of a base for pH control (Xu et al., 2015). Additionally, another advantage of the membrane electrolysis system is that the fermentation products (and by-products) do not accumulate in the fermentation broth as they transept in an acidified (by protons generated in the anode) extract free of cells. For this reason it prevents the toxicity to microorganisms due to their high accumulation on the broth (Andersen et al., 2015; Gildemyn et al., 2015). Integrated electrochemical membrane bioreactor was demonstrated for succinic acid production and in situ extraction of succinate by Pateraki et al. (2019). The bacterial strain *Basfia succiniciproducens* was cultivated on ultrafiltrated SSL as a carbon source resulting in a 45% increase in overall succinic acid production while yield and productivity were improved by 15% and 32%, respectively. The amount of NaOH was reduced by 19.3% relative to the respective control fermentation without applying the electrochemical cell (Pateraki et al., 2019a).

2.2.3 1,4-Butanediol

1,4-Butanediol (1,4-BDO) is a colourless viscous compound and one of the four stable isomers of butanediol. At room temperature this compound is a colourless, water miscible and viscous liquid. It has industrial applications as solvent, it is used in the manufacture for some types of plastics, elastic fibers and polyurethanes and its global market approaches two million t 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 1,4-BDO in a fermentation process. Using a microbial strain for the production of a metabolic products, a thorough knowledge of its metabolism and then its genetic engineering is required for the efficient production of this product. The bacterial strain *Escherichia coli* is the most common microorganism that can be engineered for direct production of biobased BDO at high levels from various sugars. Two artificial routes for 1,4-BDO biosynthesis converge at the common intermediate 4-hydroxybutyrate (4-HB). Given that, the production of 1,4-BDO is divided into two pathways: upstream enzymes for the production of 4-HB and downstream enzymes for the conversion of 4-HB into 1,4-BDO (Barton et al., 2015; Yim et al., 2011). After the fermentation stage, a suitable downstream separation and purification (DSP) process is also important to be developed, so as to provide bio-based BDO at a purity that meets industry specifications and performance requirements.

Regarding the industrial production of biobased 1,4-BDO, a California-based company, Genomatica, has developed a patented process, which uses an engineered microbe for 1,4-BDO production directly via fermentation of sugars (Patel et al., 2011). Based on this technology, a number of companies have developed direct fermentations from dextrose. BASF and Novamont are typical examples that headquarter in Europe, with Novamont to operate a 30,000 t/year 1,4-BDO plant (De Jong et al., 2020; E4tech et al., 2015). This market share only comprises a tiny fraction of the total 1,4-BDO market, which was an estimated 2,160 kt in 2021 (Mordor Intelligence, 2021). The market price for fossil-based BDO in 2013 ranged at $1.8-3.2/kg (E4tech et al., 2015).

2.2.4 Biosurfactants

Surfactants are a class of amphiphilic chemical substances that have both hydrophobic and hydrophilic domains. They are an essential part of practically every sector of modern industry. Their importance is demonstrated by the huge quantities utilized and the wide range of industries they are used to, including food and beverage, agriculture, public health, healthcare/medicine, textiles and bioremediation. Since the majority of surfactants used today for industrial applications are synthesized via organo-chemical synthesis using petrochemicals as precursors, there has been a significant push in recent decades toward the discovery of surfactants from biological/natural sources, namely biosurfactants. This is an issue not just because surfactants come from non-renewable resources but also because of their potential toxicological consequences on people and other species as well as the environment (Nikolova and Gutierrez, 2021).

The surfactants market is expected to reach $52.4 billion by 2025 from $42.1 billion in 2020, with home care products (e.g. detergents, cleaners) leading the market (Markets and Markets, 2020). The biosurfactants market is expected to reach $6.04 billion by 2029 from $4.18 billion in 2022 with household cleaners dominating the market (46.8% of the total) (Fortune Business Insights, 2021). The production of surfactants from amino acids and vegetable oils is well-known (Infante et al., 2004). High surface activity can be achieved from amphiphilic structures produced from polar amino acids/peptides (hydrophilic moiety) and non-polar long-chain compounds (hydrophobic moiety). The surfactant type (e.g. cationic, anionic, non-ionic, amphoteric) and properties (e.g. adsorption, aggregation, biological activity) is dependent on the amino acid or peptide moieties. During the Horizon2020 project PERCAL, attempts were made to produce biosurfactants from OFMSW-derived lipids and proteins for non-food applications (e.g. detergents) as substitute for petroleum-derived surfactants, such as linear alkylbenzene sulphonates, that dominate the market.

2.2.5 Poly(3-hydroxybutyrate)

Polyhydroxyalkanoates (PHAs) are a class of linear polyester that is naturally formed by direct bacterial fermentation of sugars or lipids. They are produced by bacteria to store carbon and energy, typically under physiological stress. These polymers are biodegradable and can be thermoplastic or elastomeric. Within this family, more than 150 distinct monomers can be coupled to produce compounds with vastly varied characteristics. PHAs are increasingly being employed in blending, to improve the impact resistance of PLA, for example.

PHAs were originally developed in the 1990s. Poly(3-hydroxybutyrate) (PHB) constitutes the most well-studied member of the PHAs family using renewable resources, such as biodiesel industry by-products, cereal mash, dairy industry wastewater, waste date seed oil and acid pretreated rice straw (García-Torreiro et al., 2016; Peña-Jurado et al., 2019; Salakkam and Webb, 2018b; Sindhu et al., 2013; Yousuf and Winterburn, 2017). The different types of raw materials and microorganisms that produce PHB result in a final concentration that varies from 30 g/L up to 160 g/L with productivities from 0.5 g/(L·h) up to 2.8 g/(L·h), depending on raw materials used, microorganism and operating conditions (Cavalheiro et al., 2009; Choi and Lee, 1997; Kahar et al., 2005; Koutinas et al., 2014; Kulpreecha et al., 2009; Silva et al., 2004). PHBs are biodegradable, biocompatible, and renewable and their production aims at replacing some non-renewable, petroleum-derived polymers (Koutinas et al., 2014). Biodegradable plastics are considered to be an alternative to solve environmental and social problems generated by the plastics industry from petrochemicals. PHB is similar in its material properties to polypropylene (PP), has a good resistance to moisture and aroma barrier properties. However, the cost of PHB production is mainly affected by downstream processing and therefore, the development of PHB extraction methods is required to make the overall process much simpler and cheaper.

PHB market was valued at $87.3 million in 2020 and is expected to reach at $221.14 million by 2027 at a CAGR of 14.2% over forecast period 2021-2027 (Maximize Market Rresearch, 2020). Main players operating in the global PHB market are BASF SE, Biomer, TianAnBiologic Materials

Co., Ltd., PHB Industrial S.A., BIO-ON, and TEPHA INC (Transparecy Market Research, 2021). PHB has various useful characteristics which make it an ideal candidate for different applications such as agriculture, food, and medicine. Some of them are excellent barrier properties, optical activity, and piezoelectricity. It is a partially crystalline material with high degree of crystallinity and high melting temperature. PHB is used in medical and packaging industries. It is employed as surgical implant in surgery and microcapsule in therapy. It is also used in tablet packaging, fishnets, bottles, fibers, and laminated foils. The PHB market can be divided into food & beverages, agriculture, pharmaceutical, and others. Food & beverages is the leading segment of the PHB market. Demand for biodegradable packaging films has been rising in the food & beverage industry due to its non-toxicity and properties akin to the petrochemical counterparts.

2.2.6 Poly(butylene succinate)

Poly(butylene succinate) (PBS) is a biodegradable aliphatic polyester produced by the polycondensation of SA and 1,4-BDO. 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 produced 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, 1998). 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 SA and 1,4-BDO. Given that, PBS will be an attractive biodegradable polymer that is completely produced from renewable resources (Puchalski et al., 2018).

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. 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 additives can be used to modify the PBS properties. Compared with standard petro-based plastics, PBS has similar properties to polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) (Moussa et al., 2012).

The global PBS market was valued at $276.51 million in 2021 and it is expected to expand at a

CAGR of 19.7% from 2022 to 2030 (Global Polybutylene Succinate Market Size, 2021). Its annual worldwide production capacity is 86,500 t (European Bioplastics, 2019) having various potential applications. 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 mulching films. A special feature of PBS is its blendability with other plastics, including both bio-based and conventional polymers. Even the creation of wood plastic composites is possible because of its properties. When blending PBS with PLA, its processability and mechanical properties improve. 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.

2.3 Sustainability assessment for the production of bio-based chemicals and polymers

Biorefinery development including the production of bio-based chemicals and polymers from crude renewable resources should lead to sustainable processes and products. In the circular bioeconomy era, sustainability assessment should be employed in order to assess the potential industrial implementation of a biorefinery scenario. The conventional linear production and consumption model relies on continuous growth and increasing resource throughput, while the circular production model will enhance resource efficiency towards minimization of waste disposal and improved balance considering economic, environmental and social aspects (Ghisellini et al., 2016). Circularity will be achieved by choosing the optimal combination of end-of-life (EoL) scenarios. Gargalo et al. (2016) proposed a specific framework for techno-economic and environmental sustainability analysis that can be divided into six steps: problem definition, data collection and management, deterministic techno-economic and environmental analysis, sensitivity analysis, risk quantification and finally risk assessment and decision making. This approach aids in evaluating the alternative processing options leading to the identification of the most sustainable process.

During a sustainable biorefinery development, the three pillars of sustainability should be satisfied. While this approach could be easily accepted and applied in principle, there are many challenges to be surpassed in practice, with the most important to be the measurement of the “level” of sustainability among its different aspects. The need to quantify, simplify and communicate scientific information has led to the development of specific criteria and indicators which give the opportunity to explain the performance of a process and enable the comparison among alternative technologies considering environmental, economic and social aspects (Singh et al., 2009). According to Azapagic and Perdan (2000), the standardized indicators allow for the identification of more sustainable options by offering the possibility to compare the performance of similar products produced via different processes and benchmark the performances within specific ranges, based on common standards and regulations. Life cycle thinking should be embedded in the attempt and the indicators should be expressed on the function that the system delivers. For instance, in the case of bioenergy systems, Buchholz et al. (2009a) evaluated 35 sustainability criteria considering relevance, practicality, reliability, and importance attributes with environmental criteria rated as more important and relevant (greenhouse gas balance and energy balance received the highest ratings on all four attributes), economic criteria perceived as more reliable and practical, and social criteria always rated the lowest.

In this section, the most common indicators used in biomass, biofuel, bio-based chemicals, biopolymer and bioenergy production are presented.

2.3.1 Techno-economic pillar criteria and indicators

This pillar includes the assessment of process profitability and the effect of external environmental costs. The estimation of process profitability will start with process design including the development of the process flow sheet and the estimation of material and energy balances. Plant capacity and feedstock requirements are important attributes in this assessment. The main costs that should be determined are the total capital investment (TCI) required to construct the plant and the cost of manufacture (COM) estimated during plant operation. Dheskali et al. (2020a) presented a simple and robust mathematical model for the estimation of fixed capital investment and utilities consumption of industrial bioprocesses. The total capital investment, also known as Capital Expenditure (CAPEX), is the sum of the Fixed Capital Investment (FCI) and the working capital. The COM, also known as Annual Expenditure (OPEX), is calculated on an annual basis and based on the methodology proposed by Turton et al. (2018).

Profitability assessment of one or alternative processing options is carried out via discounted cash flow analysis considering the FCI, the COM, the plant construction period, the interest rate, the income tax rate, the depreciation method, the plant life, and the construction start-up duration. Finally, sensitivity analysis (e.g. Monte-Carlo simulations) could be carried out for the assessment of variability of process parameters. The most common literature-cited techno-economic indicators assessing process profitability reported are presented in Table 2.2.

Table 2.2 presents literature-cited indicator values from different processes for the production of bio-based chemicals and polymers. In many cases, the values of indicators are quite variable due to varying plant production capacities and the different production processes employed.

Table 2.2 Techno-economic indicators representing process profitability

Indicators	**Units**	**Succinic acid**	**1,4-BDO**	**2,3-BDO**	**Lactic acid**	**Microbial oil**	**PLA**
Cost of manufacture	$\$/kg_{product}$	0.88 – 2.32	-	2.70 – 3.26	1.07	4.24	3.56
Fixed capital investment	$\$/kg_{product}$	2.88 – 16.75	-	1.29 – 3.36	3.87	2.73	10.97
Net present value	million $	99.00	-	-	234.80	-	202.10
Minimum selling price	$\$/kg_{product}$	0.99 – 2.26	1.82	1.56 – 5.10	0.56 – 5.00	0.72 – 5.8	3.33
Payback period	years	-	-	-	5.10	-	6.60
Gross profit	$\$/kg_{product}$	-	-	-	1.06	-	2.26
Net profit	$\$/kg_{product}$	-	-	-	0.89	-	1.89
Reference		(Efe et al., 2013; Ghayur et al., 2019; Klein et al., 2017)	(Satam et al., 2019)	(Koutinas et al., 2016; Maina et al., 2019)	(de Oliveira et al., 2018; Kwan et al., 2018)	(Bonatsos et al., 2020)	(Kwan et al., 2018)

Bonatsos et al. (2020) reported the techno-economic and environmental assessment of microbial oil production showing also the dependence between the raw material used and the results of the impact assessment. De Oliveira et al. (2018) reported the MSP for lactic acid production considering various substrates and downstream separation and purification processes.

External economic aspects associated with the manufacturing stage are an important factor that affects the economic feasibility of a process and should be considered along with the techno-economic costs. The term “environmental prices” addresses the welfare expenditure that is associated to the release of 1 kg of any pollutant to the environment (De Bruyn et al., 2018). Consequently, it is necessary to consider the cost of externalities and estimate the “true price” of a product or technology, as in a circular bio-economy context, the production of bio-based chemicals and polymers should be compared with their fossil counterparts. Externalities include effects on the environment, such as climate change and water pollution, and on people, such as health and safety accidents and child labour (Galgani et al., 2020).

Energy and transportation sectors are those with the most developed methodology for the estimation of externalities. The ExternE methodology (Bickel and Friedrich, 2005) provides a framework for transforming impacts that are expressed in different units into a common unit, such as monetary values. The external costs are described considering two parameters: an economic parameter representing the accounting price per unit of impact and a physical parameter representing the unit of the impact. Other similar models observed most frequently in literature are: the Tellus model (Tellus packaging study), the EPS 2000 model (Environmental priority strategies) and the ECON model (Jantzen and Pešic, 2004).

The monetization of the estimated impacts is carried out by employing average values of environmental prices considering monetary values for emissions of different pollutants, environmental implications (e.g. climate change) and impacts of environmental pollution (e.g. damage to human health) (De Bruyn et al., 2018; Gargalo et al., 2016). Pizzol et al. (2015) reviewed different monetary evaluation methods and their relevance in LCA indicators. There are still many challenges that limit the diffusion of monetization approaches, whereas the choice of the method and the budget constraint method are the best options for monetary evaluation in LCA.

Economic viability should be also assessed considering macro-economic sustainability using relevant indicators such as total value added in the economy, trade balances, foreign investments, changes in overall productivity, business opportunities, long-term profitability, energy diversity, product durability and research and development efforts (Azapagic and Perdan, 2000; Buchholz et al., 2009b; Gargalo et al., 2016; Khishtandar et al., 2017; Sadamichi et al., 2012).

2.3.2 Environmental pillar criteria and indicators

Life Cycle Assessment is used to assess the environmental impacts which are related to the production of a product. The assessment takes into consideration the entire or part of the product life cycle including raw materials, processing, transportation, use, maintenance and the EoL management after the product use phase (Biron, 2016). The general framework of the LCA is specified in ISO 14040. This framework is separated into four phases, the definition of goal and scope, the inventory analysis, the impact assessment and the interpretation of results. The goal and scope phase defines the temporal, geographic and systemic boundaries, impact categories and related indicators (e.g. GHG emissions, energy demand, land-use, waste-factor), the product's functional unit, assumptions, cut-off criteria and uncertainties from uncontainable factors of the system. The life cycle inventory phase focuses on the collection of data exploiting mass and energy balances along the entire life cycle of the product. Data quality is evaluated during the inventory analysis (Singh et al., 2018). The inventory data collected are employed in the impact assessment phase for the evaluation of environmental impacts (Singh et al., 2018). The relative contribution of each type of emission to impact categories is evaluated. Interpretation is the last LCA phase in which the life cycle inventory and impact assessment are combined in order to reach conclusions and recommendations.

The environmental impact categories commonly used in LCA studies (Nessi et al., 2018; Weiss et al., 2012) are related to non-renewable (or fossil fuel) energy use, climate change, acidification, eutrophication and ozone depletion and formation. The metrics of each environmental impact category refer to the quantitative values based on specific and representative equivalents for each of them. Global warming potential expresses the impact of each greenhouse gas on global warming using carbon dioxide (kg CO_2-eq per functional unit) as the refence gas complying with the guidelines of the Intergovernmental Panel on Climate Change (Durkee, 2006). The non-renewable (or fossil fuel) energy use, expressed as MJ of non-renewable energy use per functional unit, is the impact category which is related to the depletion of non-renewable resources (Azapagic et al., 2003). The acidification potential, expressed as SO_2 equivalents per functional unit, describes the negative impact of acidifying pollutants (e.g. SO_2, NOx) on soil, ecosystems, ground and surface water, surface water and materials (Biron, 2016). The eutrophication potential, expressed as PO_4^- equivalents per functional unit, describes excessive nutrient input into soil and water via fertilization, effluent disposal and combustion processes (Azapagic et al., 2003; Nixon, 1995; Smith, 2003). The human toxicity potential, expressed as 1,4-dichlorobenzene equivalents per functional unit, describes the factors that cause toxicological impacts to humans (Azapagic et al., 2003). The Particulate Matter Formation impact category describes the harmful effect on human health caused by emissions of particulate matter and its precursors (e.g. NOx, SOx, NH_3) (Nessi et al., 2018).

Nessi et al. (2018) presented impact categories, indicators and related impact assessment methodologies that should be applied in an LCA study. Table 2.3 presents representative indicators and values that have been estimated from various bioprocesses for the production of bio-based chemicals and polymers using various renewable raw materials. Global warming potential and fossil energy consumption are the most frequently used indicators. The wide variation of the global warming potential values occurs due to the production process and the feedstock employed. For instance, the downstream separation and purification method for succinic acid followed by González-García et al. (2018) requires large amounts of solvents and electricity, a fact that increases the total environmental impact on both global warming potential and fossil energy consumption categories.

Table 2.3 Environmental indicators

Indicators	Units	Succinic acid	1,4-BDO	Lactic acid	Microbial oil	PLA	PHB
Global warming potential	$kg_{CO2\text{-}eq.}$/ $kg_{product}$	-0.20 – 5.30	1.60 – 3.00	-0.60 – 1.20	2.9 – 11.6	0.30 – 3.20	-2.58 – 3.95
Acidification potential	$kg_{SO2\text{-}eq.}$/ $kg_{product}$	0.73	0.01	-	0.004 – 0.043	$7.0\ 10^{-3}$ – $3.8\ 10^{-2}$	0.022 – 0.028
Eutrophication potential	$kg_{PO4,eq.}$/ $kg_{product}$	0.17	-	-	0.005 – 0.045	$1.8\ 10^{-4}$ – $7.5\ 10^{-3}$	-
Fresh water/ aquatic eutrophication potential	$kg_{P\text{-}eq.}$/ $kg_{product}$	-	9.1×10^{-5}	-	-	0.80 – 1.40	$2.8\ 10^{-3}$ – $11\ 10^{-3}$
Marine eutrophication	$kg_{N\text{-}eq.}$/ $kg_{product}$	-	4.0×10^{-4}	-	-	-	-
Fossil fuel energy use	MJ./ $kg_{product}$	6.89 – 227.00	41.50	9.00 – 120.00	-	21.40 – 45.30	-28.39 – 75.97
Particulate Matter Formation	$kg_{PM10\text{-}eq.}$/ $kg_{product}$	-	2.2×10^{-3}	-	-	-	-
Ozone depletion potential	$kg_{CFC\text{-}11\ eq.}$/$kg_{product}$	13.60	2.1×10^{-7}	-	-	4.0×10^{-10} – 3.6×10^{-7}	-
Human toxicity potential	$kg_{1,4\text{-}DB\ eq./}$ /$kg_{product}$	-	-	-	-	8.5×10^{-3}	-
Photochemical oxidant formation	$kg_{NMVOC.}$/ $kg_{product}$	-	3.5×10^{-3}	-	-	-	-
References		(Cok et al., 2014; De Matos et al., 2015; Dunn et al., 2015; González-García et al., 2018; Moussa et al., 2012)	(Dunn et al., 2015; Forte et al., 2016)	(De Matos et al., 2015; Morales et al., 2015)	(Bonatsos et al., 2020)	(Broeren et al., 2017; De Matos et al., 2015)	(Kookos et al., 2019)

Besides individual bioprocesses, the environmental impact of waste refining or management has also been assessed. Joglekar et al. (2019) evaluated the environmental performance of a citrus waste biorefinery including hydrolysis, filtration, fermentation and distillation for the production of ethanol, while the solids remaining after filtration are employed for methane production via anaerobic digestion. Global warming potential is 0.4 kg CO_2-eq per kg of citrus waste, the acidification potential is 3.4 g SO_2-eq per kg of citrus waste and the eutrophication potential is 0.2 g PO_4^{3-}-eq per kg of citrus waste. Slorach et al. (2019) compare four different management practices for the treatment of food wastes. Anaerobic digestion indicated the lowest environmental impacts per t of waste in most of the categories considered in the study, having also a net-negative global warming potential.

2.3.3 Social pillar criteria and indicators

Socioeconomic indicators focus on the evaluation of human well-being as related to industrial operation in a specific region. Health and safety, job creation and satisfaction and social justice issues are some of the social aspects assessed by such indicators. There is a wide variation in the social indicators and their units identified in literature-cited studies (Kooduvalli et al., 2019). Social indicators quantify social impacts (midpoint and endpoint: describing the points of impact along the pathway of a system) that can affect people's working conditions locally, and to show impacts on a larger community level (Jørgensen et al., 2008). Along similar lines, Dreyer et al. (2006) has presented a framework for social assessment that deals with the entire life cycle of a product with emphasis given on the stages where the company has the largest influence, the materials and product manufacturing stages.

Dale and Beyeler (2001) presented a literature review presenting the key criteria for the selection of social indicators. The selected indicators should be easily, timely and cost-effectively measured. Moreover, the method of implementation and the final responses of the indicators should be unambiguous. The set of the selected indicators should be sufficient when considered collectively in order to reach a representative outcome. Indicators meeting these criteria should allow users to set targets and select the most sustainable processes Dale et al. (2013). Table 2.4 presents the most common categories evaluated in social assessment and the most representative indicators in each category.

Table 2.4 Social categories with associated indicators and units for biobased product manufacturing

Category	**Indicator**	**Reference**
Human rights/ Equality	Income inequalities Gender equity	(Blok et al., 2013; Dale et al., 2013; Ekener-Petersen et al., 2014; Fontes et al., 2018; Kooduvalli et al., 2019; Sureau et al., 2018; van Haaster et al., 2017)
Human health	Occupational Health Environmental Human Health	
Autonomy	Child Labor Forced Labor	
Safety, security and tranquility	Total employment Work days lost due to injury	
Social acceptability	Public opinion Transparency Stakeholder participation	

Chapter 3 Objectives

Environmental and social concerns and competitiveness for resources leads to the development of novel and sustainable technologies using renewable resources shifting the current production strategy from linear to circular processes. The goal of such systems thinking is to “close the loop” by becoming resource efficient through development and establishment of industrial symbiosis (Lokesh et al., 2018). Material cascading, which may be virgin raw materials, by-products or wastes resulting from any given sector, as well as development of sustainable biorefineries could be the approach to develop a resource and energy efficient, green and low-carbon economy.

Under this framework, this PhD thesis has focused on the assessment of the sustainability potential of novel biorefineries for the production of bio-based products. Succinic acid and poly(butylene succinate) (PBS) were selected as the target products while IFSS and OFMSW were employed as feedstocks for biorefinery development. Process design, TEA and LCA have been used for sustainability evaluation of all proposed biorefineries, while profitability risk assessment, LCC and social assessment methodologies have been implemented in case-specific studies.

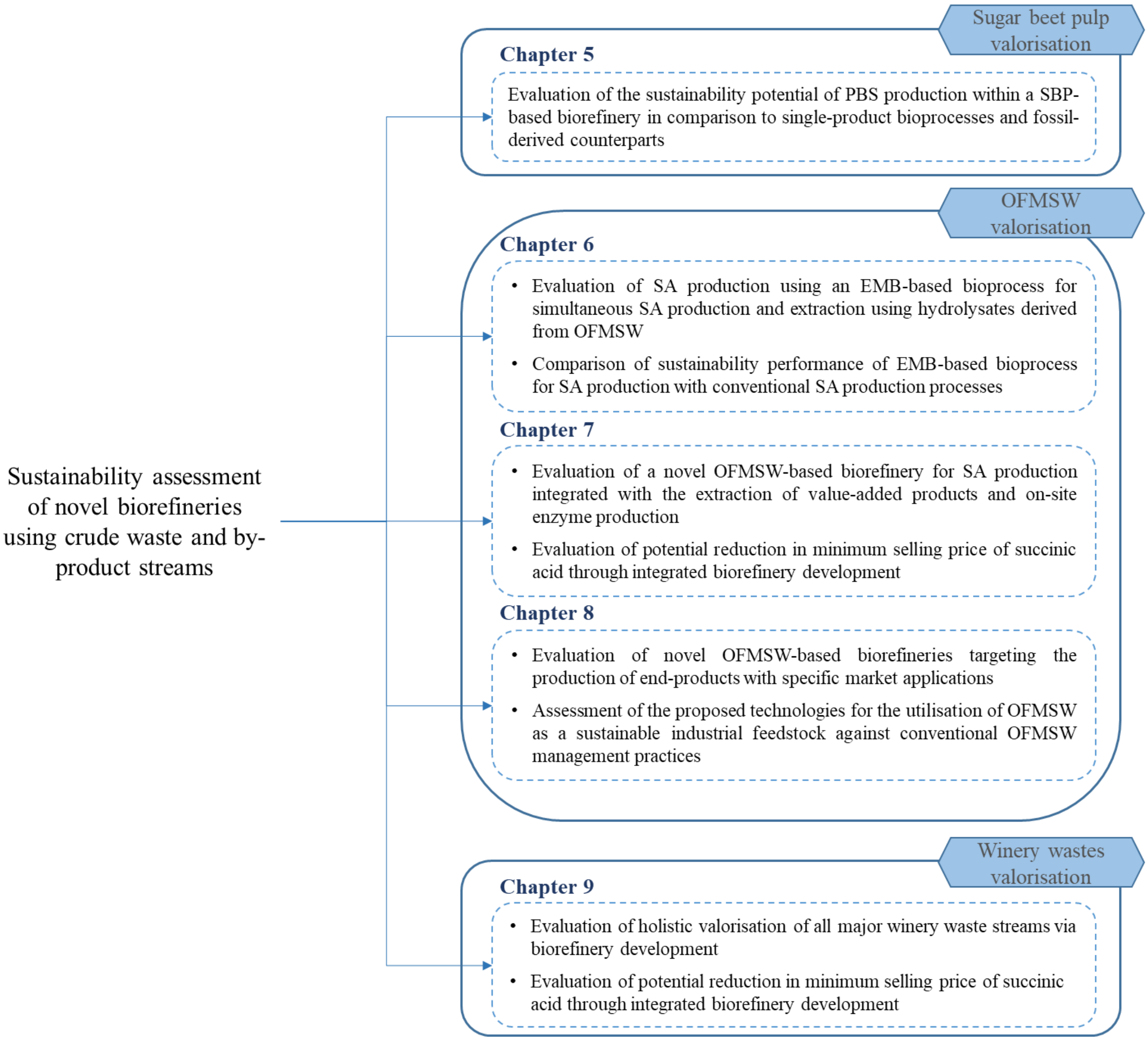
The PhD thesis is organized into three sections. In the first section (Chapter 5), TEA, LCA and LCC have been carried out to assess the sustainability of PBS production from three different renewable resources. Corn-derived glucose syrup, corn stover and SBP were evaluated as promising feedstocks for PBS production, while the study was divided into five stages, namely process design, TEA using process design data, LCA, LCC and comparison to fossil counterpart, and techno-economic risk assessment to assess process profitability.

In the second section (Chapter 6-8), OFMSW is valorised for biotechnological production of succinic acid. Initially, the sustainability assessment of succinic acid production using an integrated electrochemical membrane bioreactor (EMB) has been performed for simultaneous succinic acid production and *in situ* separation (Chapter 6). Process design, TEA, profitability risk assessment and LCA have been carried out to show the sustainability potential of the novel EMB-based bioprocess. Chapter 7 presents the sustainability assessment of an OFMSW-based biorefinery integrating the extraction of oils and proteins as well as on-site enzyme production via solid state fermentation for the hydrolysis of OFMSW polysaccharides. Process design, TEA and estimation of two environmental indicators have been carried out to show the sustainability potential of the proposed biorefinery, focusing also on the cost-competitiveness of succinic acid production. Finally, sustainability assessment of four biorefinery concepts using OFMSW for the production of one of the following end-products, namely lactic acid, succinic acid, HMAs and PUDs, combined with the simultaneous production of biosurfactants has been presented in Chapter 8. This chapter assesses the proposed technologies for the utilisation of OFMSW as industrial feedstock in the bioeconomy era as a sustainable alternative to conventional OFMSW management practices.

In the third section, Chapter 9 presents TEA, LCA and profitability risk assessment of a novel biorefinery using winery wastes for the production of bio-based succinic acid and value-added co-products, namely crude phenolic-rich extract, grape seed oil, calcium tartrate and crude tannin-rich extract. The holistic valorisation of all major winery waste streams and the potential reduction in succinic acid production cost through integrated biorefinery development are evaluated.

Figure 3.1 presents the objectives of this PhD thesis. The main objectives of this PhD thesis are:

- Sustainability assessment of novel biorefineries using crude waste and by-product streams
- Evaluation of the sustainability potential of PBS production within a SBP-based biorefinery in comparison to single-product bioprocesses and fossil-derived counterparts
- Evaluation of SA production using an EMB-based bioprocess for simultaneous SA production and extraction using hydrolysates derived from OFMSW
- Comparison of sustainability performance of EMB-based bioprocess for SA production with conventional SA production processes
- Evaluation of a novel OFMSW-based biorefinery for SA production integrated with the extraction of value-added products and on-site enzyme production
- Evaluation of novel OFMSW-based biorefineries targeting the production of end-products with specific market applications
- Assessment of the proposed technologies for the utilisation of OFMSW as a sustainable industrial feedstock against conventional OFMSW management practices
- Evaluation of holistic valorisation of all major winery waste streams via biorefinery development
- Evaluation of potential reduction in minimum selling price of succinic acid through integrated biorefinery development



Chapter 5

Evaluation of the sustainability potential of PBS production within a SBP-based biorefinery in comparison to single-product bioprocesses and fossil-derived counterparts

Chapter 6

- Evaluation of SA production using an EMB-based bioprocess for simultaneous SA production and extraction using hydrolysates derived from OFMSW
- Comparison of sustainability performance of EMB-based bioprocess for SA production with conventional SA production processes

Chapter 7

- Evaluation of a novel OFMSW-based biorefinery for SA production integrated with the extraction of value-added products and on-site enzyme production
- Evaluation of potential reduction in minimum selling price of succinic acid through integrated biorefinery development

Chapter 8

- Evaluation of novel OFMSW-based biorefineries targeting the production of end-products with specific market applications
- Assessment of the proposed technologies for the utilisation of OFMSW as a sustainable industrial feedstock against conventional OFMSW management practices

Chapter 9

- Evaluation of holistic valorisation of all major winery waste streams via biorefinery development
- Evaluation of potential reduction in minimum selling price of succinic acid through integrated biorefinery development

Figure 3.1 Objectives of the PhD thesis

Chapter 4 Materials and Methods

4.1 Introduction

During sustainability assessment of a biorefinery, process profitability, efficiency, environmental and social performance are evaluated. After the individual assessments, the external costs and benefits of the process under study (environmental and social) are estimated and factored into the economic performance of the biorefinery. All these calculations are performed under a specific time frame perspective. Sustainable biorefineries should be based on process improvement, evaluation of alternative renewable feedstocks, efficient processing, effective exploitation of unavoidable organic wastes and by-product streams and recirculation of used bio-based products from the EoL alternative stages into the manufacturing stage in line with the principles of circular bioeconomy. This approach will minimize the environmental burden caused by their current management practices and facilitate the transition to the bio-economy era.

In this chapter, the methodologies that were implemented for the sustainability assessment of the developed biorefineries are analysed. Initially, the construction of a process flow diagram is described. Afterwards, the adopted methodologies for techno-economic evaluation, life cycle assessment, life cycle costing, social assessment and profitability risk assessment are analysed, providing the basic principles and theories about each methodology.

4.2 Development of a Process Flow Diagram and Process Design

There are various design factors that should be taken into account during process design. The effort to include all these considerations in the overall design project should be quite intense, otherwise the whole performance of a biorefinery could be significantly affected, rendering the investment unprofitable. Some of the decisions that require particular attention in the development of a biorefinery are plant location, plant layout, plant operation and control, utility requirements, structural design, storage and buildings, materials handling, patent considerations as well as aspects related to environmental protection, safety and health needs of plant personnel and the public. According to Peters et al. (2003), the development of a process design involves twelve different steps (Table 4.1). However simple or complex the chemical or biochemical design is, the engineer should possess a wide variety of skills including, among others, research, market analyses, computer simulation, software programming, equipment design, cost estimation, profitability analysis and technical communications.

Table 4.1 Typical design steps for chemical and biochemical processes (Peters et al., 2003)

Number	Step
1	Recognize a societal or engineering need a. Make a market analysis if a new product will result
2	Create one or more potential solutions to meet this need a. Make a literature survey and patent search b. Identify the preliminary data required
3	Undertake preliminary process synthesis of these solutions a. Determine reactions, separations, and possible operating conditions b. Recognize environmental, safety, and health concerns
4	Assess profitability of preliminary process or processes (if negative, reject process and create new alternatives).
5	Refine required design data a. Establish property data with appropriate software b. Verify experimentally, if necessary, key unknowns in the process
6	Prepare detailed engineering design a. Develop base case (if economic comparison is required) b. Prepare process flowsheet c. Integrate and optimize process d. Check process controllability e. Size equipment f. Estimate capital cost.
7	Reassess the economic viability of process (if negative, either modify process or investigate other process alternatives)
8	Review the process again for environmental, safety, and health effects
9	Provide a written process design report
10	Complete the final engineering design a. Determine equipment layout and specifications b. Develop piping and instrumentation diagrams c. Prepare bids for the equipment or the process plant
11	Procure equipment (if work is done in-house)
12	Provide assistance (if requested) in the construction phase
13	Assist with start-up and shakedown runs
14	Initiate production

Once the biorefinery idea has been conceived, the plant design engineer creates one or more solutions to embody it. As these alternatives require different process steps and unique operating conditions, the engineer should establish separate flowsheets including, as a first step, just the reaction, separation, temperature and pressure change operations, and selecting process equipment in a task integration step. The initial simplified flowsheets that provide a favourable gross profit are further developed considering base-case designs for each flowsheet.

A detailed process flow diagram (PFD) with an inventory of steady-state material and energy balances and a designation of major equipment items is, then, developed. Utility streams are also identified in a PFD. Equipment is represented symbolically by “icons” that identify specific unit operations. A list of the equipment names along with a brief descriptive name for the equipment is created next to the PFD. The location of these equipment numbers and names roughly corresponds to the horizontal location of the corresponding piece of equipment. The convention for formatting and identifying the process equipment is given in Table 4.2. This table provides the information necessary for the identification of the process equipment icons shown in a PFD. An example of how to use this information in a PFD as well as what each number or letter mean, could be the detection of the third heat exchanger of the second Area in a biorefinery development:

E-203 identifies the equipment as a heat exchanger
E-**2**03 indicates that the heat exchanger is located in area 200 of the biorefinery
E-20**3** indicates that this specific heat exchanger is number 03 in unit 200.

The material and energy balances are generally performed using common rules of thumb of chemical engineering and validated using computer-aided process simulators. The design is always performed aiming at improving the process efficiency via separation train synthesis, heat and power integration and second-law analysis. The implementation of these optimisation approaches offers the ability to the engineer to compare the base case with other potential alternatives and recreate flowsheets that should be built in addition to, or instead of, the base-case design.

After the detailed process flowsheet development has been completed, the sizing of equipment takes place. Given a specific annual production capacity of the desired product or an annual quantity of feedstock for valorisation, the mass and energy balances' inventory developed during the design and the residence time in each unit operation, the characteristic size of each type of equipment is estimated. Table 4.2 presents the most common units of equipment employed during process design along with their corresponding characteristic size.

Table 4.2 Specific codes of units of equipment and corresponding characteristic size

Specific code	Type of equipment	Characteristic size	Unit
A-	Agitator	Power	hp
C-	Compressor	Power	kW
CF-	Centrifugal separator	Volumetric flowrate	m^3/h
CR-	Crystallizer	Mass flowrate	kg/h
DR-	Dryer	Mass flowrate	kg/h
E-	Heat exchanger	Area	m^2
EV-	Evaporator	Area	m^2
EX-	Extruder	Mass flowrate	kg/h
F-	Fermentor	Volume	m^3
R-	Reactor	Volume	m^3
T-	Distillation column	Trays Height/Diameter	Number m
V-	Vessel	Volume	m^3

4.3 Techno-economic assessment

4.3.1 Definitions

The basic terms used in the techno-economic assessment starting at the delivery of the feedstock at the gate of the industrial plant through the production of platform or intermediate products/chemicals/polymers to the production of the final bio-based marketable product are defined according to Peters et al.(2003), Turton et al. (2018) and Towler and Sinnott (2013) as follows:

Fixed capital investment

"The capital needed to supply the required manufacturing and plant facilities is called the fixed-capital investment (FCI)"

"The fixed capital investment (FCI) is the total cost of designing, constructing, and installing a plant and the associated modifications needed to prepare the plant site."

Working capital

"The working capital for an industrial plant consists of the total amount of money invested in (1) raw materials and supplies carried in stock; (2) finished products in stock and semifinished products in the process of being manufactured; (3) accounts receivable; (4) cash kept on hand for monthly payment of operating expenses, such as salaries, wages, and raw material purchases; (5) accounts payable; and (6) taxes payable.";

"The capital that is tied up in maintaining inventories of feeds, products, and spare parts, together with cash on hand and the difference between money owed by costumers (accounts receivable) and money owed to suppliers (accounts payable), is termed the working capital of the plant."

"Is the amount of capital required to start up the plant and finance the first few months of operation before revenues from the process start. Typically, this money is used to cover salaries, raw material inventories, and any contingencies."

Total capital investment

"The sum of the fixed-capital investment and the working capital is known as the total capital investment (TCI)."

Cost of Manufacture or Operating cost

"All expenses directly connected with the manufacturing operation or the physical equipment of a process plant itself are included in the manufacturing costs. These expenses, as considered here, are divided into three classifications: (1) variable production costs, (2) fixed charges, and (3) plant overhead costs."

Cost of raw materials

"Any cost of those materials that are directly consumed in making the final products; this includes chemical reactants and constituents and additives included in the product. Materials necessary to carry out process operations but which do not become part of the final product, such as catalysts and solvents, are listed separately."

Cost of labour

"The total expenditure borne by employers for employing staff and consists of employee compensation (including wages, salaries in cash and in kind, employers' social security contributions), vocational training costs, other expenditure (e.g recruitment costs, spending on working clothes and employment taxes regarded as labour costss), minus any subsidies received."

Cost of waste treatment

"any cost of the processes applied for treatment and safe disposal of waste which is produced within the production process."

Cost of utilities

"Any cost of the primary sources of raw energy for the supply of power are found in the heat of combustion of fuels and in elevated water supplies."

4.3.2 Methodological framework

With the aim of assessing the techno-economic profitability of an integrated biorefinery, the methodological framework should start by determining the target bio-based product as well as the production capacity of the industrial plant. An annual production capacity of a platform chemical constitutes a limiting factor after which the economies of scale are expected to have been reached. Then, the alternative technologies should be identified to employ the best production parameters for the process (e.g. carbon source to product conversion yield, productivity, concentration and purity of the final product). After the selection of the technology, the desired feedstock should be defined. Feedstock availability and geographic coverage are aspects that should be addressed during the supply chain network design. These parameters can ensure that renewable resources are available in the required quantities in order for the desired plant capacity to be achieved. The selection of feedstock can also be based on each feedstock potential for biorefinery development and co-products manufacture.

The main part of TEA begins by conducting the process design as described in section 4.1. The inventory developed during the design is afterwards used for further assessing the techno-economic performance of a process. The definition of the functional unit (FU) and the system boundaries of the process are performed. The results could be converted into different FUs, but the developed methodology should define the FU in which the results will be initially presented in order for future comparisons with similar alternative scenarios to be feasible. The two typical FUs for a biorefinery development approach are 1 kg (or 1 t) of the main bio-based product or 1 t of dry renewable feedstock used in the process, depending on the goal and scope of the study. The system boundaries considered in the TEA of the conversion stage for a bio-based production refer mainly to the manufacturing and downstream stages. These stages include pretreatment of feedstock and extraction of sugars, chemical or biochemical conversion into chemical intermediates, separation and purification of the intermediate products, polymerization (if applicable) and end-product formulation.

4.3.3 Estimation of Total Capital Investment

TEA calculations are based on preliminary techno-economic assessment carried out to estimate the TCI and the COM using established chemical engineering methodologies (Peters et al., 2003; Turton et al., 2018; Ulrich and Vasudevan, 2004). In this section, the TCI estimation will be analysed.

The TCI is divided into FCI and the WC. The WC pertains the cost of inventories of raw materials, supplies and final/intermediate products as well as payments of manufacturing expenses and various accounts and taxes. The FCI is divided into the manufacturing fixed-capital investment (or direct costs), which is the capital that is directly related to the plant's construction, and the non-manufacturing fixed-capital investment (or indirect costs), which include the capital that is indirectly related to the process operation. It is highly important to develop predictive models for quick estimation of FCI and utilities requirements as the precise mathematical approach developed by Dheskali et al. (2020a).

The estimation of the FCI is based on the estimation of the equipment purchase cost (Ceq.fob) or the installed equipment cost (Ceq.in) for the inside battery limits (ISBL) equipment. This methodology is sufficient for preliminary cost estimation as long as the process flow sheet, the material and energy balances and the sizing of major process equipment are available. There are various methods that have been proposed for rapid estimation of total capital investment. However, there is lack of reliable information in the case of bio-based product formation using renewable feedstocks, especially in the case of bioprocesses. Bonatsos et al. (2016) have demonstrated that the FCI exhibits a strong correlation with the installed fermentation capacity based on various techno-economic studies reported in literature-cited publications.

In order to ensure the accuracy of estimations, FCI has been estimated in this study based on the equipment purchase cost (Ceq.fob) by sizing the equipment that are included in each process flow sheet of alternative production processes and feedstocks. The design and sizing of chemical process equipment has been based on standard chemical engineering techniques and widely acceptable rules of thumb (Couper et al., 2005; Peters et al., 2003) as described in section 4.1. Given the complete equipment sizing, data from several textbooks can be used to estimate the purchased equipment cost (Humbird et al., 2011; Peters et al., 2003; Turton et al., 2018). When data are not available to calculate the Ceq.fob for the desired characteristic size, then the following equation will be used:

$$\mathrm{C_{eq}} = \frac{\mathrm{CEPCI_t}}{\mathrm{CEPCI_{t_0}}} \mathrm{C_{eq,0}} \left(\frac{\mathrm{X}}{\mathrm{X_0}}\right)^{\mathrm{n}}$$

Where the purchase cost $C_{eq,0}$ of a particular type of equipment with characteristic size X_0 is known at year t_0 and the purchase cost Ceq of the same type of equipment but different characteristic size X and/or at different year should be estimated. The exponent n is characteristic to the particular type of equipment and $CEPCI_t$ is the chemical engineering plant cost index at year t published monthly in the Chemical Engineering Magazine. The $CEPCI_t$ employed in the following sections is different in each case due to the reference year for which each process design was carried out.

The FCI is then calculated using appropriate multipliers. When the equipment purchase cost is available, then a multiplier in the range 3-6 has been proposed (Peters et al., 2003; Turton et al., 2018) in order to obtain an estimation of the FCI. The lower values of the multipliers are more appropriate when the new production facility will be an extension of an existing industrial facility and will only require minor upgrades and modifications to the outside battery limits units (OSBL) (such as utilities production area, wastewater treatment area, storage facilities, etc.). The larger values are normally proposed for larger production facilities that require major alterations of dedicated OSBL facilities. However, this is not a clear-cut decision and it is difficult to determine what an appropriate value for the multiplication factors is in order to identify them as suitable for the production of bio-based products employing bioprocessing or chemical conversion of biomass components. Given the fact that the proposed production plants will be constructed mainly from relatively expensive material (SS304 or SS316), it is envisaged that the actual FCI will be 5 × ∑Ceq (sum of purchased free on board equipment costs).

The WC is calculated on top of the FCI and is spent before the launch of plant operation as it reflects cost of raw materials and the labour cost required to begin plant operation. According to Peters et al. (2003), as credit terms extended to customers are usually based on an allowable 30-day payment period, the working capital is required because of accounts receivable ordinarily amounts to the production cost for 1 month of operation. The ratio of WC to FCI for chemical production plants varies between 15 – 20% with a potential increase to 50% or more for processes of seasonal operation. However, this may not be accurate in the case of biorefineries. Humbird et al. (2011) estimated the WC as 5% of the FCI in the case of ethanol production using lignocellulosic feedstocks, thus this percentage will be taken into account in this study.

4.3.4 Estimation of the Cost of Manufacture

The COM could be divided into the Direct Operating Costs, the Fixed Capital Related Costs and the General Expenses. Table 4.4 presents the cost items contained in these categories. Table 4.3 presents the cost items included in these categories.

Table 4.3 Factors affecting the COM for an industrial process

Factor	Description of factor
Direct costs	**Factors that vary with the rate of production**
Raw materials	Costs of feedstocks required by the process and will be calculated by the process flow sheet and material balances
Waste treatment	Costs of waste treatment to protect the environment
Utilities	Costs of utilities (e.g. steam, cooling water, process water, electricity etc.) required by the process and will be calculated by the process flow sheet and material and energy balances
Operating labour	Costs of personnel required for plant operation
Direct supervisory and clerical labour	Costs of administrative, engineering and support personel
Maintenance and repairs	Costs of labour and materials associated with maintenance
Operating supplies	Costs of miscellaneous supplies that supports daily operation not considered to be raw materials
Laboratory charges	Costs of routine and special laboratory tests required for product quality control and troubleshooting
Patents and royalties	Costs of using patented or licensed technology
Fixed costs	**Factors not affected by the level of production**
Depreciation	Costs associated with the physical plant (buildings, equipment etc.)
Local taxes and insurance	Costs associated with property taxes and liability insurance

Plant overhead costs	Catch-all costs associated with operations of auxiliary facilities supporting the manufacturing process.
General expenses	**Costs associated with management level and a administrative activities not directly related to the manufacturing process**
Administration costs	Includes salaries, other administration, buildings and other related activities
Distribution and selling costs	Costs of sales and marketing required to sell the final products. Includes salaries and other miscellaneous costs
Research and development	Costs of research activities related to the process and products. Includes salaries and funds for research-related equipment and supplies etc.

The following mathematical expression has been proposed by Turton et al. for the approximation of COM:

$$\mathrm{COM} = 0.18\times\mathrm{FCI} + 2.73\times C_{OL} + 1.23\times(C_{UT} + C_{RM} + C_{WT}) + \text{depreciation}$$

with C_{OL} standing for manufacturing labour expenses, C_{UT} standing for utilities expenses, C_{RM} standing for raw material expenses and C_{WT} standing for waste management.

The methodology that will be followed on the estimation of operating labour has been proposed by Ulrich and Vasudevan (2004), which is based on the number and type of each unit operation used in the process flow sheet. This methodology begins with accounting the number of workers necessary to operate and supervise a particular piece of process equipment that is included in the process flow sheet. The sum of workers (N_{OL}) for all unit operations represents the workers necessary to supervise the operation of an industrial plant per shift.

The methodology subsequently estimates the total number of workers required in the industrial plant by taking into consideration the duration of plant operation and the working time of each worker. For instance, let’s assume that an industrial plant that operates 24 h/day, 3 shifts/day and 365 days per year is considered, which leads to 1095 shifts per year. A single worker works approximately 8 h/shift, 5 days/ week and 49 weeks/year considering vacations and sick leave allowances. Thus, each worker will work 245 shifts/year. In order to allow for one worker being present in the plant at any time throughout the year, then 4.5 workers should be employed [(1095 shifts/year) / (245 shifts/operator/year)]. Then, the operating labour is estimated by multiplying 4.5 with N_{OL}. It should be stressed that this number represents the operating labor and not any support or supervisory staff. The operating labour should be multiplied by the number of hours that each operators work per year (8 h/day × 5 days/week × 49 weeks/year = 1960 hours) and the average labour cost in EU28.

Table 4.4 Workers per shift for representative unit operations (Ulrich and Vasudevan, 2004)

Unit operation	Workers/shift
Agitator	0.2
Compressor	0.1
Centrifugal separator	0.05
Crystallizer	0.4
Dryer	1
Heat exchanger	0.05
Evaporator	0.3
Extruder	1
Fermentor	1
Reactor	1
Distillation column	0.5
Vessel and towers	0.2

Utilities are the ancillary streams required for the operation of the process. The ancillary streams that are going to be used in this category are: steam, cooling water, electricity and process water. A process flow sheet usually represents the inside battery limits of an industrial plant including the various ancillary services or utilities used. The utilities could be:

- Purchased from a public or private utility
- Supplied by a comprehensive off-site facility that covers the utility requirements of many industrial plants situated at a common location
- Generated on-site by the same industrial plant. In this case, fixed capital costs for the unit operations required to produce each utility and their respective operating costs should be considered

The cost of utilities depends also on the fuel used for the production of each utility. Thus, in order to reduce the complexity on the estimation of the cost of each utility used in each alternative process that will be evaluated during the project, the utilities unitary costs supplied by off-sites will be considered as presented in Turton et al. (2018) (Table 4.5).

The cost of raw materials could be divided into the cost of the main renewable resources used as feedstocks and the cost of miscellaneous materials used in the operation of the plant. Table 4.6 presents the unitary cost of raw materials used during the biorefineries' development under study, derived from literature and market research. As the feedstocks utilized in each biorefinery are mainly industrial and food supply chain side streams, no cost is attributed to those raw materials. C_{RM} is estimated by multiplying the unitary raw material costs with the mass balances of each case, after developing the relevant inventories.

The estimation of waste treatment cost will be based on the material balances and information provided by Turton et al. (2018) (Table 4.5) on the waste disposal or treatment cost of various waste streams (e.g. non-hazardous, hazardous, waste water treatment through primary, secondary or tertiary processes)

Table 4.5 Utilities provided by off-sites for a plant with multiple process units (Turton et al., 2018)

Utility	**Specific type**	**Cost**
Steam (latent heat only)	LPS: 6 bar - 160°C	\$9.45/t
	MPS: 10 bar - 184°C	\$9.54/t
	HPS: 41 bar - 254°C	\$9.61/t
Water	Cooling water	\$0.0157/t
Electricity	220 V	\$0.0674/kWh
Natural gas	0.0354 GJ/std m^3	\$3.16/GJ
Waste water treatment	Primary	\$41/m^3
	Secondary	\$43/m^3
	Tertiary	\$56/m^3

Table 4.6 Unitary cost of raw materials

Raw Material	**Unitary prices (\$/t)**	**Reference**	**Raw Material**	**Unitary prices (\$/t)**	**Reference**
Glucose	230	(USDA, 2018)	Neopentyl glycol	1,500	(Alibaba.com)
Corn stover	58	(Humbird et al., 2011)	Additives for HMAs	1,894	
Sugar beet pulp	5	(www.thebeefsite.com)	Additives for PUDs	5,500	
Water	0.435	(Turton et al., 2018)	Petroleum ether	1,000	
Yeast extract	1,500	(Dourado et al., 2016)	$MgCO_3$	1,000	(ICIS, 2006)
SFM	250	(Kachrimanidou et al., 2021)	HCl	61	(ICIS, 2006)
NH_4Cl	155	(Local vendor)	NaOH	400	(Efe et al., 2013)
CO_2	150		NaCl	35	(Kazi et al., 2010)
Citric acid	220		$CaCl_2$	275	(ICIS, 2006)
H_2SO_4	80	(Alibaba.com)	$(NH_4)_2SO_4$	150	
NH_3	350	(ICIS, 2006)	KH_2PO_4	900	
Methanol	630		$MgSO_4$	300	
Ethanol	680		$NaHCO_3$	150	
Hexane	1,000	(Alibaba.com)	Na_2HPO_4	900	
Ethyl-lactate	1,110		$CaCO_3$	150	(Dimou et al., 2016)
Petroleum ether	1,000		$CaCl_2$	150	
Acetone	1,500		Vitamins	15,000	(ICIS, 2006)
KOH (85%)	400		Resins	2,900	(Local vendor)
1,6-hexanediol	3,500		Enzymes	1,000/4,240	(Alibaba.com; Humbird et al., 2011)

4.3.5 Discounted cash flow analysis and methodology for indicators selection

In the process of making an investment decision, the profit anticipated from an investment must be judged relative to some quantitative measures of profit with respect to the investment required to generate that profit. Profit is the goal of any investment, but maximizing profit is an inadequate profitability standard. Profitability is usually measured with methods that consider the time value of money giving reliable results for maximizing the overall future worth of an investment. Based on the total capital investment and the cost of manufacture that will be calculated for each biorefinery scenario, a discounted cash flow (DCF) analysis will be carried out. DCF analysis can be employed for the assessment of the profitability of the developed biorefinery demonstrating the economic efficiency of the employed process technology. In order to implement the same DCF analysis in all alternative processing scenarios, the plant construction period, the interest rate, the income tax rate, the depreciation method, the plant life, and the construction start-up duration should be specified (Table 4.7). It should be stressed that the financial assumptions presented in Table 4.7 are subject to uncertainty economic sensitivities and should be evaluated in order to identify the profitability range.

Table 4.7 Parameters of the DCF analysis (Humbird et al., 2011)

Discount rate (or interest rate)	10 %
Plant lifetime	30 years
Equity financing	100 %
Depreciation via MACRS	200% declining balance and 7 year recovery period
Corporate tax rate	35 %
Plant construction duration	3 years
% of project cost in the 1st, 2nd and 3rd year of construction	8 % - 60% - 32 %
Working capital	5 % of FCI
Salvage value	0
Land costs	0

Depreciation is an annual income tax deduction that allows recovery of the cost or other basis of certain property over the time the property is being used. Depreciation, has a significant effect on corporate cash flow. The concept of depreciation is based upon the fact that physical facilities deteriorate and decline in usefulness with time; thus, the value of a facility decreases. There are several methods for calculating depreciation (e.g. straight-line, double-declining balance, the modified accelerated cost recovery system). For all DCF analyses, the IRS-MACRS methodology will be used for depreciation estimation, as proposed by Humbird et al. (2011).

Various indicators can be used for the assessment of process profitability. Techno-economic indicators used in the international literature for process profitability evaluation are the Net Present Value (NPV), the Minimum Selling Price (MSP) and the Discounted Payback Period (DPP). A detailed list of process profitability measures considering with special consideration for energy efficiency and renewable energy systems are presented by (Short et al., 1995). A couple of additional techno-economic indicators that has been used in this study are the Optimum Plant Capacity (OPC) and the Minimum Feedstock Requirements (MFR).

The NPV of a project is one way of examining costs (cash outflows) and revenues (cash inflows) together. A NPV analysis can be composed of many different cost and revenue streams. The form of the different streams (current or constant dollars) should be known, in order for the correct discount rate to be used for the present value analysis. Alternatively, the cash flows can be adjusted to reflect the form of the discount rate. The formula for NPV can be expressed as:

$$\mathrm{NPV} = \sum_{\mathrm{n}=0}^{\mathrm{N}} \left[\frac{C\mathrm{F_n}}{(1+\mathrm{i})^{\mathrm{n}}}\right] = C\mathrm{F_0} + \frac{C\mathrm{F_1}}{(1+\mathrm{i})^1} + \frac{C\mathrm{F_2}}{(1+\mathrm{i})^2} + \cdots . + \frac{C\mathrm{F_N}}{(1+\mathrm{i})^{\mathrm{N}}}$$

where CFn is the annual cash flows received at year n, N is the total number of years corresponding to the analysis period, and i is the annual discount (interest) rate.

A positive NPV indicates that the earnings, which are generated by the biorefinery operation, exceed the anticipated costs; thus, the investment under study can become profitable. A negative NPV will result in a net loss.

The MSP stands for the market price of the end-product that results in zero NPV value at the end of the useful lifetime of the industrial plant operation and is affected by the selected annual production capacity due to the economy of scale. Figure 4.1 illustrates a descriptive algorithm to estimate the MSP as a function of NPV. The DPP is the time required, after the initiation of plant operation, to recover the capital investment. The OPC defines the capacity at which the COM or MSP reach a plateau and thereafter remain constant.

A useful techno-economic indicator is the MFR that stands for raw material needed for the manufacture of the end-product annual capacity assuming zero NPV value at the end of the useful duration of industrial plant operation (Serna-Loaiza et al., 2019). This indicator connects the supply chain stage with the production process of a bio-based value chain.

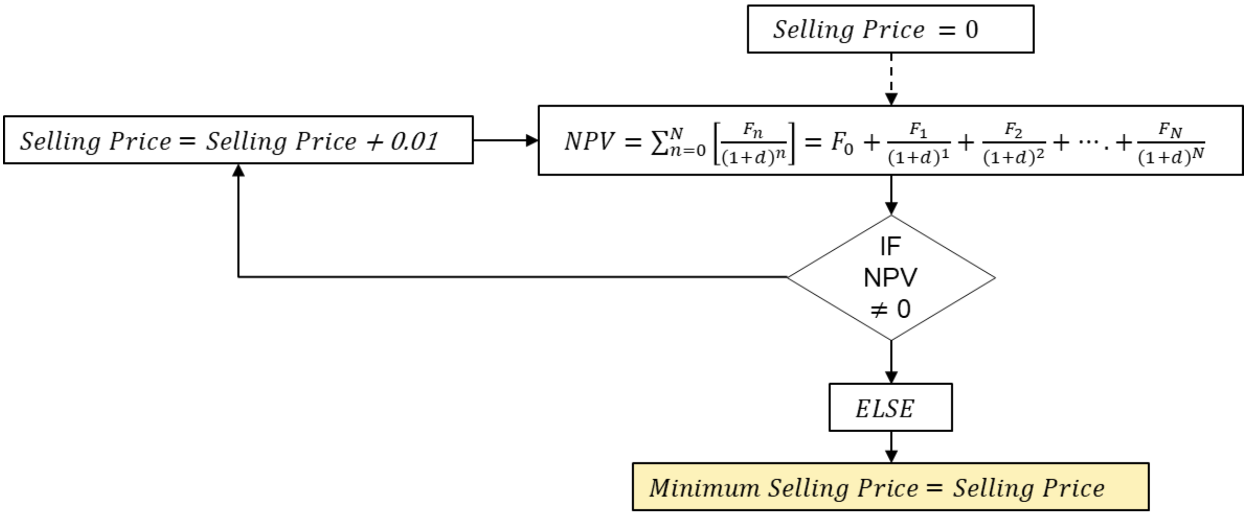


Figure 4.1 Illustrative description of minimum selling price

4.4 Life Cycle Assessment

Assessing the environmental performance of different key bioprocesses using different renewable resources is a fundamental issue in order to realize what is the impact of a specific bio-based supply chain network, how the treatment of feedstock affects the environmental impacts, how the crucial parameters of the processes can be improved and finally what the actual result of the comparison between the current scenario and the alternative solution of bioeconomy is. The outcome of the evaluation can continuously feedback the design of the whole process so as to find out the best way of utilizing the wastes for environmentally sustainable production.

The broadly accepted and extensively used LCA methodology is generally selected to quantify impacts along circular bioeconomy value chains. LCA is a structured, internationally standardised method and management tool (ISO, 2006) for quantifying the emissions, resources consumed and environmental and health impacts that are associated with products and services. LCA takes into account the product‘s full life cycle from the extraction of resources, over production, use and recycling up to the disposal of the remaining waste (Ögmundarson et al., 2020).

This methodology appeared in the late 1960s to early 1970s. In the beginning, the assessments were referred to as “Resource and Environmental Profile Analysis (REPA)” or “Ecobalances” (Hauschild et al., 2017) and the emphasis was laid on the function of recycling, solid waste management and the dilemma of using reusable products, while energy issues were not evaluated until the energy crisis in the mid-1970s. These early evaluations were more akin to the current stage of life cycle inventory (LCI), aiding at the development of a more comprehensive life cycle impact assessment framework, as constructed in the following decades. The first LCA methods for quantifying environmental impacts were published in the early 1990s, with notable examples to be the Swiss Ecoscarcity (or Ecopoints) methodology and the CML 1992 methodology (Heijungs et al., 1992).

In the 1990s, a standardization process was launched for LCA under the International Organization for Standardization (ISO) guidance, resulting in a common framework and fundamental principles. ISO 14040 (outlining principles of LCA), ISO 14041(describing life cycle inventory modelling), ISO 14042 (dealing with the necessary requirements for an impact assessment) and ISO 14043 (adding interpretation as a continuously occurring step) were constructed the outline for LCA methodology (ISO 14041, 1998; ISO 14042, 2000; ISO 14043, 2005). After updates until 2006, the family standards 14040 (14040-14044, 2006) constitute the present framework for LCA implementation (Figure 4.2). However, this effort is still being researched and developed.

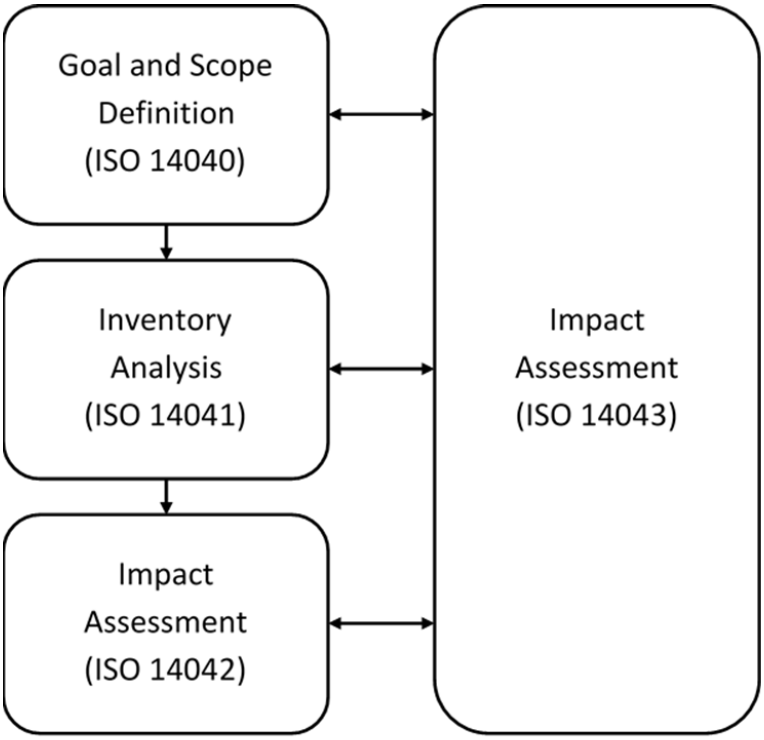


Figure 4.2 Framework of life cycle assessment according to ISO 14040-14044

This framework includes four discrete but interdependent phases that must be followed when performing an LCA: definition of goal and scope, inventory analysis, impact assessment and interpretation of the results.

4.4.1 Goal and scope

The goal and scope phase describes the reason for the LCA performance, the target audience and the strategy that will be followed for reporting the final results. Some of the factors that should be defined in this stage to ensure LCA transparency and comparability are the functional unit of the study, the system boundaries of the process, the selected impact categories and related indicators, possible assumptions and foreseeing uncertainties from uncontainable factors of the system and, possibly, the relevant perspective of the study, e.g. whether the LCA is attributional or consequential.

The FU is employed to establish a reference to which the final impacts are expressed. Systems that provide significantly diverse products, yet meet the same requirement, can be compared using the same FU. The functional unit could be linked to a quantity of required product (output-based FU) or to the quantity of the feedstock under valorisation (input-based FU). This does not reflect the ultimate function of a finished product, but it does make it possible to make comparisons among the different systems. To guarantee comparability, factors like purity and dry weight must also be considered. In the chemical industry, the most frequent output-based definition of functional units are mass (1 kg), energy content (1 MJ) and volume (m^3). However, as biorefineries are systems that deliver multiple products and introduce multifunctionality issues in the assessment, an input-based FU (1 kg of feedstock) allows to avoid the allocation between the co-products and assess the biorefinery as an overall system. If the goal requires the determination of the impact of a single co-product, the multiple FUs should be defined, then the desired allocation method could be applied.

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 are 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. A very crucial fact for the system boundaries is that these are the basis for the comparison of two independent LCA studies. Comparison between two studies can be made only if they have the same system boundaries. To minimize issues of comparability, the whole life cycle of a process, from raw material extraction to waste disposal, should be included within the system limits, a process known as “cradle-to-grave” assessment. However, the most preferable approach in the literature is the “cradle-to-gate” assessment, providing the environmental impacts from raw material extraction to final product ready to depart the factory gate. Selecting a cradle-to-gate assessment is the proper decision when the main scope is to identify the hotspots of a process and compare different technologies that result in similar final products. However, to allow for fair comparisons, the same sub-processes, e.g. feedstock pretreatment, downstream processing, possible heat and power co-generation), must be included.

LCA perspectives are broadly classified into two types: attributional LCA (A-LCA) and consequential LCA (C-LCA). According to ILCD handbook (2010), A-LCA approach depicts the potential environmental impacts that can be attributed to a system over its life cycle or the boundaries under study. The modelling is performed using measurable data, built on stoichiometric connections between inputs and outcomes. The main focus of the study is on the selected functional unit and the general system, while variation in the results during comparisons are explained by technical differences between technologies rather than economic or other exterior factors from the background system. On the other hand, C-LCA aims at identifying the consequences that a decision in the foreground system has for other processes and systems of the economy, both in the analysed system's background system and on other systems. The consequential life cycle inventory modelling principle is also called “change-oriented” or "effect-oriented" (ILCD Handbook, 2010), since it is dependent on interactions between demand for inputs, price elasticities, supply, and market impacts of co-products Brander et al. (2008). Most studies in industry and research are based on A-LCA, as they prefer to focus on their own “product” (responsibility) and its related supply chain in a specified reference period and area perspective.

4.4.2 Life Cycle Inventory (LCI)

During the life cycle inventory phase (LCI), data for consumption of resources and utilities are collected as well as the quantities of waste flows and emissions caused in each stage of production are estimated. The analysis investigates all of the processes that are part of the product system, and the flows are scaled in line with the product reference flow provided by the functional unit. Moreover, the data quality is assessed during the developed of the inventory.

As most product systems are comprehensive, inventory analysis frequently relies on data that are derived from databases with unit processes or cradle-to-gate data, presenting the input and output flows for one unit process, such as material production, heat or electricity generation, transportation or waste management. Environmentally extended input-output analysis can be used to assist and qualify inventory data collecting. This stage results in the development of the life cycle inventory, which is a list of quantified physical elementary flows for the product system expressed on the basis of the FU. This inventory is subsequently employed for the assessment of the environmental performance of the system under study.

4.4.3 Life Cycle Impact Assessment (LCIA)

The evaluation and quantification of the potential environmental impacts of the process is performed in the impact assessment phase by analyzing the data of the LCI. This phase provides indicators, in terms of several impacts categories, to evaluate the product life cycle on the selected FU basis considering the contributions of all the stages of the production process (Singh et al., 2018).

ISO guidelines provide only a general approach for the LCIA phase and do not specifically define the environmental categories or characterization factors that should be used. The adaption of a specific method depends mainly on the goal and scope of the study, the sector at which the study is aimed and the future targets of the study. Areas of Protection (human health, natural environment and natural resources, ILCD handbook, 2010) with which the study is intended to deal is also an important criterion when selecting an LCIA method. The various LCIA models differ fundamentally due to changes in temporal scales, geographical coverages and differences in the focus of research at the institutions where assessment methods are developed (Dekker et al., 2020). As a result, the outcomes and conclusions of an LCA frequently rely on the LCIA approach used.

According to ISO 14044, the indicator that characterize an impact category can be located anywhere along the impact route, connecting inventory data through consecutive environmental impacts to the damage that they cause on the areas of protection (Goedkoop et al., 2013). Midpoint indicators are located somewhere along the impact pathway, to relatively early stages in the cause–effect chain, and group LCI results in the so-called midpoint categories, which follow a problem-oriented approach and translates impacts into environmental themes. On the other hand, endpoint methods are damage-oriented and try to model the cause–effect chain, up to the Areas of Protection.

Two of the most common methodologies used for LCIA in 1990s were the CML (developed at Centrum voor Milieukunde Leiden) and the Eco-indicator 99 (developed by PRé Consultants). CML employs a midpoint approach, meaning that the LCI is translated to contribution to different mechanisms for environmental issues (Heijungs et al., 1992), while Eco-indicator 99 uses an endpoint approach linking the environmental impacts with the final Areas of Protection (Goedkoop et al., 2001). As a response to a request for a more comprehensive framework, with both midpoint and endpoint indicators, ReCiPe 2008 was developed in the beginning of this century (Goedkoop et al., 2013). This thesis focuses on the midpoint categories, which are more direct and therefore have a lower degree of uncertainty, thus the midpoint categories of the most updated versions of CML and ReCiPe methodologies will be reported in the following sections. The CML methodology was carried out for comparison purposes with LCA indicators reported in literature-cited publications (Cok et al., 2014). The ReCiPe methodology was used because the LCC framework used in this study (De Bruyn et al., 2018) has been developed using this methodology. Table 4.8 presents the midpoint categories of ReCiPe 2008 along with the corresponding indicators, their units and a short description for each category. Each environmental indicator is quantitatively estimated based on case-specific equivalents.

Table 4.8 Impact categories at midpoint level for ReCiPe 2008 (Goedkoop et al., 2009).

Impact Category	Midpoint indicator	Unit	Explanation
Land use	Agricultural land occupation	m^2a	The amount of agricultural area occupied in m^2 and the time of occupation in years. At midpoint level there is no differentiation to land use types.
Climate change	Climate change	kg CO_2-eq.	Greenhouse gasses in the atmosphere absorb infrared radiation leading to increased global temperature. The global warming potential (GWP) is quantified relative to that of CO_2 over a defined period of time. The GWP depends on both the specific thermal radiation absorption and the lifetime of a substance
Fossil fuel depletion	Fossil fuel depletion	kg oil-eq.	Fossil resources like natural gas, oil and coal are limited.
Toxicity	Freshwater ecotoxicity	kg 1,4-DCB-eq.	Environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical.
Eutrophication	Freshwater eutrophication	kg P-eq	Phosphorus enrichment of seawater leads to adverse ecological effects.
Toxicity	Human toxicity	kg 1,4-DCB-eq.	Environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical.
Ionizing radiation	Ionizing radiation	kg U^{23} -eq.	Routine releases of radioactive material in the nuclear fuel cycle damage humane health.
Toxicity	Marine ecotoxicity	kg 1,4-DB-eq.	Environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical.
Eutrophication	Marine eutrophication	kg N-eq.	Nitrogen enrichment of seawater leads to adverse ecological effects.
Mineral resource depletion	Metal depletion	kg Fe-eq.	Many metals are not destroyed after their use, but the cost pf extraction can be higher. The mineral depletion potential (MDP) is quantified relative to the burden that current resource extraction of a metal puts on future extraction relative to extracting 1 kg iron.
Land use	Natural land transformation	m^2	The land area that is transformed from one use to another. The land use types (forest, tropical forest, sea and ocean) can be recognized as natural land. A negative value corresponds to transformation to natural land. The natural land transformation potential (NLTP) makes no difference to land use types at midpoint level.

Ozone depletion	Ozone depletion	kg CFC-11-eq.	Depletion of stratospheric ozone result in increased damaging UVB- radiation.
Health damage due to PM10 and ozone	Particulate matter formation	kg PM_{10}-eq.	Fine Particulate Matter (PM) with a diameter of less than 10 μm (PM10) causes health problems when inhaled. Emissions of substances like sulfur dioxide ammonia and nitrogen oxides can lead to the formation of PM.
Health damage due to PM10 and ozone	Photochemical oxidant formation	kg NMVOC-eq.	Ozone formed at ground level from photochemical reactions of NO_X and air pollutants have a negative impact on human health and vegetation. Ozone formation potential (OFP) is quantitated as the marginal change in the 24h-average European concentration of ozone due to a marginal change in emission of the substance and is expressed in Non Methane Volatile Organic Compounds (NMVOCs) equivalents.
Acidification	Terrestrial acidification	kg SO_2-eq.	Emission of some inorganic substances to air increase the acidity in the soil (via rain) to harmful levels.
Toxicity	Terrestrial ecotoxicity	kg 1,4-DCB-eq.	Environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical.
Land use	Land use	m^2a	Describes the amount in m^2 of urban area, like mineralextraction sites or traffic area, occupied and the time of occupation in years. At midpoint level there is no differentiation to land use types.
Water depletion	Water depletion	m^3 water-eq.	Expresses the total amount of water used.

4.4.4 Interpretation

Life cycle interpretation should occur at every stage in an LCA but more systematically when obtaining life cycle inventory and impact assessment results. The results of the study are interpreted in order to answer the questions posed in the goal and scope phase. Moreover, conclusions are drawn, the limitation of the LCA study are defined based on the main results and the selected comparisons and recommendations are provided for further elaboration.

4.5 Life Cycle Costing

Except for the main economic performance of a process, there are also external costs (also termed “externalities”) that are not directly related to the manufacturing process but affects the total economic feasibility of a bio-based value chain. More specifically, externalities are quantifiable costs (negative externalities) or benefits (positive externalities) that occur when the actions of an industrial plant have an effect on other stakeholders (Hunkeler et al., 2008). Most of the time, these effects are related to the environmental impacts occurred during the operation for the production process as well as the social impact of the plant. Consequently, the consideration of the cost of externalities is a crucial factor for a techno-economic evaluation to be complete and reliable. Moreover, this practice offers the opportunity for objective comparisons between bio-based products and their fossil counterparts in a circular bioeconomy context.

Environmental impacts are generally characterized in terms of human health (health and occupational health impacts), human welfare (aesthetic, materials and resource use impacts), environmental resources (biodiversity/endangered species, coastal and other marine ecosystems, groundwater, terrestrial ecosystems impacts), and global systems impacts (global, environmental, physical, psychological, socioeconomic/cultural impacts).The non-environmental impacts are associated with market failure (asymmetry in the labor market and geographical rigidity), government intervention failure (policies that cause higher or lower taxes than those if the interventions did not exist) and energy security (over-reliance on imported energy) (Galán et al., 1995). Assessing the economic dimensions of impacts is a controversial issue which has extensively been discussed in literature. The triptych "Quantification, Valuation, Monetization" was the preliminary methodology for expressing the environmental externalities (Bemow et al., 1991). Some of the models observed are the followings:

1. Environmental prices handbook (De Bruyn et al., 2018): Environmental prices are constructed prices for the social cost or pollution, expressed in euros per kilogram pollutant. Environmental prices thus indicate the loss of economic welfare that occurs when one additional kilogram of the pollutant finds its way into the environment. In this methodology, the environmental prices are presented at pollutant level, at midpoint level and at endpoint level. The methodology used in this report is designed to harmonize the values at pollutant, midpoint and endpoint level, to achieve consistent valuation of the impacts or pollution in the EU28.
2. True Price (Galgani et al., 2020): The true price methodology implements the principles of remediation by identifying the following four types of costs that, when appropriately combined, form the remediation cost for an impact: 1) Restoration costs, 2) Compensation costs, 3) Prevention costs of re-occurrence and 4) Retribution costs. True price makes external costs explicit by assessing and monetising them on a per-unit basis. The sum of all external costs assessed in this way is called the “true price gap”. The true price gap can be compared directly to the market price of the product by adding the two values to get to the true price. The true price can be interpreted as how much the product truly costs. It includes costs to the buyer (the market price) and the costs to external stakeholders (the true price gap).
3. ExternE (Bickel and Friedrich, 2005): EU-US EPA, 1991-2005. It refers to the energy sector

and is an approach of calculating environmental external costs as it was developed during the “ExternE project-series”, called Impact-Pathway-Approach. The impact pathway assessment is a bottom-up-approach in which environmental benefits and costs are estimated by following the pathway from source emissions via quality changes of air, soil and water to physical impacts, before being expressed in monetary benefits and costs. The tool and data for calculating environmental external costs according to the Impact-Pathway-Approach are implemented in the EcoSense model.

4. AQBAT (AQBAT, 2020): Canadian Government, 2011. It concerns the air quality and health. It is a computer application developed by Health Canada which is designed to estimate the human health impacts of changes in Canada’s ambient air quality. Also, it is used to estimate the benefits (positive impacts) or damages (negative impacts) of proposed regulatory initiatives related to outdoor air quality. It allows the user to define a wide range of scenarios combining pollutants, health endpoints, geographic areas and scenario years consists of a Microsoft Excel file with numerous controls to enable the user to define, run, examine and save the inputs and outputs for specific scenarios contains sheets of historical and projected population data, pollutant concentration data, annual baseline health endpoint occurrence rates, and Health Canada endorsed concentration-response functions and health endpoint valuations utilizes the @Risk add-in software to perform Monte-Carlo simulations, which allow the user to examine the effects of uncertainties on estimated health impacts.
5. TCBA (Kander et al., 2015): Canada (VTPI), ongoing (last update 2016). It concerns the transport sector and its equation is presented below.

Thus the TCBA inventory for country s is given by the equation:

$$\text{TCBA}^{s} = \sum_i f_i^s + \sum_{i,r\neq s} q_i^r \# x_i^{rs} - \sum_{i,r\neq s} q_i \# x_i^{sr}$$

6. HECT (Sampson, 2018): European Commission, 2008 & 2014. It concerns the transport sector.
7. Stepwise (Stepwise, 2006): EU, 2005-2006, It concerns products. The Stepwise method applies a new approach to monetisation that avoids some of the problems of earlier cost-benefit assessments that have been criticized of incompleteness and high uncertainty in relation to monetarization of environmental impacts. The Stepwise method carries all impacts forward to a single score, either monetary units or QALYs (Quality Adjusted Life Years) while maintaining the option of providing results at midpoint categories (environmental themes) or damage categories (human well-being, biodiversity, and resource productivity).
8. Environmental Priority Strategies (EPS, 2000): Swedish research & industry, 1998-1999. It

concerns products. EPS is a systematic approach to choose between design options in product and process development. Its basic idea is to make a list of environmental damage costs available to the designer in the same way as ordinary costs are available for materials, processes and parts. The designer may then calculate the total costs over the products life cycle and compare optional designs.

In this thesis, the monetization of the estimated impacts is carried out by employing average values of environmental prices, provided from De Bruyn et al. (2018). The determined environmental impacts are converted into monetized values using representative environmental prices for each impact category (e.g. pollutant emissions, climate change, human health). The principal stages for the implementation of methodology are:

1. Definition of the activity to be assessed and the background scenario where the activity is embedded. Definition of the important impact categories and externalities.
2. Estimation of the impacts or effects of the activity (in physical units). In general, the impacts allocated to the activity are the difference between the impacts of the scenario with and the scenario without the activity. Given the selection of the monetisation methodology, the ReCiPe Mid/Endpoint methodology, version 1.08, will be employed for the impact assessment.
3. Monetisation of the impacts, leading to external costs. Table 4.9 presents the monetisation factors for environmental impacts

Table 4.9 Midpoint level environmental prices (adopted from De Bruyn et al., 2018)

Impact Category	**Unit**	**Monetary Value**
Climate Change	€/kg $CO_{2\text{-eq}}$	0.0566
Stratospheric Ozone Depletion	€/kg $CFC\text{-}_{11\text{-eq}}$	30.4000
Human Toxicity	€/kg 1,4 $DCB_{\text{-eq}}$	0.0991
Photochemical Oxidant Formation	€/kg $NMVOC_{\text{-eq}}$	1.1500
Fine Particulate Matter Formation	€/kg $PM_{10\text{-eq}}$	39.2000
Ionizing Radiation	€/kg kBq $U_{235\text{-eq}}$	0.0461
Acidification	€/kg $SO_{2\text{-eq}}$	4.9700
Freshwater Eutrophication	€/kg $P_{\text{-eq}}$	1.8600
Marine Eutrophication	€/kg $N_{\text{-eq}}$	3.1100
Terrestrial Ecotoxicity	€/kg 1,4-$DB_{\text{-eq}}$	8.6900
Freshwater Ecotoxicity	€/kg 1,4-$DB_{\text{-eq}}$	0.0361
Marine Ecotoxicity	€/kg 1,4-$DB_{\text{-eq}}$	0.0074

4. Assessment of uncertainties, sensitivity analysis.
5. Analysis of the results, drawing of conclusions.

The complete LCC of a bio-based value chain is the summary of the MSP estimated by TEA and the cost of externalities. The desired comparisons between the different bio-based technologies or possible fossil counterparts should be made based on the final LCC and not considering only the cost derived from TEA.

4.6 Social Assessment

Social indicators quantify social impacts (midpoint and endpoint: describing the points of impact along the pathway of a system) that can affect people's working conditions locally and show impacts on a larger community level. Socio-economic indicators focus on the evaluation of human well-being as related to industrial operation in a specific region. The relation between environmental and social aspects, job creation and satisfaction and moderate utilization of resources are some of the social aspects assessed by such indicators. There is a wide variation in the frameworks for social assessment, social indicators and quantification of the impacts which are identified in literature-cited studies (Dreyer et al., 2006; Kooduvalli et al., 2019).

As Dale et al. (2013) stated, the key criteria for the selection of indicators for the social assessment of bioenergy sustainability are strongly associated with information availability about socio-economic conditions of the selected industry and geographic region, as emphasis will be given on the stages where the company has the most considerable influence, the materials and product manufacturing stages. Consequently, some of the conditions that the selected indicators should satisfy are:

- Applicability: Easy, timely and cost-effective to be measured
- Sensitivity and responsiveness to both natural and anthropogenic factors
- Clarity concerning what is measured and how measurements are made
- Predictability of impending changes or changes that can be averted with management action
- Comparability with measurements of performance across different contexts

Indicators which meet these criteria allow users to set targets and create incentives for continuous improvement towards the development of sustainable processes. For the social assessment of the OFMSW biorefinery for the production of market products in this thesis, the methodology presented by Aristizábal-Marulanda et al. (2020) will be followed, as it fulfils most of the above criteria by quantifying social aspects.

A set of 8 indicators related to workers and local community stakeholders are evaluated considering the people who may be impacted by the implementation of each biorefinery facilities. The selected indicators are estimated using information derived from the simulation of the processes as well as accessible information regarding the European Union statistics. All indicators are calculated for each country of EU-27 in order for comparisons among countries to be feasible. Table 4.10 summarizes the stakeholders, subcategories and indicators used to evaluate the social impacts of the developed biorefineries, while Table 4.11 presents detailed explanations as well as the equations to calculate the indicators as mentioned above.

Table 4.10 Social indicators used in the study to evaluate the social impact of OFMSW biorefinery development.

Stakeholder	Subcategory	Indicator
Workers	Children labour	Children in employment, total (5 – 17 years)
	Fair salary	Living wage, per month Minimum wage, per month
	Working time	Hour of work per employee
Local community	Local employment	Job generation
	Access to material resources	Level of facility water use (related to the industrial sector) Level of facility water use (related to actual renewable resources)
	Safe and healthy living conditions	Relative contribution of GHG emissions

Table 4.11 Explanation of social indicators used to perform social analysis.

Indicator	Equation	Symbol	Units
Children in employment, total (5 – 17 years)	$\mathrm{CLindustrial} = \frac{\text{Children in employment}}{\text{Total in the country}} \times 100$	CL: Children labour	-
Living wage, per month	$\mathrm{LW} = \frac{\text{Total salary per month}}{\text{Living wage per month}} \times 100$	LW: Living wage	%
Minimum wage, per month	$\mathrm{MW} = \frac{\text{Total salary per month}}{\text{Minimum wage per month}} \times 100$	MW: Living wage	%
Hour of work per employee	-	WH: Work hours	h/employee
Job generation	-	N employees	-
Level of facility water use, sector	$\mathrm{FWU}_{\mathrm{sector}} = \frac{\text{Wprocess} + \text{Wcooling}}{\text{Windustrial water withdrawal}} \times 100$	FWU: Facility water use	%
Level of facility water use, country	$\mathrm{FWU}_{\mathrm{total}} = \frac{\text{Wprocess} + \text{Wcooling}}{\text{Wtotal water withdrawal}} \times 100$	W: Volume flow of water (m3/year)	
Relative contribution of gaseous emissions	$\mathrm{RCGE} = \frac{\mathrm{CO}_{2-\mathrm{eq}}\ \text{released}}{\mathrm{CO}_{2-\mathrm{eq}}\ \text{in each country}} \times 100$	$RCGE$: Relative contribution of gas emissions.	%

Stakeholder: Workers

The social impact that is imputed to the workers' stakeholder category is evaluated considering the child labour, fair salary and working time as subcategories. Each subcategory is assessed through the calculation of the four indicators presented in Table 4.10. The first indicator refers to the estimation of the total children in employment. The developed biorefineries are considered to be constructed in an EU-27 country and therefore are aligned with the Directive 94/33/EC regarding the protection of young people at work. The Directive's main objective is to prohibit the employment of children, having as an only exception the children's work under certain conditions for cultural, artistic, sporting or advertising activities. Employment in the industrial sector is strictly forbidden and consequently this indicator is zero in all case studies (Directive 94/33/EC).

The second subcategory (i.e. fair salary) involves the calculation of the monthly salary of workers of the chemical industry and the comparison to the living wage and the minimum wage of the reference country. Living wage describes the adequate living standard of a country, including costs for nutritious food, water, shelter, clothing, education, healthcare, transportation and communication, while the minimum wage is a national legally binding obligation on employers and defined as the minimum amount of remuneration that an employer is required to pay. The information related to living and minimum wages in EU-27 is extracted from WageIndicator.org (WageIndicator, 2022), where values are calculated based on living cost prices.

Finally, the last working time subcategory considers as indicator the number of hours of work per employee. This indicator is calculated considering the duration of plant operation and the working time of each worker. It is assumed that the industrial plant that operates 24 h/day, 7 days/week, 3 shifts/day and 7920 h per year, while a single worker works approximately 8 h/shift, 5 days/ week and 47 weeks/year considering vacations and sick leave allowances. Thus, each worker will work 235 shifts/year. In order to allow for one worker being present in the plant at any time throughout the year, then 4.5 workers should be employed, working 37 h per week (24 h/day × 7 days/week / 4.5 workers). This value is compared to the working hours of each county of EU-27 (European Statistics, 2022).

Stakeholder: Local community

The social impact caused in the local community by the implementation of the OFMSW biorefineries is evaluated considering three subcategories related to local employment, the use of natural resources and the healthy living conditions.

The subcategory local employment assesses the job generation that occurs because of the construction of the industrial plant. The operating labour is estimated by multiplying 4.5 (derived from the assumption that is analyzed in the "Workers" section) with N_{OL}, e.g. the summary of workers required for all units of equipment of each biorefinery. More specifically, the estimation of the number of workers of each biorefinery is based on the methodology developed by Ulrich et al. (2004). This methodology presents an estimation of the required workers per shift for the proper operation of each unit of equipment and depends on the number of units for each type of equimpment and the selected annual production capacity. It should be stressed that this number represents the operating labour and not any support or supervisory staff. Along with jobs created by producing greener chemicals, additional jobs can be created by switching from chemical feedstocks to renewable raw materials.

The second subcategory (i.e. access to material resources) evaluates whether the access of local communities to material resources is restricted because of commercial or industrial activities in their regions. The implementation of a new facility increases the demand for natural resources, which can lead to the depletion and conflict of different actors over these resources. This subcategory involves the calculation of the level of facility water use. This metric is evaluated as the ratio between the mass flow of water used in the biorefinery (cooling water + process water) and the total water used in the industrial sector and available in the country. For this, the AQUASTAT database, created by the Food and Agriculture Organization of the United Nations (FAO), was used to find the value of the total industrial water withdrawal and total water withdrawal (Aquastat, 2022). Industrial water withdrawal refers to the annual quantity of self-supplied water withdrawn for industrial uses, not connected to the public distribution network. It can include water from primary renewable and secondary freshwater resources, as well as water from over-abstraction of renewable groundwater or withdrawal from fossil groundwater, direct use of agricultural drainage water, direct use of (treated) wastewater, and desalinated water. On the other hand, the term total water withdrawal describes the annual quantity of water withdrawn for agricultural, industrial and municipal purposes.

Finally, the safe and healthy living conditions subcategory includes the comparison of the GHG emissions of each biorefinery with the overall GHG emissions of the selected country. Information about the GHG emissions of the EU-27 countries is derived from the Carbon Dioxide Information Analysis Center (Index Mundi, 2022).

4.7 Profitability risk assessment

Despite the comprehensive frameworks and the well-established methodologies that are followed for the sustainability assessment of a biorefinery, there are many challenges and uncertainties that should be handled. The main uncertainties can be related to the process design and economic model development (e.g. conversion yield, fermentation time and final broth concentration, cost of utilities etc.) or can be affected by various aspects of the main bio-based products and feedstocks of the biorefinery under study (e.g. market prices, demand, feedstock biomass cost, seasonality etc.). To surpass this problem and make it possible to decrease the risk of uncertainty for the investment, risk assessment modelling is crucial.

To integrate the uncertainties consideration during the development of a biorefinery, a range of useful methods in combination with mathematical modelling and simulations are employed. Techno-economic and sensitivity analysis can be used to identify the effects of operational conditions and specific performance targets that should be met in order to make the desired bio-based process economically feasible. Furthermore, probabilistic models can be used to perform qualitative risk analysis aiming to expose venture's risks. The outcome of the probabilistic models is the probability distribution of the financial outcome when all inputs, representing the uncertainty parameters, are iterated at the same time. Monte-Carlo method is usually employed as sampling method due to reduced computing costs and the availability of computational software (Dheskali et al., 2020b).

After techno-economic evaluation, a single-point sensitivity analysis is carried out in each case study to assess the sensitivity to process (e.g. conversion yields in feedstock pre-treatment/fractionation, hydrolysis, fermentation and chemical conversions) and economic (e.g. utility costs, market prices) parameters. The analysis is performed using MATLAB software by changing one variable at a time with case-specific limits (i.e. reasonable minima and maxima that were selected for each variable). Subsequently, Monte Carlo sensitivity analysis was carried out on the most important variables to compute the cumulative probability function of the Net Present Value (NPV) of a specific process using the methodology of Khazen and Dubi (1999). A Monte-Carlo simulation (MCS) is a model used to predict the probability of different outcomes which are affected by distinct parameters. It is one of the well-developed stochastic approaches to quantify risk/uncertainty in economic assessments, by investigating the ranges and probability distributions of values for economic performance (Mandegari et al., 2018; Pavan et al., 2019).

The methodology for performing MCS can be described by the following steps:

1. *Determination of all uncertainty parameters*

The uncertainty parameters of the process under study are determined as random process variables inputs within a specific range.

2. *Selection of specific uncertainty parameters that mainly affect the system under study.*

This selection is considered after the sensitivity analysis performance

3. *Specification of the upper and lower limits for the selected uncertainty parameters (range) and selection of distribution curve for each parameter*

In this method the values of the input uncertainties are randomly selected from adjusted distributions curves such as normal, lognormal uniform and triangular, among others.

Usually the input uncertainties of a production process are described by a probability density function (PDF). While the estimation of average quantities by means of evaluating averages is the underlying idea of the Monte-Carlo method, the process of sampling a realization of a random variable form a given distribution is an essential part of its practical application. A mathematical algorithm or process which, for a given PDF f(x) and cumulative distribution function (CDF) F(x) generates an outcome x, and such that for every given value x_0 the condition:

$$\mathrm{P}[\mathrm{x} \leq \mathrm{x}_0] = \mathrm{F}(\mathrm{x}_0)$$

is fulfilled, is a proper sampling procedure. A random variable realization generated by a proper sampling procedure is indistinguishable from a random variable generated in a process controlled by PDF f(x). Consider the equation

$$\int_{-\infty}^{\mathrm{x}} \mathrm{f}(\mathrm{x}')\mathrm{dx}' = \mathrm{F}(\mathrm{x}) = \mathrm{u} \quad \text{solved for } \mathrm{x}[0, 1],$$

Below the formula of uniform and triangular distributions, the ones that have been adopted in the different cases during the thesis, are presented.

The random variable x follows a uniform distribution (U, Figure 4.3) within the specific range [L, R] when the PDF is described as:

$$\mathrm{f}(\mathrm{x}) = \begin{cases} \dfrac{1}{\mathrm{R}-\mathrm{L}}, & \mathrm{L} \leq \mathrm{x} \leq \mathrm{R} \\ 0, & \text{otherwise} \end{cases}$$

and the CDF is described as:

$$F(x) = P(X \leq x) \begin{cases} 0, & x \leq L \\ \dfrac{x-L}{R-L}, & L \leq X < R \\ 1, & x \geq R \end{cases}$$

When a random variable x follows a triangular distribution, the PDF is described as:

$$f(x) = \begin{cases} \left(\frac{2}{R - L}\right) \cdot \left(\frac{x - L}{M - L}\right), & L \leq x \leq M \\ \left(\frac{2}{R - L}\right) \cdot \left(\frac{R - x}{R - M}\right), & M \leq x \leq R \\ 0, & x < L, x > R \end{cases}$$

where L is the lower limit, M is the peak location and R is the upper limit. Figure 4.4 illustrates the form of PDF and CDF of a triangular distribution.

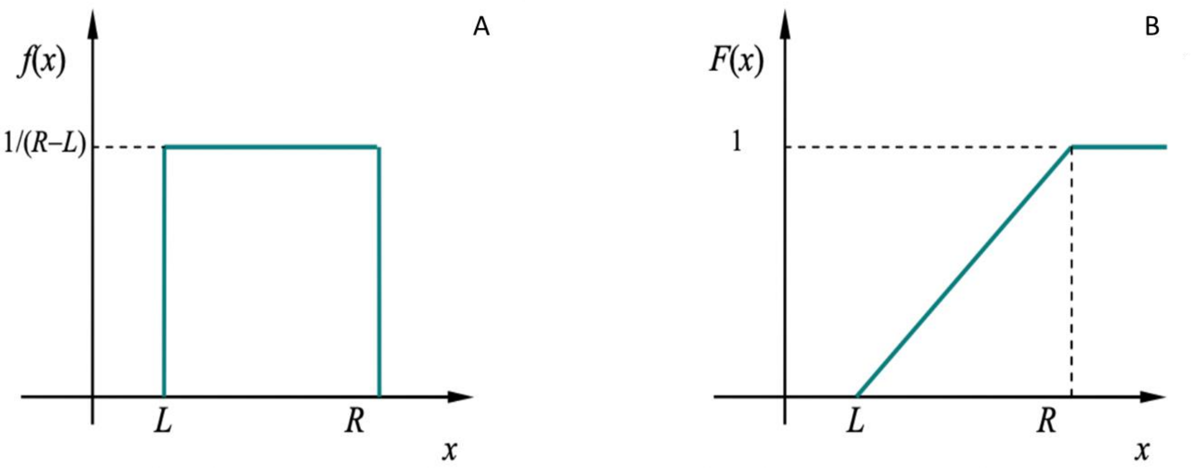


Figure 4.3 Uniform distribution curve. PDF (a), CDF (b).

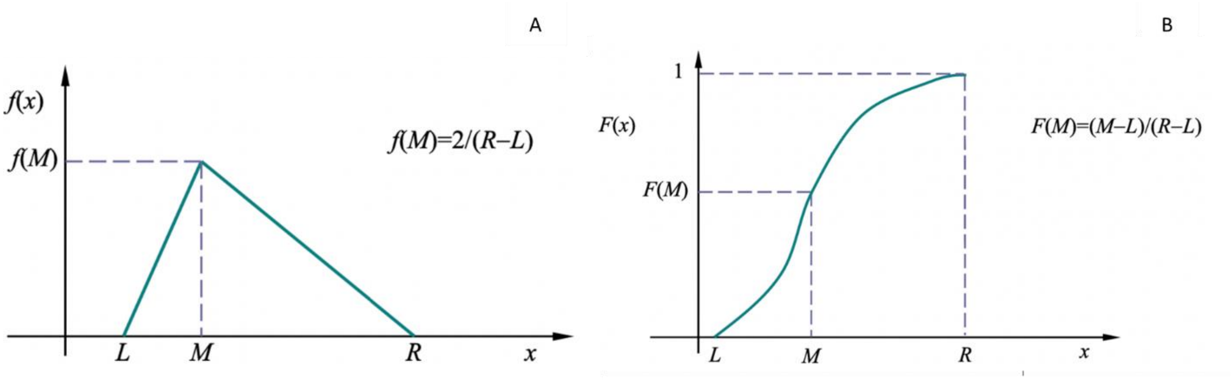


Figure 4.4 Triangular distribution curve. PDF (a), CDF (b).

4. *The sampling is carried out for sufficient iterations and the profitability indicators are estimated*

The procedure of obtaining a random variable realization x by solving the above equations is called CDF sampling method. MATLAB software (The MathWorks, Inc.) provides a “sampling” capability, with appropriate functions that each time select random variables from the probability density functions of the uncertain parameters. Each model is iterated million times by changing in each iteration the combination of the selected parameters. The randomly selected uncertain parameters as well as other input variables related to each biorefinery development are "input" into the main computational model which calculates the NPV using the Discounted Cash Flow (DCF) method.

5. *Statistical analysis of the profitability indicators*

After the implementation of the methodology, the results are expressed as the cumulative distribution function (CDF) of the indicator under study. If NPV is utilized as sustainability indicator, the CDF evaluates the probability of the NPV to be positive and therefore the investment to be profitable.

Chapter 5 Sustainability assessment of poly(butylene succinate) production using renewable resources

5.1 Introduction

In 2019, global plastic production reached ca. 370 million t with an annual increase of 2.5% (Plastics Europe, 2019). Fossil resources are used for the production of the vast majority (99.4%) of plastics (European Bioplastics, 2019; Plastics Europe, 2019). The transition towards the bio-economy era necessitates the production of bio-based and biodegradable polymers. Poly(butylene succinate) (PBS) is among the most widely used biopolymers with annual worldwide production capacities of 86,500 t (European Bioplastics, 2019). PBS is a biodegradable polyester produced via polycondensation of succinic acid (SA) and 1,4-butanediol (BDO). Although bio-based SA is a versatile platform chemical, the expected industrial growth has not been achieved mainly due to competition with low petroleum prices. Bio-based BDO is a chemical intermediate with various applications (textiles, electronics, automotive, consumer goods, etc.). It has been produced by Novamont via fermentation since 2016 at an annual production capacity of 30,000 t (Genomatica, 2016). PBS has similar properties to polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) (Moussa et al., 2012).

Conventional single-product bioprocesses using corn-derived glucose syrup as carbon source for the production of succinic acid and 1,4-butanediol lead to higher production costs than their fossil-derived counterparts. For instance, the market price of PBS ($4.0/kg) is higher than GPPS ($1.08-2.00/kg) (Plastic Insight, 2018). Agricultural residues (3.7×10^9 t) and food supply chain waste (1.3×10^9 t) produced in EU countries (Eurostat, 2019a) could be used for biorefinery development leading to sustainable bio-economy business models including biopolymer production (Kachrimanidou et al., 2021). Novel biorefinery concepts should ensure both economic benefits and low environmental impact (Thomassen et al., 2019). Thus, the sustainable production of PBS within novel biorefineries should be demonstrated via techno-economic evaluation (TEA), life cycle assessment (LCA) and life cycle costing (LCC) as compared to conventional petroleum-derived benchmarks.

The main aim of this chapter is to demonstrate the sustainability potential of PBS production within a biorefinery using sugar beet pulp (SBP), which is a widely available industrial by-product in EU (10.35 million t/year) (Ioannidou et al., 2020). The wet SBP remaining after hot water sugar extraction from sugar beets is pressed, dehydrated and pelletized to facilitate its preservation and transportation. The dried SBP pellets are currently used as low nutritional value animal feed, while dehydration requirements contributing ca. 35% of the total energy requirements at the sugar mill (Mujumdar, 2014; Zheng et al., 2012). The biorefinery concept employed in this study utilizes the low-value wet SBP for the separation of a crude pectin-rich extract as co-product and the production of LA, SA and BDO via fermentation using the carbohydrate content of SBP.

TEA and LCA of SA and BDO production as well as LCA of PBS production have been reported using renewable feedstocks (Dickson et al., 2021; Forte et al., 2016; Patel et al., 2018; Tecchio et al., 2016). There are no LCC studies based on process design, TEA and LCA for the production of PBS employing either single-product processes or multi-product biorefinery concepts.

The main novelty of this study is to evaluate the sustainability potential of PBS production within the SBP-based biorefinery via TEA, LCA, LCC and techno-economic risk assessment using Monte-Carlo simulations in comparison to single-product bioprocesses using corn glucose syrup and corn stover (CS) as well as GPPS as fossil-derived counterparts. Corn-derived glucose syrup was used as the base case conventional scenario. Corn stover was selected as a representative agricultural residue that is widely studied in bioprocess development. This study has been divided into 5 different stages:

Stage 1: Process design of PBS production using literature-cited experimental data to simulate pretreatment, fermentation, downstream separation and purification (DSP) and polymerization stages when glucose syrup, corn stover and SBP were used as feedstocks.
Stage 2: TEA using the process design data (e.g. sizing of equipment, material and energy balances) for the estimation of PBS production costs at different plant capacities.
Stage 3: LCA of PBS production using the CML 2001 methodology for comparison purposes with literature-cited environmental indicators.
Stage 4: LCC of PBS production including manufacturing costs and environmental externality costs estimated with the ReCiPe 1.08 methodology according to De Bruyn et al. (2018).
Stage 5: Techno-economic risk assessment via Monte-Carlo simulations of PBS production to assess process profitability at varying process and economic parameters.

5.2 Description of the process and feedstocks

The material and energy balances of PBS production processes from the three feedstocks were validated using UniSim (Honeywell). Every process flow diagram (Figures 5.1 and 5.2) operates 7,920 h/y. Process design was carried out at various annual plant capacities (10-120 kt PBS). The functional unit employed is 1 kg (or 1 t) of PBS.

5.2.1 Corn stover pretreatment

The pretreatment process (Area 100, Figure 5.1) has been adopted from the 2011 NREL report on bioethanol production from corn stover (Humbird et al., 2011). The corn stover used in this study contains cellulose (35.1%, db), hemicellulose (28.9%, db) and lignin (15.8%, db). Initially, milled corn stover is fed into the receiving bins after its delivery in the factory. The pre-treatment reactor system includes a feedstock receiving system (S-101) followed by a vertical vessel with a long residence time for steam-heating. The vertical presteamer tank (M-101) is designed for a residence time of up to 10 min 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. The remaining solids enter the horizontal pretreatment reactor (M-102), which operates at 5.5 atm, 158°C and 5 min. Dilute sulfuric acid (22.1 mg acid/dry g of biomass) is added in this reactor using 30% (w/w) total solids. 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 pretreatment reactor is discharged into a blowdown tank (V-101). The tank temperature is held at 130°C via pressure control. The outflow enters the oligomer conversion tank (V-102), where it is held at 130°C for 20–30 min. After this stage, the hydrolysate slurry containing 30 wt% total solids and 16.6 wt% insoluble solids at atmospheric pressure is added into the final tank of chemical pre-treatment (V-103). Here, the slurry is diluted with water to facilitate enzymatic hydrolysis using cellulase in the next stage. Ammonia gas is added into the dilution water to increase the hydrolysate pH to 5. The residence time is 30 min and the dilution cools the slurry to 75°C.

Chemical pretreatment leads to low glucan conversion into glucose (9.9%), whereas xylan is almost completely converted into xylose. Enzymatic hydrolysis using cellulase leads to cellulose conversion into glucose. The neutralized, diluted hydrolysate from chemical pre-treatment is firstly cooled and then mixed with cellulase at 48°C. The total solids loading is 20 wt%. The first stage of enzymatic hydrolysis begins in a continuous, high-solids loading reactor (V-104). The residence time in this first stage is 24 h, thus low cellulose hydrolysis is achieved. The continuous high-solids loading hydrolysis reactor 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 per g cellulose to achieve 90% conversion into glucose.

Hydrolysis continues in the next reactor (V-105) where the main hydrolysis takes place at 48°C.

After 60 h, the glucose concentration is increased from 8.81 kg/m3 to 73.66 kg/m3. The saccharified stream is centrifuged (CF-101) in order to isolate the remaining lignin and finally the sugar-rich hydrolysate stream is concentrated and cooled in order to enter the fermentation stage.

5.2.2 Sugar beet pulp pretreatment

It has been assumed that SBP is used directly as side stream from sugar beet processing plants without drying. The SBP side stream is assumed to contain 30 g solids per 100 g SBP. The SBP used in this study contains free sugars (2.73%, db), cellulose (22.7%, db), hemicellulose (36.6%, db), pectin (22.8%, db), lignin (1.16%, db) and protein (11.4%, db).

The first stage in SBP pretreatment (Area 100, Figure 5.1) includes the extraction of pectin based on data provided by Dávila et al. (2015) and Zheng et al. (2013). SBP is fed into the mixing tank (V-106) along with dilute hydrochloric acid at 100°C. The tank is designed for a residence time of 1 h. The outflow is centrifuged (CF-102) to separate the remaining solid fraction of SBP from the liquid fraction. Sodium hydroxide is used for neutralisation of the liquid stream, which is subsequently concentrated using a mechanical vapor recompression (MVR) - forced circulation evaporator system (EV-101). The concentrated pectin-rich liquid stream is, then, mixed with ethanol (93% v/v) to precipitate the pectins that are recovered via centrifugation. The amount of ethanol used is twice the volume of the pectin-rich liquid stream. The wet pectin stream recovered is dried (DR-101). The final step is the recycling of ethanol via distillation (T-101).

After the extraction of pectins, the remaining SBP solids are processed via chemical pretreatment and enzymatic hydrolysis to convert cellulose and hemicellulose into C5 and C6 sugars using the process employed in the case of corn stover (section 5.2.1). This process should be sufficient for complete cellulose and hemicellulose hydrolysis due to the significantly low lignin content in SBP.

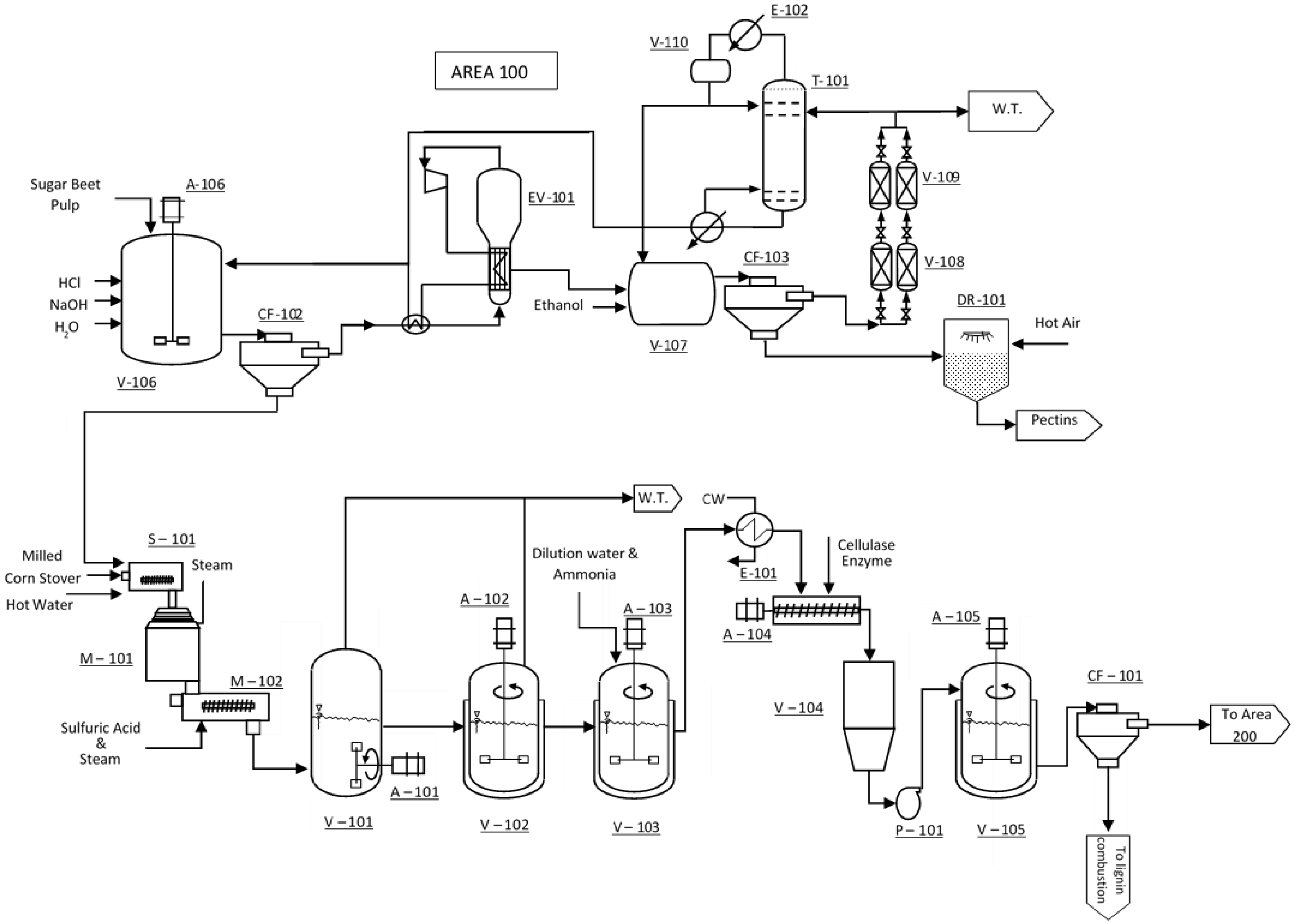


Figure 5.1 Process flow diagram for pretreatment of corn stover and sugar beet pulp

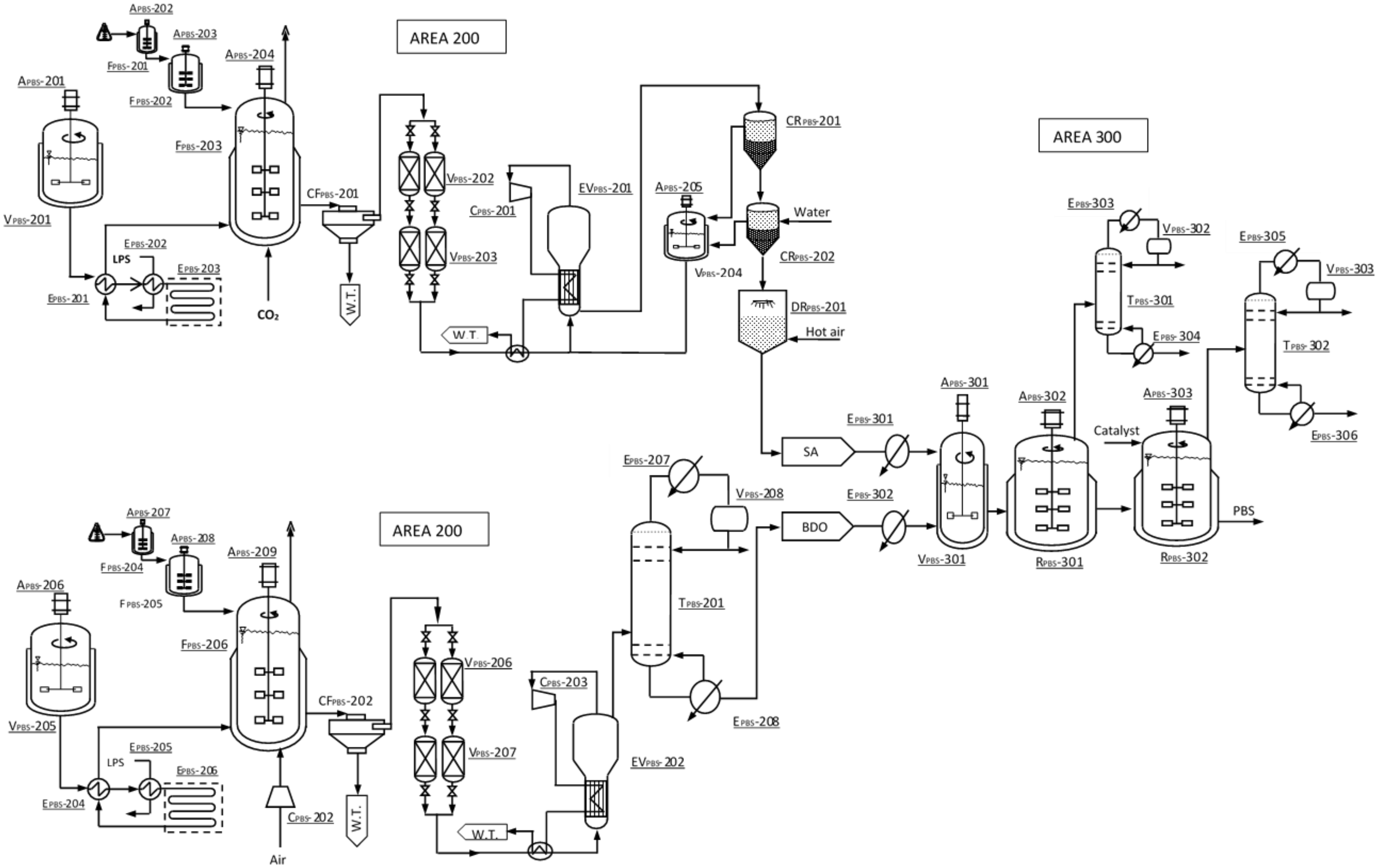


Figure 5.2 Process flow diagram for PBS production

5.2.3 Succinic acid production and purification

Literature-cited studies reporting high SA production efficiencies (expressed as yield, productivity and final succinic acid concentration) during fermentation on glucose (Table 5.1) were initially selected. Techno-economic evaluation was subsequently carried out for all selected cases to identify the most profitable fermentation. This approach was followed in order to evaluate all parameters (e.g. nutrients used for fermentation media formulation, aerobic vs facultative anaerobic conditions) influencing bioprocess profitability. Case 2 exhibited the best techno-economic performance (Cost of Manufacture = \$2.18/kg) and thus the simulation of PBS production was carried out using the parameters presented by Ma et al. (2011) (final SA concentration: 101.0 g/L, yield: 0.78 g/g, productivity: 1.18 g/(L·h). The techno-economic evaluation of the fermentation stage was carried out according to Dheskali et al. (2017).

The SA production plant consists of two main sections (Figure 5.2, AREA 200), namely bioconversion and DSP. The bioconversion stage begins with mixing (V_{PBS}-201) of process water with the carbon source and nutrients (e.g. nitrogen sources, minerals) followed by continuous heat sterilization of fermentation media via two heat exchangers and a holding tube (E_{PBS}-201 to E_{PBS}-203). Media are sterilized at 140°C and then cooled to the fermentation temperature (37°C) before addition into the bioreactors (F_{PBS}-203). The inoculum used is 10% (v/v) of the fermentation broth per bioreactor. The pH is maintained at 6.7 with 10 M NaOH solution added during fermentation. $MgCO_3$ is added at the beginning of fermentation. CO2 is used during fermentation due to metabolic requirements in the reductive TCA cycle to produce SA.

Table 5.1 Literature-cited fermentation efficiencies on succinic acid production

	Bacterial strain	**Yield (g/g)**	**Productivity (g/Lh)**	**SA concentration (g/L)**	**Reference**
Case 1	*Mannheimia succiniciproducens* LPK7	0.76	1.80	52.4	(Lee et al., 2006)
Case 2	*Escherichia coli* AFP111	0.78	1.18	101.0	(Ma et al., 2011)
Case 3	*E. coli* AFP111	1.10	1.30	99.2	(Vemuri et al., 2002)
Case 4	*Actinobacillus succinogenes* CGMCC1593	0.75	1.30	60.2	(Liu et al., 2008)
Case 5	*A. succinogenes* FZ53	0.82	1.98	103.4	(Guettler et al., 1995)
Case 6	*E. coli* KJ060	0.92	0.90	86.6	(Jantama et al., 2008)

The main metabolic by-product is acetic acid (1.67 g/L). The same fermentation efficiency has been assumed in the case of corn stover and SBP derived hydrolysates based on the existence of other *Escherichia coli* strains (e.g. *E. coli* AFP184) consuming efficiency C5/C6 sugars and potential strain engineering for fermentation efficiency improvements (Khunnonkwao et al., 2018; Sawisit et al., 2015).

The appropriate number of bioreactors depends on the desired production capacity and the maximum volume of bioreactors. Table 5.2 presents the optimal parameters for the design of fermentation stage in various annual capacities estimated according to Dheskali et al. (2017).

In the DSP stage, the fermented broth is centrifuged (CF_{PBS}-201) to remove the bacterial biomass. The biomass free broth is then fed into the activated carbon columns (V_{PBS}-202) for decolorisation and impurity removal. The decolorized effluent is fed into cation-exchange resin columns (V_{PBS}-203) to transform organic acid salts into their corresponding organic acids. The acidified liquid stream is then mixed with the stream that comes from the crystallizers (CR_{PBS}-201-202) before it is concentrated using the MVR-forced circulation evaporator system (EV_{PBS}-201). The evaporation unit consists of a preheater that heats up the temperature of the broth from 37°C to 100°C and an MVR-forced circulation evaporator system that concentrates the broth until the SA concentration reaches 214 kg/m^3. The concentrated liquid is subsequently treated via crystallisation in continuous crystallizers (CR_{PBS}-201-202) at 4°C. Two crystallisation stages are carried out. The wet succinic acid crystals are dried in a spray dryer (DR_{PBS}-201), while the remaining liquid is recycled at the evaporation stage. The SA crystal purity achieved is higher than 99.5%, while the overall succinic acid recovery yield in the DSP is ca. 95% (w/w). The DSP followed in this study has been presented by Alexandri et al. (2019b).

Table 5.2 Optimal bioreactor parameters for succinic acid production at various annual production capacities

Annual capacity (t)	**10,000**	**20,000**	**30,000**	**40,000**	**60,000**	**80,000**
Uploading time τ_{ul} (h)	23	18	15	13	7	6
Loading time τ_l (h)	5	3	3	4	4	3
Number of batches (N_b)	356	456	547	631	1,172	1,368
Number of bioreactors (N_f)	5	6	7	8	14	16
Working volume of bioreactor V_b (m^3)	278.12	434.25	543.02	627.64	506.88	579.01

5.2.4 BDO production and purification

Bioprocess design on BDO production (Figure 5.2, AREA 200) has been based on the fermentation efficiency reported by Burgard et al. (2016) using a genetically engineered *E. coli* strain. The final concentration of BDO is 125 g/L with a yield of 0.4 g/g and a productivity of 3.5 g/(L·h). A similar BDO production efficiency is also feasible in crude hydrolysates rich in C5/C6 sugars (personal communication). The bioconversion section is designed and scheduled (e.g. optimal batch duration, number of bioreactors, total volume of each bioreactor) (Table 5.3) according to Dheskali et al. (2017). The pH is held at 7 during fermentation, while microaerobic conditions are used (0.02 vvm). Besides BDO, the main by-products produced at the end of fermentation are 4-hydroxybutyrate (4-HB, 5.71 g/L), acetic acid (3.82 g/L), γ-butyrolactone (GBL, 1.32 g/L) and ethanol (0.71 g/L).

In the DSP stage, BDO is purified to 99.7% purity with recovery yield of 92%. The microbial biomass is initially removed via centrifugation (CF_{PBS}-202). The bacterial mass free liquid stream is processed through a series of cation- (V_{PBS}-206) and anion-exchange (V_{PBS}-207) resin columns to remove the minerals and organic acid salts that are present in the fermentation broth. The outlet liquid stream is subsequently concentrated using a MVR-forced circulation evaporator system (EV_{PBS}-202) up to a BDO concentration of 632.6 g/L. BDO is purified via distillation (T_{PBS}-201) at atmospheric pressure and 180°C in order to separate the water and GBL.

5.2.5 PBS polymerization

The unit operations and the process conditions for the polymerization of PBS (Figure 5.2, AREA 300) were taken from Kamikawa et al. (2013). This process is divided into three sections, the preparation of raw materials, esterification and polymerization. BDO and SA are initially mixed in a mixing tank (V_{PBS}-301) at a molar ratio of 1.3:1 and 80°C using low pressure steam (LPS). The liquid outflow enters the esterification reactor (R_{PBS}-301), after it is heated to 180°C.

Table 5.3 Optimal bioreactor parameters for BDO production at various annual production capacities

Annual capacity (t)	**10,000**	**20,000**	**30,000**	**40,000**	**60,000**	**80,000**
Uploading time τ_{ul} (h)	13	10	10	10	8	8
Loading time τ_l (h)	2	3	3	3	3	3
Number of batches (N_b)	635	826	826	826	1,032	1,032
Number of bioreactors (N_f)	4	5	5	5	6	6
Working volume of bioreactor V_b (m^3)	125.98	193.70	290.56	387.41	465.12	620.15

The esterification reaction is carried out for 3 h at 230°C and 1 bar. The vapor stream is distilled (T_{PBS}-301) to recycle the unreacted BDO. Ester polymerization is a polycondensation reaction in the presence of titanium tetrabutoxide as catalyst with a concentration of 2000 ppm (with respect to succinic acid) (R_{PBS}-302). The temperature of the reaction is 240°C and the vacuum applied is 2 torr. After 16.5 h, the final product from the polycondensation reactor contains PBS with molecular weight of 70,000 Da. The vapor stream of the reactor is initially cooled and compressed and then distilled (T_{PBS}-302) so as to recover the remaining BDO. The produced PBS is cooled, pelletized (not included in this study) and stored.

The simulation is performed in Honeywell UniSim considering the following assumptions. The first assumption is related to the thermodynamic data of the ester and PBS added in the software as hypothetical components. Their properties were determined using estimation methods, namely Joback for ester (Joback and Reid, 1987) and Van Krevelen for PBS (Van Krevelen and Te Nijenhuis, 2009). Another assumption is the use of an average molecular weight for PBS based on Kamikawa et al. (2013). Finally, owing to the lack of data about the specific reaction rate of polycondensation, a stoichiometry reaction for polymerization is assumed.

5.3 Techno-economic assessment

The stages of feedstock pretreatment (including pectin extraction in the case of SBP), fermentation, DSP and polymerization have been included in the estimation of FCI per kg PBS at different plant capacities (10-120 kt/y) (Figure 5.3a). Different plant capacities were evaluated to identify the one where a constant FCI per kg value is reached (58.63 kt_{PBS}/year). The lowest FCI per kg is estimated in the case of glucose, while the highest FCI per kg is estimated when SBP is employed. The estimation of equipment size, purchase equipment cost and FCI for the OPC for PBS production are presented in Tables 5.4 and 5.5.

Figure 5.3b present the COM for all case studies at various plant production capacities (10-120 kt/y). When SBP is employed, the highest COM is estimated due to the incorporation of pectin extraction. In the case of glucose and corn stover, the calculated COM is similar for both feedstocks. More specifically, the estimated COM is $2.63/kg for glucose and $2.56/kg for corn stover at 58.63 kt annual PBS production capacity.

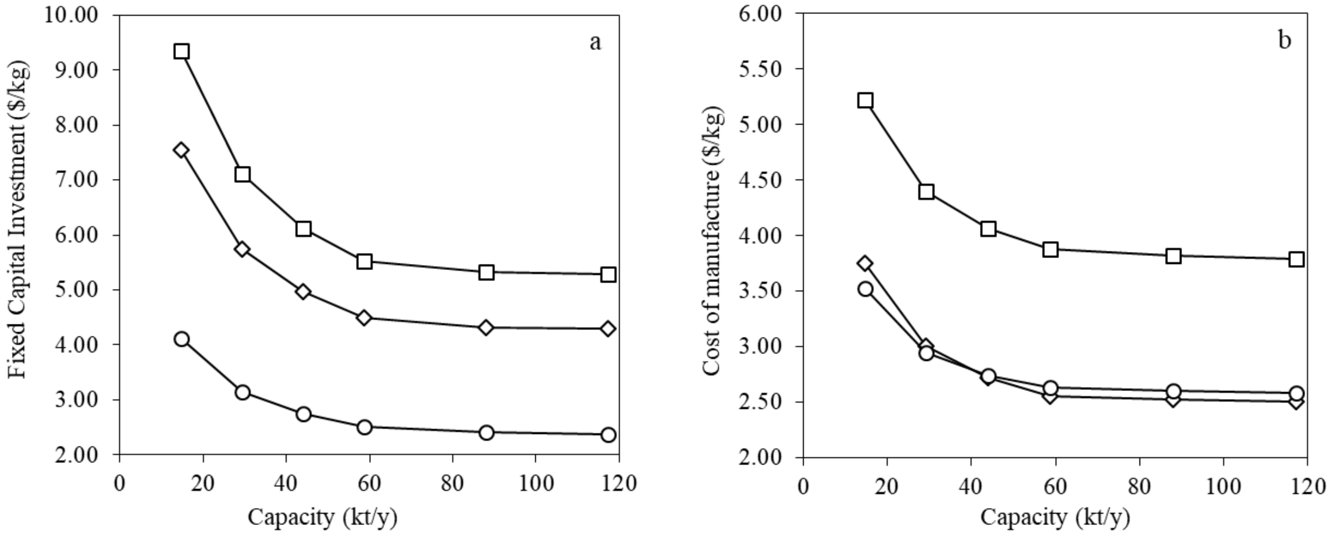


Figure 5.3 Fixed Capital Investment (a) and Cost of manufacture (b) for PBS production as a function of annual production capacity using glucose syrup (o), corn stover (◊) and SBP (□) as feedstocks

Table 5.4 Characteristic size, utility requirements and purchase equipment cost of the most important unit operations in pectins extraction for the production of 58,630 t/y PBS (OPC).

Characteristic size	**Value**	**Utility**	**FOB Cost (Cp@2017,M$)**
Working volume of V-106 (m^3)	652.05	Electricity 4,810,700 kWh/y Steam 653,866 t/y	1.714 [a]
Number of EV-101	5	Electricity 94,713,725 kWh/y	3.728 [b]
Area of EV-101 (m^2)	886.33		
Number of trays in T$_{PBS}$-201	26	Steam 67,468 t/y	1.321 [b]
Height of T$_{PBS}$-201 (m)	35.85	Cooling water 3,285,038 t/y	
Mass flow rate of DR$_{PBS}$-201 (kg/h)	9,523	Electricity 265,600 kWh/y	4.241 [b]

[a] Peters et al., 2003; [b] Turton et al., 2018, 2003;

Table 5.5 Characteristic size, utility requirements and purchase equipment cost of the most important unit operations for the production of 58,630 t/y PBS (OPC)

Characteristic size	**Value**	**Utility**	**FOB Cost (Cp@2017, M$)**
Succinic acid production process			
Area of E_{PBS}-201 (m^2)	665.76	-	0.244 [a]
Area of E_{PBS}-202 (m^2)	52.23	Steam 7,959 t/y	0.039 [a]
Number of F_{PBS}-203	8	Electricity 37,843,784 kWh/y	11.17 [a]
Working volume of F_{PBS}-203 (m^3)	627.64	Cooling water 5,832,670 t/y	
Area of EV_{PBS}-201 (m^2)	582.41	Electricity 11,312,451 kWh/y Steam 24,571 t/y	0.830 [b]
Mass flow rate of CR_{PBS}-201 (kg/h)	32,417	Electricity 7,750,860 kWh/y	0.741 [b]
Mass flow rate of CR_{PBS}-202 (kg/h)	12,020	Electricity 325,386 kWh/y	0.451 [b]
Mass flow rate of DR_{PBS}-201 (kg/h)	561.17	Electricity 23,860,000 kWh/y	3.712 [b]
1,4–butanediol production process			
Area of E_{PBS}-204 (m^2)	547.92	-	0.202 [a]
Area of E_{PBS}-205 (m^2)	42.98	Steam 6,431 t/y	0.035 [a]
Number of F_{PBS}-206	5	Electricity 24,638,292 kWh/y	4.763 [a]
Working volume of F_{PBS}-206 (m^3)	387.41	Cooling water 3,675,789 t/y	
Area of EV_{PBS}-202 (m^2)	458.67	Electricity 9,802,717 kWh/y Steam 9,644 t/y	0.721 [b]
Number of trays in T_{PBS}-201	8	Steam 28,053 t/y	0.127 [b]
Height of T_{PBS}-201 (m)	17.55	Cooling water 933,609 t/y	
PBS polymerization			
Volume of R_{PBS}-301 (m^3)	30.74	Electricity 226,755 kWh/y Steam 19,627 t/y	0.10 [b]
Number of R_{PBS}-302 (m^3)	6	Electricity 1,405,299 kWh/y	0.464 [b]
Volume of R_{PBS}-302 (m^3)	31.75	Steam 199,044 t/y	
Number of trays in T_{PBS}-302	8	Steam 5,848 t/y	0.108 [b]
Height of T_{PBS}-302 (m)	5.12	Cooling water 691,235 t/y	
		Total workers	36

[a] Dheskali et al., 2017; [b] Turton et al., 2018, 2003;

The MSP for PBS production at various plant capacities is presented in Figure 5.4. For comparison purposes, the market prices for PBS was considered as \$4/kg$_{PBS}$ (E4tech et al., 2015). Although further processing of the crude pectin extract may be needed depending on the final market application, no further processing has been considered. The selling price of the crude pectin extract was assumed at \$4/kg. This market price is significantly lower than the current pectin market prices for conventional food applications, such as low methoxy pectin (\$11−12/kg) (Ciriminna et al., 2016). The production cost of orange peel derived pectin is \$3.76/kg (Dávila et al., 2015). Thus, conservative market price (\$3-4/kg) has been assumed in this study that is lower than pectin market prices for conventional food applications. Future studies should evaluate further processing requirements of crude pectin extracts for the production of marketable products.

When SBP was used, the revenue from crude pectin extract sales as co-product is also considered leading to lower MSP than glucose syrup and corn stover for both biopolymers (Figure 5.4). More specifically, the MSP of PBS production from SBP is 54.3% lower than the respective MSP values estimated in glucose-based processes at the plant capacity where the lowest MSP is reached. At a crude pectin extract market price of \$4/kg$_{pectin}$, the MSP$_{PBS}$ is lower than the current market price of PBS (\$4.0/kgPBS) at all production capacities evaluated. When a crude pectin extract market price of \$3/kg$_{pectin}$ was considered, the MSP$_{PBS}$ calculated in this study is higher than the current market price of PBS (data not shown).

Table 5.6 presents OPC, COM, MSP, DPP and MFR values for all case studies. The lowest MSP and DPP values were estimated when SBP was used for PBS production.

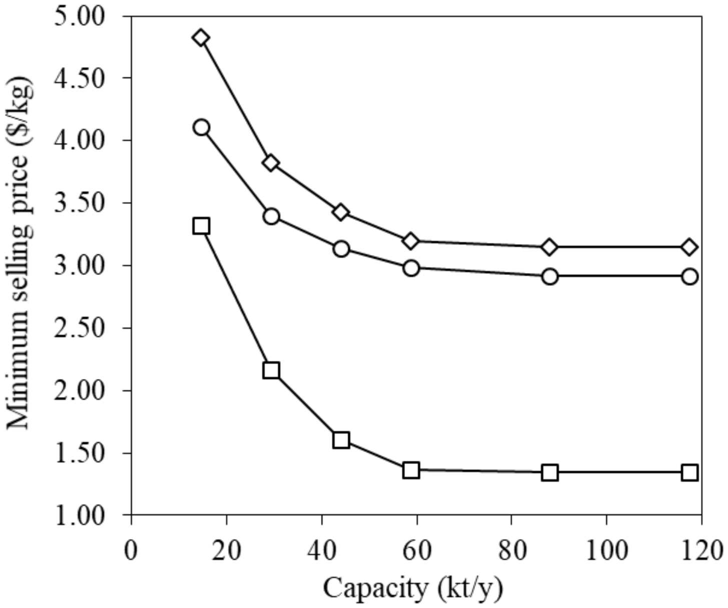


Figure 5.4 Minimum selling price for production as a function of annual production capacity using glucose syrup (o), corn stover (◊) and SBP (□) as feedstocks.

Table 5.6 TEA indicators for PBS production at the optimum plant capacity considering pectin-rich extract market price of $4/kg. A 70% water content has been assumed for SBP.

PBS	OPC (kt/year)	COM ($/kg)	MSP ($/kg)	DPP (year)	MFR (kt/year)
Glucose	58.63	2.63	2.99	7	151.28
Corn stover	58.53	2.56	3.20	9	314.67
Sugar beet pulp	58.63	3.88	1.37	6	865.18

The lowest MSP value of PBS production ($1.37/kg) from SBP is lower than the market prices of GPPS ($1.72/kg) (taken from www.alibaba.com), while the lowest MSP values estimated when glucose syrup and corn stover were used are higher than the market prices of GPPS. The MFR can be associated with the availability of SBP or corn stover in different geographic regions. The MFR presented in Table 5.6 in the case of SBP (0.86 million t) corresponds to wet SBP with 70% water content, indicating that drying and pelletisation have not been considered. Based on FAOSTAT data for 2018, France, Germany and Poland produced annually 2.34 million t, 1.55 million t and 0.85 million t of SBP pellets with 7% moisture content (FAO, 2018). If the MFR presented in Table 5.6 is expressed as dried SBP pellets with 7% moisture content, then the MFR for SBP would be 0.28 million t for PBS and 0.12 million t for PLA production. Therefore, the utilization of PBS for PBS production is feasible in these three countries as the required SBP quantities are available.

France, Romania and Hungary are the main countries producing corn in EU-28. The ratio of corn stover to corn grain production is 1 kg/kg (Murphy and Kendall, 2013). However, around 0.3 kg corn stover per kg corn grain is assumed to be available for biopolymer production in order to use the remaining corn stover in the agricultural field to minimize soil erosion. Thus, the corn stover that is available annually for biopolymer production is 3.8 million t, 5.6 million t and 2.4 million t in France, Romania and Hungary, respectively (FAO, 2018). Table 5.6 shows that the MFR for corn stover is 0.314 million t for PBS production. This quantity is also available in the specific three countries.

5.4 Life Cycle Assessment

5.4.1 Goal and scope

The aim of the LCA is to assess the environmental performance of PBS production using corn-derived glucose syrup, corn stover and SBP. A “cradle-to-gate” LCA approach has been followed for PBS production considering 1 kg of final product as functional unit. The system boundaries for the LCA includes the cultivation, pretreatment and fractionation of feedstocks, fermentation and purification stages, and polymerization for biopolymer production.

5.4.2 Life Cycle Inventories

Material and energy related data for agricultural cultivation of corn grain, stover and sugar beet are presented in Table 5.7. On-field emissions from corn and sugar beet cultivation, due to the application of agrochemicals and field management, were estimated using various literature-cited methods. In particular, N_2O, CO_2 (Nemecek et al., 2014), NH_3, NO_2 (EEA, 2013) and pesticides (European Commission, 2018) were considered to account for air emissions. NO_3^- and P leaching, P runoff (Emmenegger et al., 2009), pesticides (European Commission, 2018) and heavy metals (Durlinger et al., 2017) were considered to account for emissions to waterbodies. Heavy metals (Durlinger et al., 2017) and pesticides (European Commission, 2018) were considered in relation to soil emissions.

Process design was employed to generate mass and energy inputs and outputs (inventories) for all processes under study. Tables 5.8-5.10 present the PBS production inventories from the three different feedstocks, respectively.

Table 5.7 Main parameters for cultivation of corn and sugar beet (per hectare)

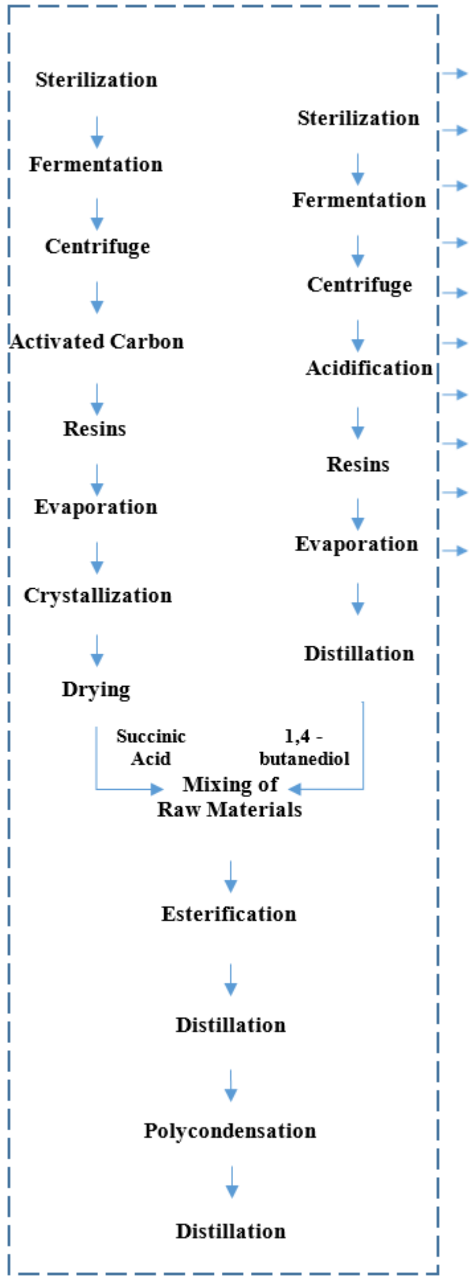
Agriculture (inputs)	**Corn** (Durlinger et al., 2017)	**Sugar beet** (Muñoz et al., 2014)
Yield product	Grain (9.3 t/ha)	Beet (84.65 t/ha)
Yield by-product	Stover (2.79 t/ha)	-
Cattle manure (Solid)	1070 kg	-
Poultry manure (dried)	284 kg	-
Urea, as N	23.6 kg	-
Nitrogen fertiliser, as N	104 kg	103 kg
Phosphate fertiliser, as P	25 kg	30 kg
Potassium fertiliser, as K	61 kg	121 kg
Lime	400 kg	100 g
Sulphur	1.3 kg	-
Pesticides	4.3 kg	3 kg
Seeds	17.8 kg	2 kg
Baling	4 p*	-
Energy	3500 kWh	1680 kWh

*The unit p considers 4 times baling process

Table 5.8 Developed inventory for PBS production from glucose

Raw Materials		
Glucose	2.7700	kg/kg$_{PBS}$
Water	24.6813	kg/kg$_{PBS}$
CO_2	0.1788	kg/kg$_{PBS}$
NaOH	0.2204	kg/kg$_{PBS}$
$MgCO_3$	0.3439	kg/kg$_{PBS}$
HCl	0.5216	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$_{PBS}$
Others	0.0003	kg/kg$_{PBS}$

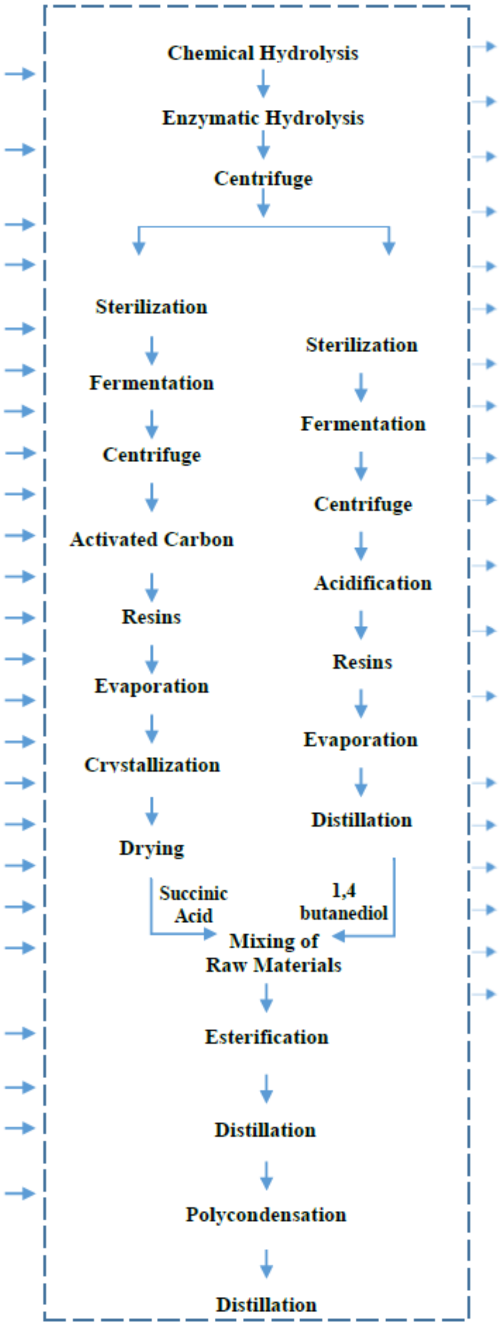
Utilities		
Electricity	1.3832	kWh/kg$_{PBS}$
Cooling Water	213.40	kg/kg$_{PBS}$
Steam (160 °C)	0.1406	kg/kg$_{PBS}$
Steam (254 °C)	4.3288	kg/kg$_{PBS}$



Total output		
PBS	1	kg/kg$_{PBS}$
Succinic acid	0	kg/kg$_{PBS}$
BDO	0.159	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	25.29	kg/kg$_{PBS}$
NaCl	1.31	kg/kg$_{PBS}$
CO_2 (biogenic)	0.914	kg/kg$_{PBS}$

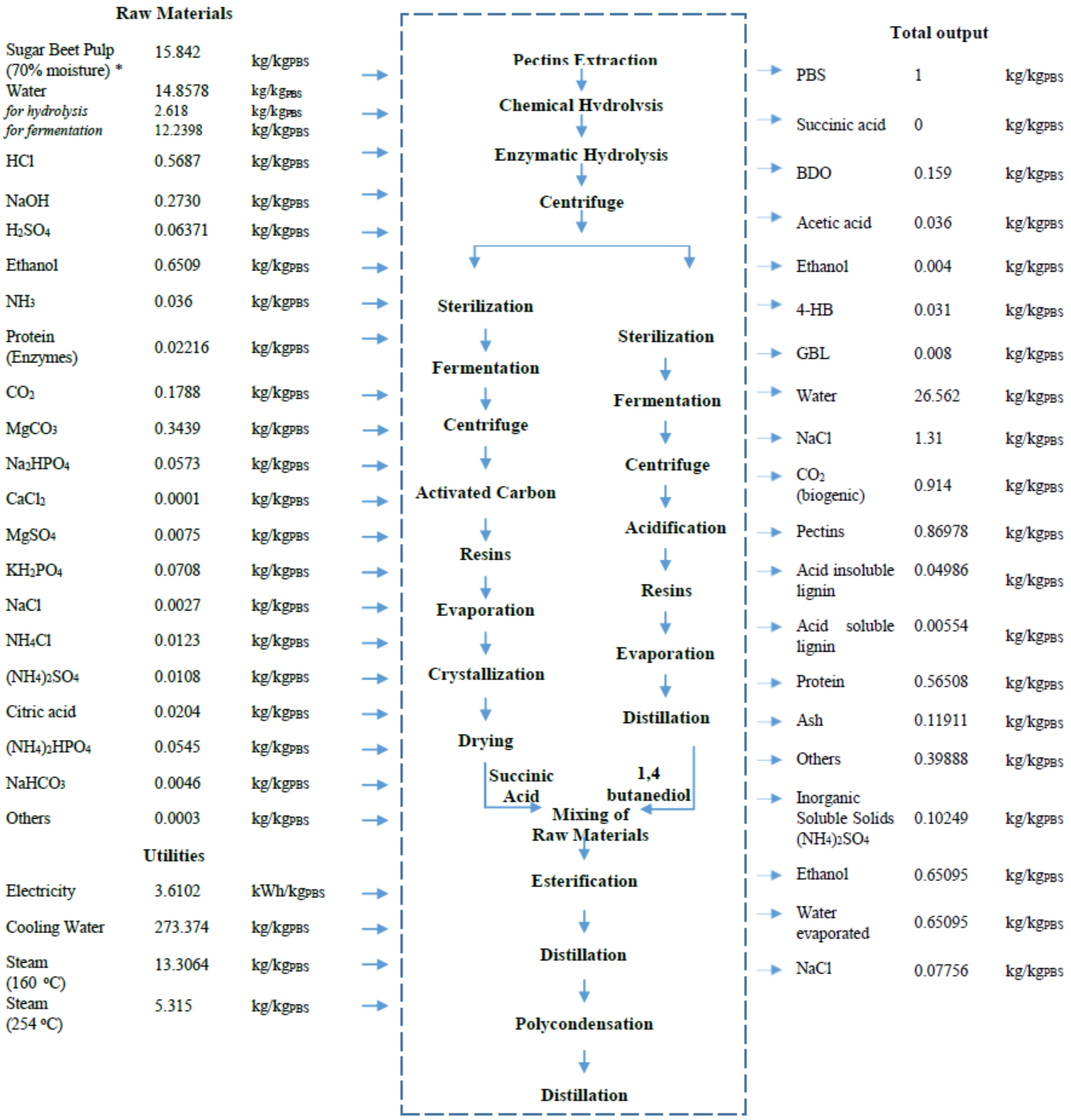
Table 5.9 Developed inventory for PBS production from corn stover

Raw Materials		
Corn Stover	5.7616	kg/kg$_{PBS}$
Water	24.681	kg/kg$_{PBS}$
for hydrolysis	18.2543	kg/kg$_{PBS}$
for fermentation	5.4852	kg/kg$_{PBS}$
H_2SO_4	0.1108	kg/kg$_{PBS}$
NH_3	0.0554	kg/kg$_{PBS}$
Protein (Enzymes)	0.0277	kg/kg$_{PBS}$
CO_2	0.1788	kg/kg$_{PBS}$
NaOH	0.2204	kg/kg$_{PBS}$
$MgCO_3$	0.3439	kg/kg$_{PBS}$
HCl	0.5216	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$_{PBS}$
Others	0.0003	kg/kg$_{PBS}$
Utilities		
Electricity	0.8709	kWh/kg$_{PBS}$
Cooling Water	213.45	kg/kg$_{PBS}$
Steam (160 °C)	0.0000	kg/kg$_{PBS}$
Steam (254 °C)	0.0000	kg/kg$_{PBS}$



Total output		
PBS	1	kg/kg$_{PBS}$
Succinic acid	0	kg/kg$_{PBS}$
BDO	0.159	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$_{PBS}$
Water	26.448	kg/kg$_{PBS}$
NaCl	1.31	kg/kg$_{PBS}$
CO_2 (biogenic)	0.914	kg/kg$_{PBS}$
Sugar Oligomers	0.0831	kg/kg$_{PBS}$
Organic Soluble Solids	0.8033	kg/kg$_{PBS}$
Inorganic Soluble Solids ($(NH_4)_2SO_4$)	0.1385	kg/kg$_{PBS}$
Furfurals	0.0277	kg/kg$_{PBS}$
Cellulose	0.0554	kg/kg$_{PBS}$
Xylan	0.0277	kg/kg$_{PBS}$
Lignin	0.6925	kg/kg$_{PBS}$
Protein	0.1662	kg/kg$_{PBS}$
Other Insoluble Solids	0.2493	kg/kg$_{PBS}$

Table 5.10 Developed inventory for PBS production from sugar beet pulp



Raw Materials		
Sugar Beet Pulp (70% moisture) *	15.842	kg/kg_{PBS}
Water	14.8578	kg/kg_{PBS}
for hydrolysis	2.618	kg/kg_{PBS}
for fermentation	12.2398	kg/kg_{PBS}
HCl	0.5687	kg/kg_{PBS}
NaOH	0.2730	kg/kg_{PBS}
H_2SO_4	0.06371	kg/kg_{PBS}
Ethanol	0.6509	kg/kg_{PBS}
NH_3	0.036	kg/kg_{PBS}
Protein (Enzymes)	0.02216	kg/kg_{PBS}
CO_2	0.1788	kg/kg_{PBS}
$MgCO_3$	0.3439	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}
Others	0.0003	kg/kg_{PBS}
Utilities		
Electricity	3.6102	kWh/kg_{PBS}
Cooling Water	273.374	kg/kg_{PBS}
Steam (160 °C)	13.3064	kg/kg_{PBS}
Steam (254 °C)	5.315	kg/kg_{PBS}

Total output		
PBS	1	kg/kg_{PBS}
Succinic acid	0	kg/kg_{PBS}
BDO	0.159	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}
Water	26.562	kg/kg_{PBS}
NaCl	1.31	kg/kg_{PBS}
CO_2 (biogenic)	0.914	kg/kg_{PBS}
Pectins	0.86978	kg/kg_{PBS}
Acid insoluble lignin	0.04986	kg/kg_{PBS}
Acid soluble lignin	0.00554	kg/kg_{PBS}
Protein	0.56508	kg/kg_{PBS}
Ash	0.11911	kg/kg_{PBS}
Others	0.39888	kg/kg_{PBS}
Inorganic Soluble Solids $(NH_4)_2SO_4$	0.10249	kg/kg_{PBS}
Ethanol	0.65095	kg/kg_{PBS}
Water evaporated	0.65095	kg/kg_{PBS}
NaCl	0.07756	kg/kg_{PBS}

*water content from SBP: 11.089 kg_{water}/kg_{PBS}

Cultivation of corn grain and stover

This process was adapted from the Agrifootprint® LCA database (Durlinger et al., 2017). The corn cultivation process is a conventional agricultural system that makes use of both chemical and organic fertilizers, in addition to pesticides and soil additives, such as lime and sulphur. It has been assumed that corn is cultivated in France with an annual yield of 9.3 t/ha. France was chosen due to the high availability in corn stover (Wietschel et al., 2019). It was assumed that only 30% (2.79 t/ha) of the corn stover is harvested and baled each year. Stover is an important soil conditioner and agent against soil erosion. Therefore, care must be taken not to compromise the quality of the soil

(Murphy and Kendall, 2013). The baling process is included in the system boundary. As this process delivers two products (corn grain and stover), economic allocation was chosen to assign the environmental burdens for each product. Corn grain and stover market prices were taken as $174.5/t (FAO, 2018) and $58.5/t (Humbird et al., 2011).

Corn grain refining and starch hydrolysis

Inventory data for corn grain processing has been taken from Renouf et al. (2008). The wet milling process is employed involving enzymatic starch hydrolysis. Impurities are initially removed from the corn grains. The wet milling process separates the germ from the kernel and the starch from the gluten leading to the production of various co-products such as corn oil, corn gluten feed and corn gluten meal (Ramirez et al., 2008). Enzymatic hydrolysis converts the starch into glucose at 95% conversion yield. As this process generates many co-products, economic allocation was applied to allocate the environmental impacts of each product. The market prices for glucose syrup, corn oil, gluten feed and gluten meal were considered as $230/t, $624/t, $123/t and $518/t, respectively (United States Department of Agriculture and Economic Research Service, 2018).

Cultivation of sugar beet

The sugar beet cultivation process was adapted from Muñoz et al. (2014). The farming stage is a conventional agricultural system that makes use of chemical fertilizers, pesticides and the soil additive lime. It is considered that sugar beet is cultivated in France with an annual yield of 84 t/ha. France was chosen because it is one of the main producers of sugar beet in Europe (Eurostat, 2019a). During the harvesting process, the leaves are separated from the beet. In this study, it was assumed that 100% of the beet leaves are left in the field as soil conditioning. Therefore, no allocation is necessary in this process, as it only delivers sugar beet as a product. The harvested sugar beet goes to a sugar processing plant.

Sugar beet pulp production

Inventory data concerning the production of SBP was adapted from Renouf et al. (2008). The beet root is washed to remove impurities (e.g. sand and stones) and subsequently cut into small “cosettes” that are diluted in hot water in a process called diffusion. SBP is the by-product of the diffusion process. The raw juice goes through a purification process with the addition of lime and carbon dioxide to remove impurities from the beet juice, producing lime fertilizer as a by-product. In a traditional sugar mill, the purified raw juice undergoes a crystallization process that produces sucrose and molasses as by-product. However, this process does not consider the recovery of molasses. The SBP by-product is mainly used as animal feed in the form of dry pellets. However, industrial fermentation processes may rely on wet beet pulp that has a very low market value. The market prices considered in this study for the economic allocation are \$370/t (United States Department of Agriculture and Economic Research Service, 2018), \$116/t (Durlinger et al., 2017) and \$5/t (www.thebeefsite.com) for sugar beet juice, lime fertiliser and wet SBP, respectively. The market price of beet juice was considered the same as sucrose (Tomaszewska et al., 2018).

5.4.3 Life Cycle Impact Assessment

LCA was carried out using two different methodologies, CML 2001 (Jan. 2016) and ReCiPe 1.08 (Guinée et al., 2002). The CML methodology was used as the most cited methodology for environmental assessment (Ioannidou et al., 2020) to compare the environmental impact of PBS production estimated in this study using the three feedstocks with literature-cited data. The ReCiPe methodology was employed for the estimation of environmental externality costs because this method is used in the LCC methodology reported by De Bruyn et al. (2018) (see section 5.5). The system boundaries, the functional unit and the assumptions are the same to those considered in the CML methodology.

Figure 5.5 presents the LCA indicators (GWP 100 years, ADP fossil, AP, EP and HTP) for PBS production using the three feedstocks and utilizing the CML 2001 (Jan. 2016) methodology. In the case of corn stover, combustion of lignin for energy production has been considered. The environmental performance of GPPS has been also presented as the fossil counterparts of PBS.

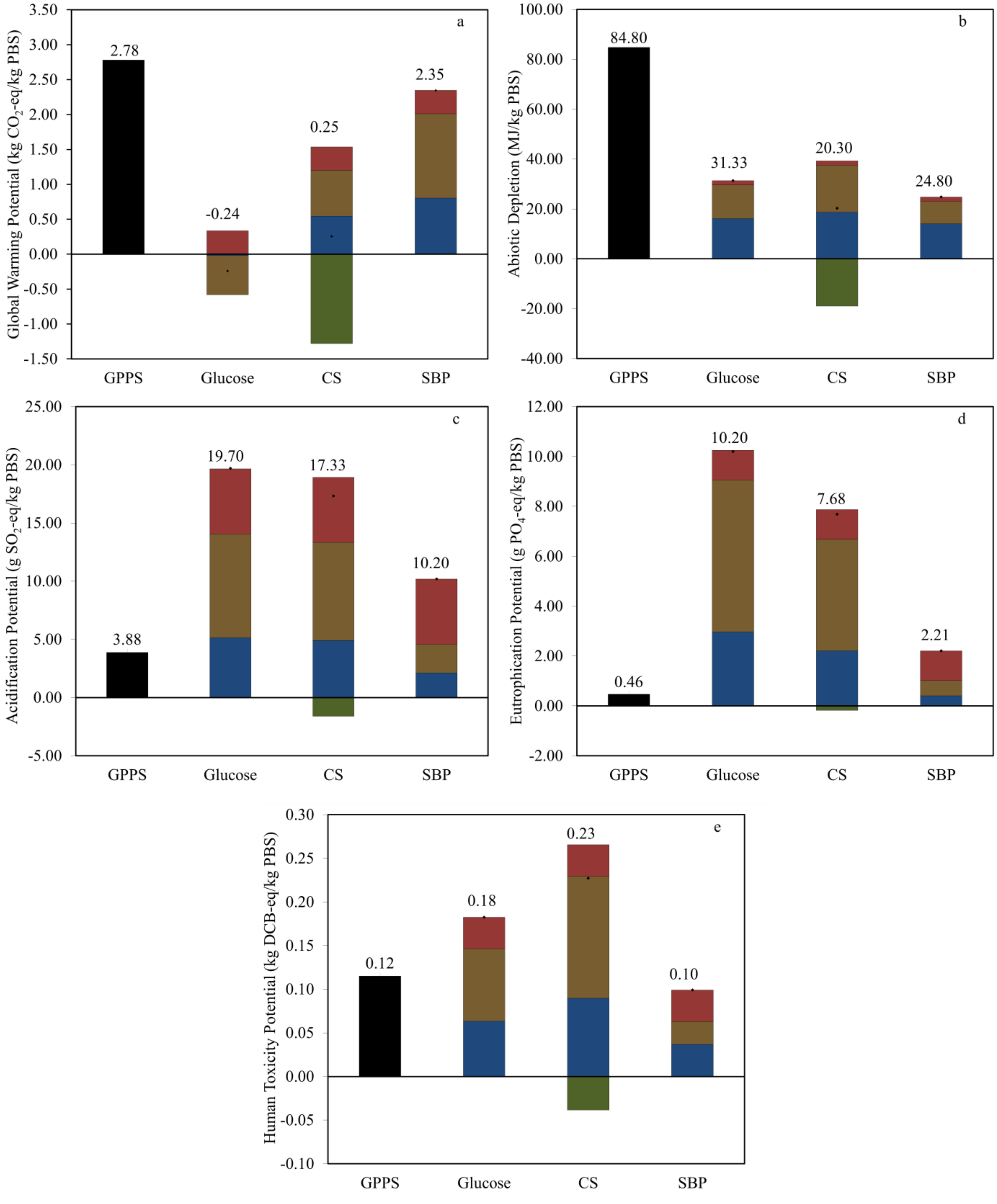


Figure 5.5 LCA for PBS production from glucose, corn stover and SBP. The environmental impacts of the fossil counterpart (GPPS) is also presented. Bars have been color-coded based on the contribution of each production stage: diamond – net total impact, black – fossil-based counterpart, blue – succinic acid, brown – BDO, red – polymerization, green – savings from lignin combustion. Monomer production include the environmental impacts of pretreatment, fermentation and DSP stages. Labels indicate the net total impact of each process.

The greenhouse gas (GHG) emissions of PBS production from glucose syrup, corn stover and SBP are -0.24 kg CO_2-eq/kg$_{PBS}$, 0.25 kg CO_2-eq/kg$_{PBS}$ and 2.35 kg CO_2-eq/kg$_{PBS}$, respectively. The GHG emissions of the bioprocess producing PBS is 2.31 kg CO_2-eq/kg$_{PBS}$ considering only fermentation, DSP and polymerization stages, excluding the impact of the raw material. The negative environmental impact of GWP in the case of glucose syrup occurs because the biogenic CO2 of corn cultivation (-2.55 kg CO_2-eq/kg$_{PBS}$) is taken into consideration. The same assumption has also been considered for corn stover, as agricultural residue of corn cultivation. However, the pretreatment of corn stover and the lower economic allocation owing to the lower price of corn stover than corn grain, increases the environmental impact to 1.54 kg CO_2-eq/kg$_{PBS}$. The combustion of lignin for energy generation plays a vital role in the final impact, as the lower consumption of utilities in the bioprocess decreases the final impact to 0.25 kg CO_2-eq/kg$_{PBS}$. SBP has the highest environmental impact among the three feedstocks. Biogenic CO_2 is also taken into account due to sugar beet cultivation. However, the high utility requirements in SBP pre-treatment contributes to a high environmental impact of the whole process (2.35 kg CO_2-eq/kg$_{PBS}$). It should be stressed though that allocation of GHG emissions and other environmental impacts to pectin should be carried out when marketable products are developed.

Patel et al. (2018) reported a GWP of approximately 2.2 kg CO_2-eq/kg$_{PBS}$ for PBS production from corn grain, while a GWP of approximately 0.77 kg CO_2-eq/kg$_{PBS}$ was reported when corn stover was used (without considering the conversion of PBS into a specific end-product in both cases). The results reported by Patel et al. (2018) have been estimated without taking into account the biogenic CO_2 associated with corn cultivation. If the results of this study are expressed without taking into consideration biogenic CO_2 from corn cultivation, the GHG emissions are 2.31 kg CO_2-eq/kg$_{PBS}$, which is similar to the reported value for PBS production from corn grain. Tecchio et al. (2016) reported that GHG emissions of PBS production range from 4.17 to 6.34 kg CO_2-eq/kg$_{PBS}$. The reported environmental impacts are higher than the results estimated in this study. The difference is mainly attributed to the fact that the PBS considered by Tecchio et al. (2016) is partly bio-based, i.e it is obtained only from bio-based succinic acid while the BDO is produced from fossil resources. The GWP of the bio-based PBS produced from the three feedstocks is lower than its petroleum-based counterpart GPPS (2.78 kg CO_2-eq/kg$_{GPPS}$ according to PlasticsEurope). Moreover, the GWP of the fossil-derived PBS (6.6 kg CO_2-eq/kg$_{PBS}$) is significantly higher than the bio-based PBS (Moussa et al., 2012).

The ADP fossil varies between 20.3 and 31.33 MJ/kg$_{PBS}$ (Figure 5.5b). The fossil-energy requirements of the PBS production process are 15.8 MJ/kg$_{PBS}$. The lowest ADP fossil occurs when corn stover is employed, as lignin combustion reduced fossil-energy requirements. The ADP fossil of GPPS is 84.80 MJ/kg_{GPPS} (PlasticsEurope), 2.7-fold higher than the ADP fossil of PBS production from glucose syrup. Patel et al. (2018) reported ADP fossil values for PBS production of 75 MJ/kg_{PBS} for corn grain and 50 MJ/kg_{PBS} for corn stover. Tecchio et al. (2016) reported an ADP fossil value for PBS production of 140 MJ/kg_{PBS}, a value equal to the fossil-based PBS (Moussa et al., 2012).

AP (Figure 5.5c) corresponds to 19.7 g SO_2-eq/kg_{PBS}, 17.33 g SO_2-eq/kg_{PBS} and 10.2 g SO_2-eq/kg_{PBS} for glucose syrup, CS and SBP, respectively. EP (Figure 5.5d) corresponds to 10.2 g PO_4-eq/kg_{PBS}, 7.68 g PO_4-eq/kg_{PBS} and 2.21 g PO_4-eq/kg_{PBS} for glucose, CS and SBP, respectively. PBS production from glucose syrup exhibits the worst AP and EP performance. The AP and EP values of GPPS are 3.88 g SO_2-eq/kg_{GPPS} and 0.46 g PO_4-eq/kg_{GPPS}, which are significantly lower than PBS production. The cultivation of the agricultural crops has a significant contribution in these two impact categories and therefore the AP and EP values of the fossil-based polymer are lower. HTP (Figure 5.5e) corresponds to 0.18 kg DCB-eq/kg_{PBS}, 0.23 kg DCB-eq/kg_{PBS} and 0.10 kg DCB-eq/kg_{PBS} for glucose syrup, CS and SBP, respectively. The HTP of GPPS is 0.12 kg DCB-eq/kg_{GPPS}. SBP presents the lowest HTP value among the three feedstocks and GPPS, as sugar beet depicts better environmental performance than corn. It should be mentioned that to the best of our knowledge, there are no literature-cited data on AP, EP and HPT for bio-based PBS production.

5.5 Life Cycle Costing

Based on the LCC methodology of De Bruyn et al. (2018), the ReCiPe 1.08 methodology was used for the estimation of environmental assessment indicators (Table 5.11) that was subsequently converted into monetized values (Table 5.12) (Goedkoop et al., 2013). The total cost of externalities for GPPS is lower than the cost of externalities for PBS production from all three feedstocks. The indicators that predominantly contribute to the cost of externalities for GPPS are climate change, particulate matter formation, photochemical oxidant formation and terrestrial acidification. In the case of PBS, the most influential indicators are climate change (mainly when SBP is used), particulate matter formation, terrestrial acidification and terrestrial ecotoxicity. Among the three renewable feedstocks, the use of SBP led to the lowest total environmental externality costs ($0.346/$kg_{PBS}$).

Table 5.11 Environmental impact of GPPS and PBS production from various feedstocks (unit/kg) using the ReCiPe 1.08 methodology

Impact category	**Unit**	**GPPS**	**PBS (glucose)**	**PBS (CS)**	**PBS (SBP)**
Climate change (CC)	kg CO_2-eq.	2.78	-0.22	0.75	2.34
Freshwater ecotoxicity (FEC)	kg 1,4 DB-eq.	5.96×10^{-4}	5.72×10^{-3}	3.82×10-^{3}	7.30×10^{-4}
Freshwater eutrophication (FEU)	kg P-eq.	3.01×10^{-6}	7.17×10^{-5}	-4.60×10^{-6}	6.94×10^{-5}
Human toxicity (HT)	kg 1,4-DB-eq.	7.06×10^{-2}	1.62×10^{-1}	1.17×10^{-1}	1.05×10^{-1}
Ionizing radiation (IR)	U235-eq.	8.71×10^{-2}	3.37×10^{-1}	3.75×10^{-1}	3.97×10^{-1}
Marine ecotoxicity (MEC)	kg 1,4-DB-eq.	1.20×10^{-3}	2.59×10^{-3}	1.76×10^{-3}	7.41×10^{-4}
Marine eutrophication (MEU)	kg N-eq.	1.92×10^{-4}	1.53×10^{-2}	9.08×10^{-3}	2.36×10^{-3}
Ozone depletion (OD)	kg CFC-11-eq.	5.45×10^{-15}	8.63×10^{-14}	7.02×10^{-10}	4.39×10^{-10}
Particulate matter formation (PM)	kg PM_{10}-eq.	1.30×10^{-3}	4.23×10^{-3}	2.58×10^{-3}	2.12×10^{-3}
Photochemical oxidant formation (POF)	kg NMVOC-eq.	3.06×10^{-2}	1.00×10^{-2}	5.81×10^{-3}	5.70×10^{-3}
Terrestrial acidification (TA)	kg SO_2-eq.	4.06×10^{-3}	1.70×10^{-2}	1.01×10^{-2}	7.16×10^{-3}
Terrestrial ecotoxicity (TE)	kg 1,4-DB-eq.	1.28×10^{-5}	7.78×10^{-3}	5.38×10^{-3}	2.88×10^{-4}

Table 5.12 Cost of externalities expressed as $/kg for GPPS and PBS production from glucose syrup, corn stover and SBP

Impact category	**GPPS**	**PBS (glucose)**	**PBS (CS)**	**PBS (SBP)**
Climate change	0.184	-0.015	0.050	0.155
Freshwater ecotoxicity	2.51×10^{-5}	2.41×10^{-4}	1.61×10^{-4}	3.08×10^{-5}
Freshwater eutrophication	6.54×10^{-6}	1.56×10^{-4}	-9.99×10^{-6}	1.51×10^{-4}
Human toxicity	0.008	0.019	0.014	0.012
Ionising radiation	0.005	0.018	0.020	0.021
Marine ecotoxicity	1.04×10^{-5}	2.23×10^{-5}	1.52×10^{-5}	6.39×10^{-6}
Marine eutrophication	0.001	0.056	0.033	0.009
Ozone depletion	1.93×10^{-13}	3.06×10^{-12}	2.49×10^{-8}	1.56×10^{-8}
Particulate matter formation	0.060	0.194	0.118	0.097
Photochemical oxidant formation	0.041	0.013	0.008	0.008
Terrestrial acidification	0.024	0.099	0.058	0.042
Terrestrial ecotoxicity	1.30×10^{-4}	0.079	0.055	0.003
Total	**0.322**	**0.463**	**0.356**	**0.346**

Figure 5.6 presents the life cycle costs of PBS and its fossil counterpart. The MSP presented in Table 5.6 and the total externality costs presented in Table 5.12 has been used for the estimation of life cycle costs for PBS production. The MSP was used in order to incorporate the effect of biorefinery development in the overall assessment where the revenue from crude pectin-rich extract sales has been considered. The market price of GPPS ($1.72/kg) and the total externality cost presented in Table 5.12 has been used for the estimation of the life cycle cost of GPPS. Figure 5.6 illustrates that the life cycle costs of PBS is lower than GPPS, only in the case of SBP where the crude pectin-rich extract has been considered as co-product at market prices of $4/kg. The life cycle cost of SBP-derived PBS is 13% lower that the life cycle cost of GPPS. These results do not include the EoL phase and thus could be further improved considering that the fossil-derived products have a higher environmental impact than bio-based products in the EoL stage. In any case, it is illustrated that only biorefinery concepts can lead to sustainable production of PBS provided that marketable applications are developed for pectin-rich extracts.

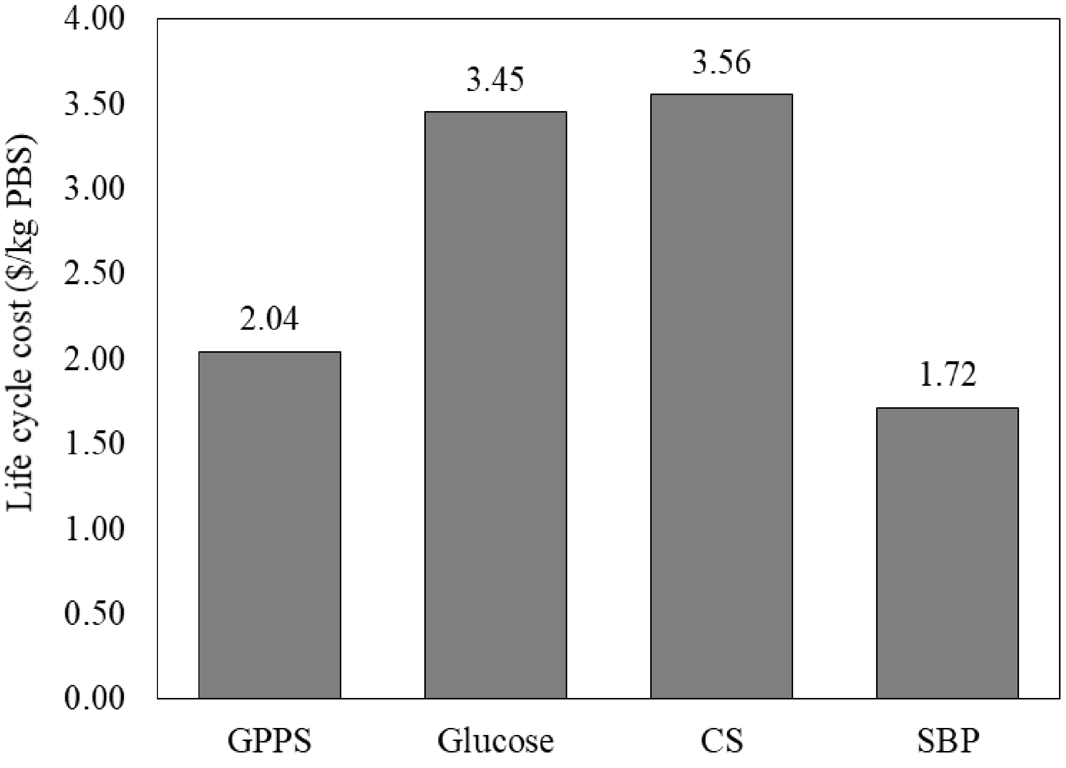


Figure 5.6 Life cycle costing of PBS production considering the sum of the MSP estimated when each biopolymer is derived from glucose syrup, corn stover or SBP (Table 5.6) and the total externality costs presented in Table 5.12. The life cycle cost of fossil-derived counterpart (GPPS) has been estimated considering the sum of market price and the total external cost presented in Table 5.12.

5.6 Profitability risk assessment

The analysis is carried out by developing a techno-economic model (based on the results of process design and TEA) that evaluates the sensitivity to varying process and economic parameters considering that PBS is sold at the current market price of its fossil counterpart (\$1.72/kg_{GPPS}). A single-point sensitivity was initially carried out using MATLAB by changing one variable at a time with case-specific limits. The most important variables (i.e., fermentation duration, unitary cost of steam, electricity cost, succinic acid market price, sugar to BDO conversion yield) identified via single-point sensitivity are presented in Table 5.13, while their distribution curves are presented in Figure 5.7. Monte-Carlo simulations were subsequently carried out to identify the probability to develop a profitable process for PBS production by estimating the NPV using the most important variables and their corresponding value ranges presented in Table 5.13. The design parameters used in the techno-economic model are the ones presented in the process design section, while case-specific design parameters are presented in Table 5.13. It should be pointed out that the total sugar to BDO (0.32, 0.40, 0.48 g/g) conversion yields have been varied at these three distinct values.

Table 5.13 Process variables, design parameters and assumed PBS market price used in Monte-Carlo simulations for risk assessment of process profitability of PBS production

Process variables	Range	Design parameters	Values
Fermentation duration of BDO production process (h)	20-50	Optimum PBS annual production capacity (kt/year)	58.6
Cost of steam (\$/t)	9.45-9.61	BDO annual production capacity (kt/year)	40
Electricity cost (\$/kWh)	0.0674-0.08	Succinic acid annual production capacity (kt/year)	40
Succinic acid market price (\$/kg)	1.0-2.0	BDO concentration at the end of fermentation (kg/m^3)	125
Total sugar to BDO conversion yield (kg_{BDO}/kg_{TS})	0.32, 0.4, 0.48		
Assumed PBS market price equal to GPPS (\$/kg_{PBS})		1.72	

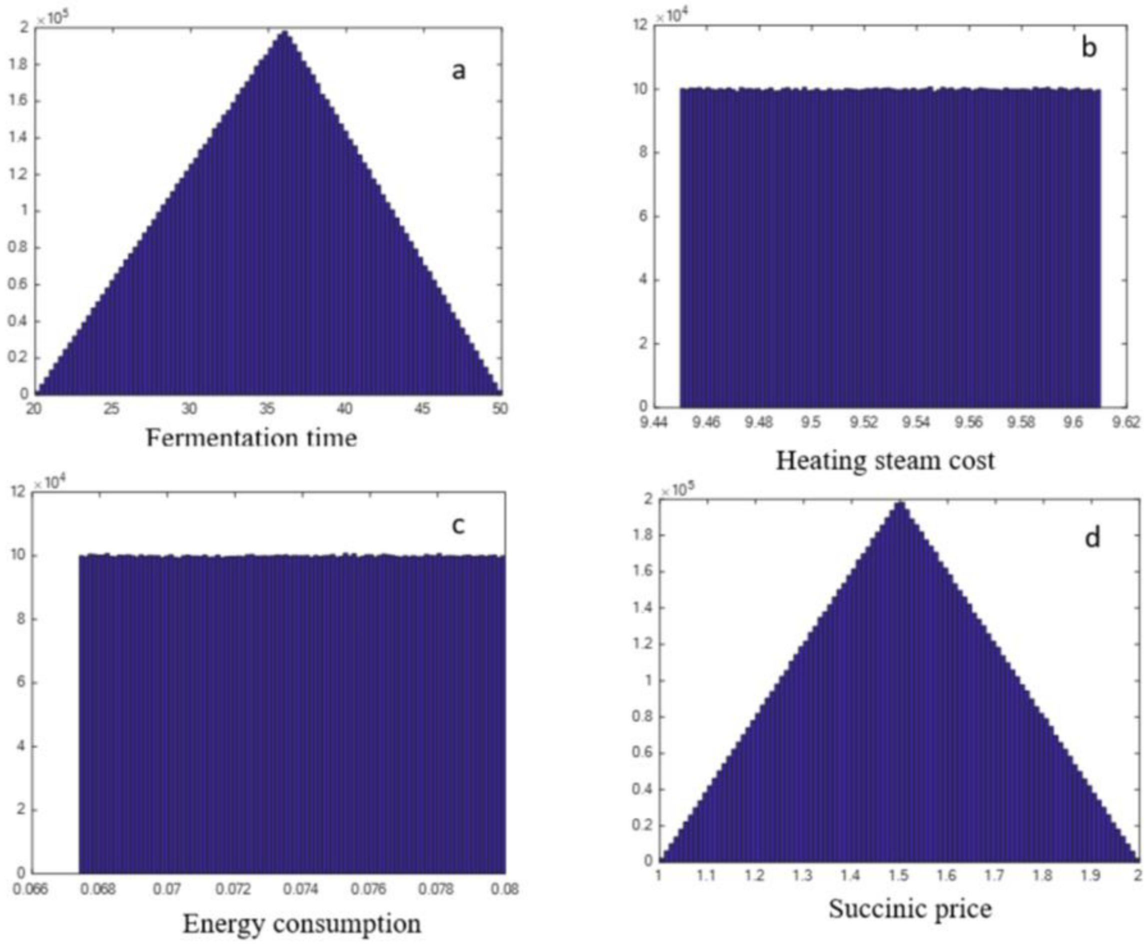


Figure 5.7 Input uncertainties. a) 1,4-BDO fermentation time (h), b) heating steam cost ($/t), c) electricity cost ($/kWh), d) succinic market price ($/kg).

The Monte-Carlo simulations carried out in the case of PBS production from SBP considered four different market prices for crude pectin extracts ($3, 4, 5 and 6 /$\text{kg}_{\text{pectin}}$). Figure 5.8a presents the probability of NPV to be positive, and thus the process to be profitable, in the case of PBS production considering the market price of GPPS and the lowest sugar to BDO conversion yield (0.32 $\text{g}_{\text{BDO}}/\text{g}_{\text{TS}}$). The probability for positive NPV is 100% when the pectin selling price is higher than $4/kg, while the probability to achieve positive NPV is 98% when the pectin selling price is $3/kg.

Figure 5.8b shows that the probability of NPV to be positive is zero when PBS and is produced from corn stover considering three different fermentation yields. Figure 5.8c shows that the probability to achieve positive NPV is zero when PBS is produced from glucose syrup considering three different glucose syrup market prices (170, 230 and 290 $/t). Thus, PBS production from corn stover and glucose syrup will not be profitable if PBS is sold at the market price of GPPS. The main conclusion of the risk assessment study is that only the potential development of a biorefinery concept using SBP could lead to a profitable process when the biopolymer is sold at price equal to those of its fossil counterpart. This would be feasible though as long as marketable products from crude pectin-rich extracts are developed.

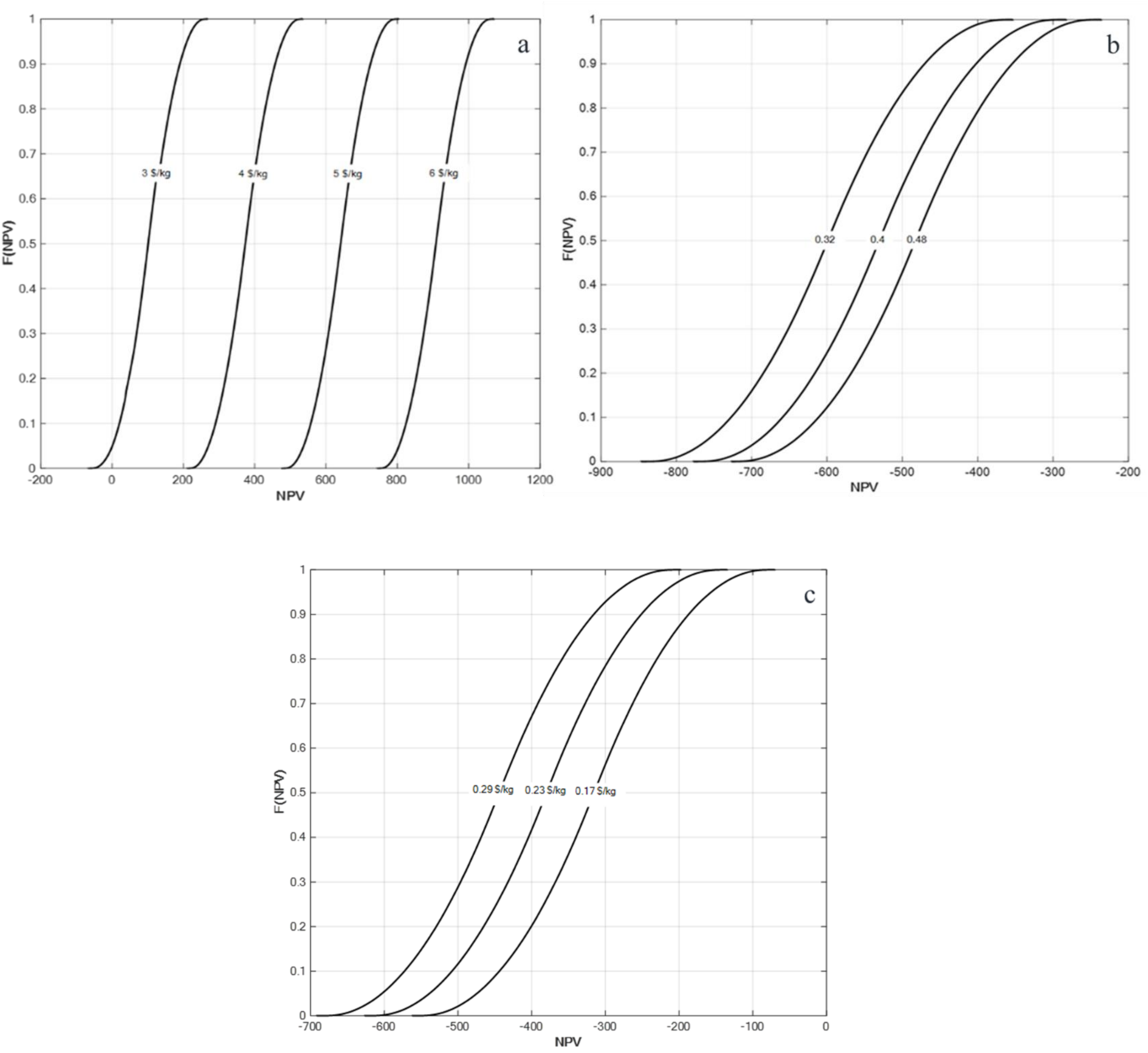


Figure 5.8 Probability to achieve positive NPV (million $) for PBS production from: a) SBP at different market prices of crude pectin extracts ($3-6/kg pectin) and at the lowest BDO conversion yield (0.32 g_{BDO}/g_{TS}) , b) corn stover at three different total sugar to BDO conversion yields, namely 0.32 g_{BDO}/g_{TS}, 0.4 g_{BDO}/g_{TS} and 0.48 g_{BDO}/g_{TS} and c) glucose syrup at the highest conversion yield (0.48 g_{BDO}/g_{TS}) and at three different glucose market prices ($170/t, $230/t, $290/t). The Monte-Carlo simulations have been carried out considering a market prices of PBS equal to those of GPPS ($1.72/kg).

Chapter 6 Sustainability assessment of succinic acid production from OFMSW using an electrochemical membrane bioreactor

6.1 Introduction

SA has been considered as one of the most important platform chemicals in the circular bioeconomy era (Chandel and Segato, 2021). Its global production capacity in 2021 was 16,000-30,000 t, with the major manufacturing companies being BASF, Myriant and Corbion among others (Mordorintelligence, 2021). SA could be used in various applications, including food, pharmaceuticals, biopolymers, such as poly(butylene succinate) and polyester polyols, lubricants and adhesives. Despite the high commercial prospects of industrial SA production and the significant investments that started around 2009, the commercialization of SA did not meet the expectations mainly due to the limited use of this intermediate into final products (Bettenhausen, 2021). The higher market price of bio-based succinic acid ($2.9/kg) as compared to the combined bio- and fossil-based succinic acid ($2.5/kg) (Stylianou et al., 2021), is one of the issues that impedes bio-based succinic acid market growth.

Minimizing manufacturing costs is crucial for bio-based SA to compete with petro-based SA production. The cost of downstream separation and purification (DSP) of SA accounts for around 60% of the total production costs (Kurzrock and Weuster-Botz, 2010). The main DSP processes for industrial SA recovery are crystallization (Reverdia) (Van De Graaf et al., 2010), Mg-based process (BASF and Corbion), precipitation (Myriant) and electrodialysis (used in the past by BioAmber) (Jansen and van Gulik, 2014). SA production can be achieved either by bacterial cultures at neutral pH or by yeast cultures at low pH during fermentation where the acidification step is no longer required. Although the conventional industrial DSP technologies offer many advantages, including few unit operations, low technological barriers and mature commercialization level, the high energy and chemical requirements increase the succinic acid production cost (Jansen and van Gulik, 2014). Novel DSP technologies should be developed to minimise utility and chemical requirements and integrate fermentative SA production (preferably at low pH) with SA extraction and purification.

Membrane electrolysis is an electrochemical extraction technology that has been employed for carboxylate recovery. Bioreactor operation could be integrated with an electrolysis cell using an anion exchange membrane by recirculating the fermentation broth through the cathode compartment during fermentation. As a consequence, anions are transported across the anion exchange membrane under the driving force of an electrical potential into the anode compartment. An integrated electrochemical membrane bioreactor (EMB) has been used for simultaneous organic acid (e.g. succinic acid, caproic acid, acetic acid) production and in situ separation (Gildemyn et al., 2015; Pateraki et al., 2019b). The EMB leads to simultaneous separation, acidification and concentration of SA in the anode compartment, while less DSP stages are required, including cell removal by centrifugation, decoulorisation using activated carbon and acidification of the succinate salts produced in conventional bacterial cultures. Furthermore, the production of OH- during water reduction in the cathode compartment leads to pH regulation during fermentation and therefore lower NaOH requirements. These advantages lead to the reduction of chemical consumption for SA recovery and thus to lower production cost and environmental impacts.

It has been also reported that the utilization of an EMB can also improve the fermentation efficiency of succinic acid production. Pateraki et al. (2019) reported that using an EMB in SA production by the bacterial strain *Basfia succiniciproducens* led to 45% higher SA production, 15% higher yield, 32% higher productivity and 19.3% lower NaOH consumption than conventional bacterial cultures. Stylianou et al. (2023) used the EMB with an engineered *Yarrowia lipolytica* yeast for the production of 23% higher SA production, 16% higher yield, 35% lower NaOH consumption and no significant change in productivity than conventional yeast cultures. The SA-rich solution from the anolyte could be purified via evaporation, crystallisation and drying at 95% recovery yield and purity higher than 99.9% (Stylianou et al., 2021)

Industrial SA purification with the EMB technology requires high electricity consumption. Stylianou et al. reported that the coulombic efficiency and electricity requirements of SA extraction were in the range of 56.8-73.5% and 2.1-3.4 kWh/kg_{SA}. Thus, the utilisation of renewable electricity (e.g. photovoltaics) will minimize significantly the environmental impact of the whole process. Furthermore, the use of yeasts rather than bacteria cultures for SA production can lead to higher coulombic efficiencies for the electrolysis membrane operation. The absence of CO_2 supply when yeast cultures are used for SA production results in reduced energy requirements as no competing anion species (e.g. carbonic acid) are extracted through the anion exchange membrane.

This chapter presents the sustainability assessment of SA production using an EMB for simultaneous SA production and extraction using a genetically engineered *Y. lipolytica* strain cultivated on hydrolysates derived from the organic fraction of municipal solid waste (OFMSW). Sugar-rich OFMSW hydrolysates have been used widely for fermentative production of various bio-based chemicals and polymers (e.g. succinic acid, lactic acid, polyhydroxyalkanoate), hydrogen and biogas (López-Gómez et al., 2019; Song et al., 2021; Sousa et al., 2021; Stylianou et al., 2020; Yahya et al., 2021) due to the widespread availability of this feedstock in EU countries14. Process design, techno-economic assessment (TEA), profitability risk assessment (PRA) using

Monte-Carlo simulations and Life Cycle Assessment (LCA) have been carried out to show the sustainability potential of the proposed process. The novelty of this study lies on the demonstration that the proposed EMB-based technology improves the sustainability aspects of SA production when compared to the performance of conventional SA production processes.

6.2 Description of the process

Figure 6.1 illustrates the process flow diagrams for OFMSW hydrolysate production (Area 100) and the fermentation and DSP stages of SA production and purification using the EMB technology (Area 200). Material and energy balances and sizing of unit operations have been carried out via process design using the UniSim (Honeywell) software. The plant operates 7,920 h/year, while process design and economics have been carried out at various annual plant capacities (5,000 – 100,000 t_{SA}/year). The functional unit employed for expressing economic and environmental performance of the process is 1 kg SA.

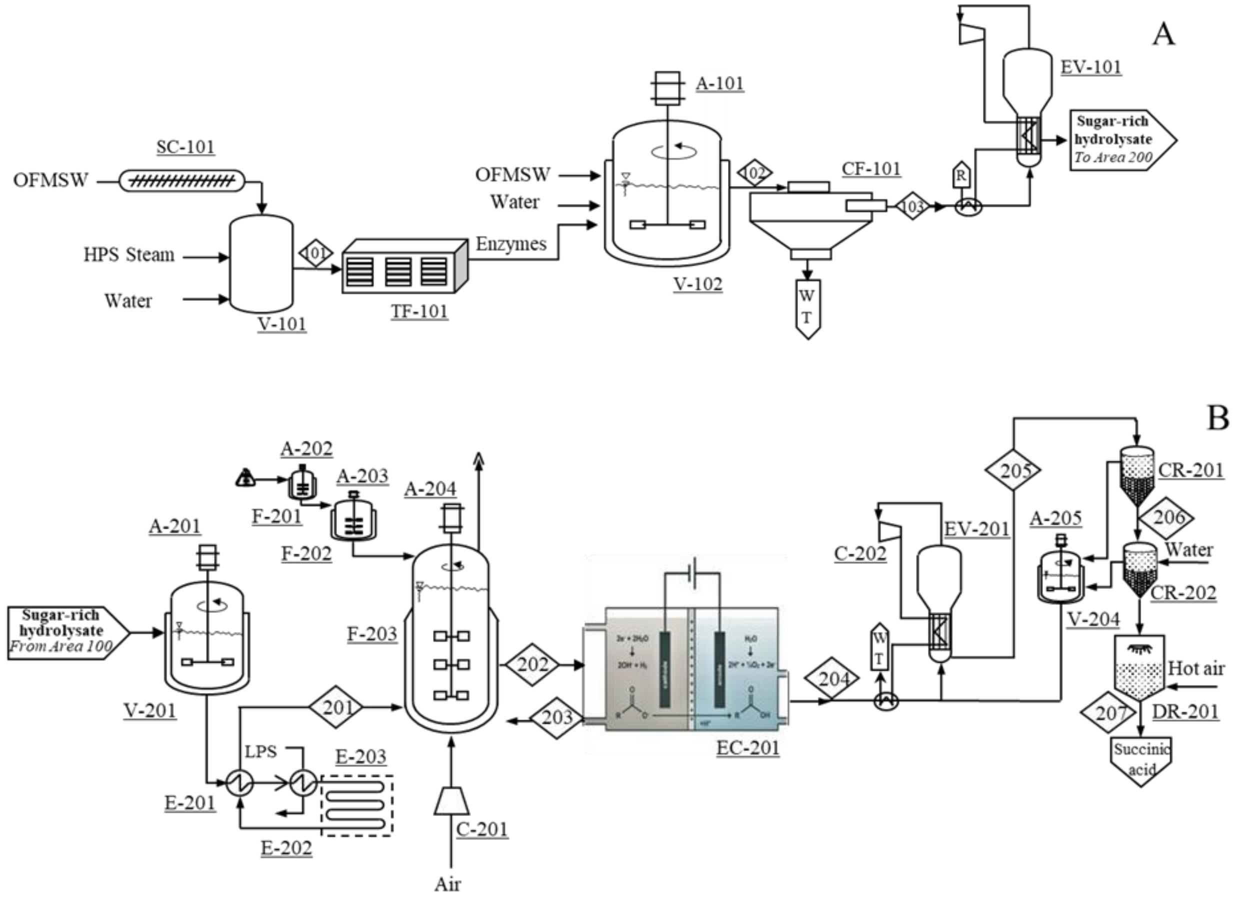


Figure 6.1 Process flow diagram of succinic acid production from OFMSW including enzyme production and OFMSW hydrolysis (Area 100) (A) and succinic acid production via fermentation followed by DSP (Area 200) (B)

The OFMSW composition used in this study has been presented by Stylianou et al. (2020), considering an average 30% of OFMSW content in MSW and 75% moisture content. OFMSW hydrolysis has been carried out using crude enzymes produced via solid state fermentation (SSF) with the fungal strain *Aspergillus awamori* using OFMSW as solid support. The onsite production of crude enzymes by SSF has been reported by Ladakis et al. (2022). Figure 6.1A illustrates the production of crude enzymes by SSF and the enzymatic hydrolysis of OFMSW with crude enzymes. Area 100 begins with the production of crude enzymes via SSF (TF-101) that lasts for 81 h to achieve the highest enzyme activities. The required OFMSW stream for SA production is mixed with the SSF solids and hydrolysis is performed (V-102) for 20 h at 50°C. Temperature control was achieved with low-pressure steam (LPS). After hydrolysis, a centrifugal separator (CF-101) was employed to separate the residual solids from the sugar-rich OFMSW hydrolysate. A fraction of the hydrolysate (stream 103) was concentrated up to 700 g/L via evaporation (EV-101). The OFMSW hydrolysate was used at the beginning of fermentation as feedstock, while the concentrated OFMSW hydrolysate (700 g/L sugars) was used as feeding solution.

Area 200 presents the SA production and DSP process using the EMB system (Figure 6.1B). The OFMSW hydrolysate from Area 100 and the required nutrients were initially sterilized in continuous mode using three heat exchangers (E-201, E-202, E-203). The fermentation medium is subsequently fed into the bioreactor (F-203). The fermentation efficiency used in this study has been reported by Stylianou et al. (2023) (66.7 g_{SA}/L, 0.51 g_{SA}/gtotal sugars yield and 0.78 g/(L·h) productivity). The optimization of bioreactor design was focused on the estimation of loading duration, uploading duration, bioreactor volume, number of bioreactors per batch and batches per year. Fermentation efficiency parameters were used in bioreactor design optimization with the mathematical software GAMS according to the methodology described by Dheskali et al. (2017). Table 6.1 presents the optimal bioreactor design parameters at 50,000 t_{SA}/year production capacity. The inoculation bioreactor train (F-201, F-202) was used for inoculum preparation and the compressor C-201 was employed for aeration purposes due to the aerobic nature of *Y. lipolytica*.

The bioreactor has been integrated with a membrane electrolysis cell (EC-201) using an anion-exchange membrane for simultaneous SA production and in situ separation. The coulombic efficiency of SA extraction is 66.2% (Stylianou et al., 2023), while energy consumption is 2.6 kWh/kg_{SA}. The anolyte solution containing concentrated SA is processed via evaporation (EV-201), crystallization (CR-201/202) and drying (DR-201) according to the conventional DSP reported by Alexandri et al. (2019b). The recovery of SA crystals reached 95% and the purity was higher than 99.9% as reported by Stylianou et al. (2023).

Table 6.1 Optimal bioreactor parameters for succinic acid production at various annual production capacities

Annual capacity (t)	10,000	20,000	30,000	40,000	50,000	60,000
Uploading time τ_{ul} (h)	18	15	10	7	6	5
Loading time τ_l (h)	3	3	3	4	3	3
Number of batches (N_b)	435	522	783	1,118	1,305	1,566
Number of bioreactors (N_f)	6	7	10	14	16	19
Working volume of bioreactor V_b (m^3)	344.6	574.3	574.3	536.3	574.3	574.3

The conventional DSP process includes centrifugation for bacterial cell removal, activated carbon for colourisation if the fermentation broth, cation exchange resins for acidification of SA, evaporation, crystallization and drying. The bioprocess results for the conventional *Y. lipolytica* fermentation (54.4 g_{SA}/L, 0.44 g_{SA}/g_{TS}, 0.82 g/L/h productivity) and the DSP for SA purification have been presented by Alexandri et al. (2019b).

6.3 Techno-economic assessment

Figure 6.2 illustrates the FCI and COM of SA production using the integrated EMB system at various plant capacities (5-100 kt/y). The OPC is defined as the SA production capacity where economies of scale are reached. At the OPC (50,000 t_{SA}/year), the FCI and COM are \$6.1/kg_{SA} and \$2.6/kg_{SA}, respectively. Table 6.2 presents the characteristic size of each unit operation, utility requirements, FOB purchased costs, FCI (M\$305.37), C_{UT} (M\$24.46) and C_{OL} (M\$5.41) at the OPC (50,000 t_{SA}/year). The bioreactors (F-203/A-204), enzyme production system (SC-101/V-101/TF-101) and electrochemical cell (EC-201) contribute ca. 36%, 18% and 8% of the FCI. The main utility cost is electricity consumed by the electrochemical cell, air compressor and agitation.

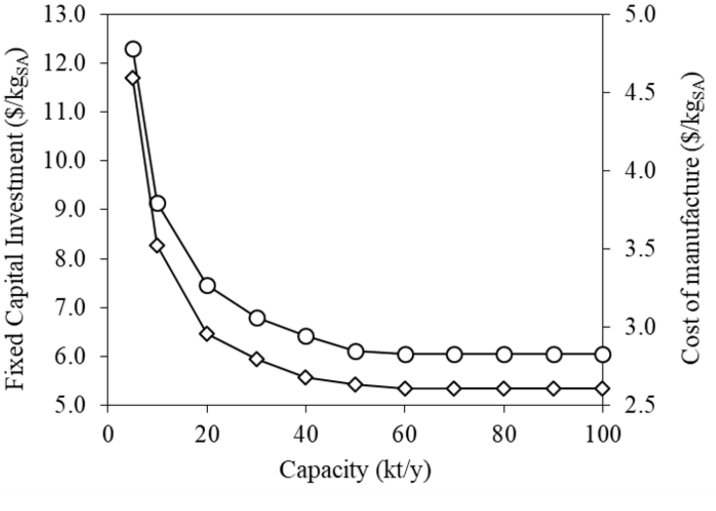


Figure 6.2 FCI (○) and COM (◊) of succinic acid production (Areas 100 and 200) at various annual capacities (5-100 kt/year) employing an integrated EMB system

Table 6.2 FOB purchase equipment cost (Cp), FCI, workers, COL, utility requirements and CUT for 50,000 t/year succinic acid production capacity and annual wet OFMSW treatment capacity of 1,153,402 t/y

	Unit	**Unit operation**	**No of units**	**CEPCI$_{t0}$ [d]**	**Characteristic size (X$_t$) [e]**	**C$_p$@2018 (M$)**	**Electricity (kWh/year)**	**Steam (t/year)**	**Cooling water (t/year)**
Area 100	SC-101	Screw conveyor[a]	1	390.6		3.793	8,544,388		
	V-101	Mixing tank[b]	8	521.9	V=921.57 m^3	4.331			
	TF-101	Tray SS bioreactors[c]	1	390.6	A=2,949.01 m^2	2.982			
	V-102	Mixing tank[b]	1	521.9	V=5,461.2 m^3	1.407		83,620	
	A-101	Agitator[b]	5	521.9	P=781.17 hp	3.272	23,068,051		
	CF-101	Centrifugal separator[c]	2	444.2	Q=91.02 m^3/h	1.712	736,560		
	EV-101	Evaporator[a]	3	521.9	A=738.24 m^2	2.928	6,621,730		
	Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
	Workers A100		5						
	Total C$_p$ A100 (M$)					20.425			
	FCI A100 (M$)				**5 × Total C$_p$ =**	**102.130**	**C$_{UT}$ A100 (M$/y) = 3.404**		
Area 200	E-201	Heat exchanger[b]	1	444.2	A=814.04 m^2	0.316			
	E-202	Heat exchanger[b]	1	444.2	A=63.95 m^2	0.046		15,062	
	E-203	Holding tube[b]	1	500	l=0.12 m	0.154			
	F-203	Bioreactor[b]	16	521.9	V=717.92 m^3	10.608			9,384,986
	A-204	Agitator[b]	16	521.9	P=855.76 hp	11.478	71,620,114		
	C-201	Compressor[b]	16	521.9	W=639.25 kW	4.435	71,743,589		
	F-201/202	Seed bioreactor[b]	1	521.9	V=71.80 m^3	0.198			
	A-202/203	Seed agitator[b]	1	521.9	P=85.75 hp	0.049			
	EC-201	Electrochemical cell[c]	1	567.6	A=2,557.71 m^2	4.669	131,500,000		
	EV-201	Evaporator[a]	2	521.9	A=711.73 m^2	2.711	29,029,652	23,445	
	CR-201	Crystalizer[a]	1	525.4	M=40,522 kg/h	0.964	9,688,575		
	CR-202	Crystalizer[a]	1	525.4	M=15,025.3 kg/h	0.588	406,733		
	DR-201	Dryer[a]	1	525.4	M=701.46 kg/h	4.432			
	Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
	Workers A200		25						
	Total C$_p$ A200 (M$)					40.648			
	FCI A200 (M$)				**5 × Total C$_p$ =**	**203.238**	**C$_{UT}$ A200 (M$/y) = 21.055**		
	Total FCI A100-200 (M$)					**305.368**			
	Total C$_{OL}$ A100-200 (M$)					**5.410**	**Total C$_{UT}$ A100-200 (M$/y) = 24.459**		

Area 100 alone for the onsite production of crude enzymes at the OPC results in a sugar production cost of \$180/t$_{sugars}$ that is associated with 1,153,402 t$_{OFMSW}$/year feedstock requirement. This sugar production cost is lower than the cost of corn-derived glucose syrup (\$230/t) (USDA, 2018) used in conventional bioprocesses. The COM (M\$131.62) at the OPC has been estimated using the FCI, C_{UT} and C_{OL} presented in Table 6.2 and the C_{RM} (M\$25.86) presented in Table 6.3.

As the OFMSW management fees vary (\$35-118/t) depending on the country and the region (Hogg, 2002), the most conservative scenario has been used in this study (\$35/t$_{OFMSW}$). DCF analysis was carried out at the OPC for the estimation of NPV and MSP (Case 1 in Table 6.4) considering either no OFMSW management fees (NPV_1=M\$-203.3, MSP_1=\$3.51/kg$_{SA}$) or the lowest reported OFMSW management fees as revenues (NPV_2=M\$74.6 and MSP_2=\$2.7/kg$_{SA}$). The MSP_2 is lower than the market price of bio-based SA (\$2.94/kg$_{SA}$) (E4tech et al., 2015).

Table 6.4 presents the techno-economic performance of SA production by the integrated EMB system (Case 1) and a conventional bioprocess for SA production by *Y. lipolytica* reported by Stylianou et al. (2021) (Case 2). In Case 2, the fermentation was carried out using a dual pH strategy where pH 6 was used until 30 h followed by pH reduction to 5.5 until the end of fermentation. The DSP stage of Case 2 includes centrifugation for cell removal, activated carbon for decolourisation and cation exchange resins for SA acidification (Stylianou et al., 2021) besides evaporation, crystallisation and drying that are also included in Case 1. Although higher SA concentration (66.7 g$_{SA}$/L) and yield (0.51 g$_{SA}$/gsugars) were achieved in Case 1, a slightly higher productivity (0.82 g/L/h) was achieved in Case 2. The comparison between the two processes was initially focused on the fermentation and DSP stages, excluding the upstream stage of OFMSW hydrolysis (results not presented in Table 6.4). Following this scenario, the unitary production cost of Case 2 (\$2.06/kg$_{SA}$) is slightly lower than Case 1 (\$2.13/kg$_{SA}$) due to the higher productivity achieved in case 2 and the high electricity requirements in Case 1.

Table 6.3 Raw materials cost (CRM) for the annual production of 50,000 t/y succinic acid

Material	Amount (t/y)	Total cost (M\$/y)
NaOH	14,000	5.600
Yeast extract	13,450	20.155
Process water	237,465	0.103
Total C_{RM} (M\$)		**25.858**

Table 6.4 Comparison of techno-economic and environmental indicators for integrated EMB system (case 1) and conventional bioprocess (case 2)

	Case 1	Case 2
Fermentation efficiency data		
Yield ($g_{SA}/g_{total\ sugars}$)	0.51	0.44
Productivity (g/L/h)	0.78	0.82
Concentration (g/L)	66.7	54.4
Coulombic efficiency (%)	66.2	
NaOH reduction (%)	35%	-
Techno-economic data based on 50,000 t_{SA}/year production		
Capacity OFMSW (t/year)	1,153,402	1,336,898
FCI (M$)	305.37	319.98
FCI (\$/kg$_{SA}$)	6.11	6.40
COM (M$)	131.62	132.91
COM (\$/kg$_{SA}$)	2.63	2.66
MSP$_1$ (\$/kg$_{SA}$)	3.51	3.60
MSP$_2$ (\$/kg$_{SA}$)	2.70	2.64
Techno-economic data based on 1,153,40 t_{OFMSW}/year usage		
Capacity SA (t/year)	50,000	43,137
FCI (M$)	305.37	286.49
FCI (\$/kg$_{SA}$)	6.11	6.64
COM (M$)	131.62	117.25
COM (\$/kg$_{SA}$)	2.63	2.72
MSP$_1$ (\$/kg$_{SA}$)	3.51	3.67
MSP$_2$ (\$/kg$_{SA}$)	2.70	2.74
Environmental performance (grid electricity)		
GWP (kg CO_2-eq/kg$_{SA}$)	3.87	3.97
ADP (MJ/kg$_{SA}$)	45.92	47.89
AP (g SO_2-eq/kg$_{SA}$)	7.41	7.42
EP (g PO_4-eq/kg$_{SA}$)	0.89	0.94
HTP (kg DCB-eq/kg$_{SA}$)	0.15	0.14
Environmental performance (100% renewable electricity - photovoltaics)		
GWP (kg CO_2-eq/kg$_{SA}$)	0.81	1.39
ADP (MJ/kg$_{SA}$)	15.73	22.62
AP (g SO_2-eq/kg$_{SA}$)	1.87	2.56
EP (g PO_4-eq/kg$_{SA}$)	0.25	0.39
HTP (kg DCB-eq/kg$_{SA}$)	0.29	0.25

* MSP$_1$: \$0/t OFMSW; MSP$_2$: \$35/t OFMSW;

If all SA production stages are considered (Table 6.4), the techno-economic performance has been evaluated considering either 50,000 t_{SA}/year production capacity or 1,153,40 t_{OFMSW}/year feedstock usage for both Cases 1 and 2. These alternative scenarios were considered because the lower sugar to SA conversion yield achieved in Case 2 results in higher revenues from OFMSW management fees when the same SA production capacity is considered. When no OFMSW management fees are considered, the MSP$_1$ of Case 1 (\$3.51/kg$_{SA}$) is always lower than the MSP$_1$ of Case 2 (\$3.6-3.67/kg$_{SA}$), especially in the case that the same OFMSW feedstock capacity is considered where

4.3% lower MSP_1 is achieved by Case 1 for the production of 15.9% higher annual SA production capacity (50,000 t_{SA}/year). When OFMSW management fees are considered, the MSP_2 of Case 1 (\$2.7/kg_{SA}) is higher than the MSP_2 of Case 2 (\$2.64/kg_{SA}) because higher OFMSW feedstock usage (1,336,898 t/year) is needed in Case 2 for the production of the same SA capacity (50,000 t_{SA}/year). When the same OFMSW feedstock usage (1,153,40 t_{OFMSW}/year) is considered, then the MSP_2 for Cases 1 and 2 is similar.

Case 1 shows higher techno-economic performance than Case 2 when lower annual SA production capacities are considered where economies of scale have not been achieved. For instance, considering 461,361 t_{OFMSW}/year feedstock usage, corresponding to 20,000 t_{SA}/year (Case 1) and 17,254 t_{SA}/year (Case 2), then the MSP_2 of Case 1 (\$3.22/kg_{SA}) is 5.6% lower than the MSP_2 of Case 2 (\$3.41/kg_{SA}).

6.4 Profitability risk assessment

The variables used in the PRA were fermentation duration (71-107 h), steam cost (\$8-12/t), electricity cost (\$0.06-0.2/kWh) and C_{RM} (M\$20.68-31.03). The PRA was carried out for 50,000 t_{SA}/year production capacity. PRA has been carried out considering the following four scenarios: i) \$2.94/kg_{SA} bio-based SA market price (E4tech et al., 2015) and \$35/t_{OFMSW} management fees, ii) \$2.50/kgSA combined fossil- and bio-based market price (E4tech et al., 2015) and \$35/t_{OFMSW} management fees, iii) \$2.94/kg_{SA} and \$70/t_{OFMSW} (Hogg, 2002) , and iv) \$2.50/kg_{SA} and \$70/t_{OFMSW}. Figure 6.3 presents the probability of NPV to be positive when the four scenarios are considered. At \$35/t_{OFMSW} management fees, the probability to achieve positive NPV is ca. 15% when \$2.94/kg_{SA} bio-based SA market price is considered, while the NPV is always negative when \$2.50/kg_{SA} market price is considered. At \$70/t_{OFMSW} management fees, the probability to achieve positive NPV is 60% when \$2.50/kg_{SA} is considered, while the probability to achieve positive NPV is over 90% when \$2.94/kg_{SA} market price is considered.

The profitability of SA production from OFMSW is dependent on the development of a multi-product biorefinery concept exploiting also the protein and lipid fractions besides the carbohydrate fraction that is used as fermentation feedstock. Ladakis et al. (2022) reported varying MSP (\$1.13-2.39/kg_{SA}) for SA production from OFMSW using a conventional bioprocess depending on OFMSW management fees and co-product market prices, considering lipids and protein valorisation that were removed before enzymatic hydrolysis of polysaccharides. Combining renewable energy utilisation for SA production and separation in the EMB system and a biorefinery approach from OFMSW could lead to enhanced profitability.

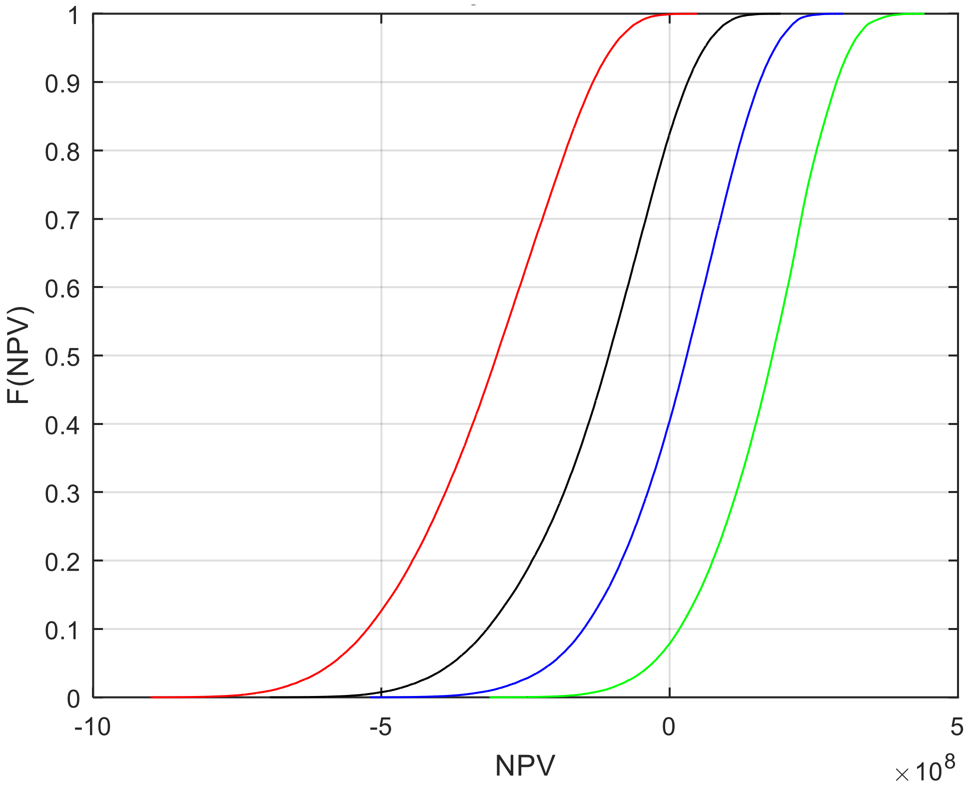


Figure 6.3 Probability to achieve positive NPV (M$) in: i) SA sold at $2.94/kg$_{SA}$ and OFMSW management fees at $35/t (black), ii) SA sold at $2.50/kg$_{SA}$ and OFMSW management fees at $35/t (red), iii) SA sold at $2.94/kg$_{SA}$ and OFMSW management fees at $70/t (green) and iv) SA sold at $2.50/kg$_{SA}$ and OFMSW management fees at $70/t (blue).

6.5 Life Cycle Assessment

6.5.1 Goal and scope

The aim of the LCA study is to assess the environmental performance of SA production using the EMB system. The system boundaries were set as "cradle-to-gate" including the enzymatic hydrolysis of OFMSW, the fermentation stage and the DSP of SA crystals, while the functional unit for the evaluation of all processes is considered as 1 kg of final product. The environmental indicators of both the EMB-based bioprocess and the conventional bioprocess have been estimated for comparison purposes.

6.5.2 Life Cycle Inventory

The life cycle inventory that includes the mass and energy inputs per kg of SA is presented in Table 6.5. The inventory was developed based on the process flow diagrams and the process design simulations.

Table 6.5 Life cycle mass and energy inventory expressed per kg produced SA

Inputs (unit/kg$_{SA}$)		**Outputs (unit/kg$_{SA}$)**	
Material/Utility	**Value**	**Material/Utility**	**Value**
NaOH (kg)	0.28	Succinic acid (kg)	1
Yeast extract (kg)	0.27		
Process water (kg)	4.749		
Electricity (kWh)	7.656		
Steam (kg)	2.442		
Cooling water (kg)	0.188		

Two different types of electricity have been employed to estimate the final environmental performance of the process, i.e. conventional electricity production mix (grid) and electricity derived from photovoltaics as source of renewable energy. The later was used because electricity requirements in the EMB-based bioprocess is high and therefore the use of renewable energy is important to ensure process sustainability. It has been assumed that OFMSW has no individual environmental impact as the impact depends on its final management system.

6.5.3 Life Cycle Impact Assessment

The LCA software GaBi was used to perform the environmental assessment of the proposed process by employing the CML2001 (Jan. 2016) methodology (Guinée et al., 2022) The selected impact categories which are used to express the final environmental results into quantitative indicators are Global Warming Potential (GWP 100 years), Abiotic Depletion (ADP fossil), Acidification Potential (AP), Eutrophication Potential (EP) and Human Toxicity Potential (HTP), as the most frequently used in the literature.

Environmental indicators for Cases 1 and 2 considering either conventional grid electricity mix or renewable electricity are presented in Table 6.4. Similar or slightly lower indicator values are observed in Case 1 when grid electricity mix is considered. For instance, GWP values are similar, while ADP in Case 1 is 4.1% lower than Case 2. The beneficial environmental performance of the EMB system is demonstrated when renewable electricity is used where all indicators, except for HTP, are significantly lower in Case 1 than Case 2. The GWP of Case 1 (0.81 kg CO_2-eq/kg$_{SA}$) is 41.7% lower than Case 2 (1.39 kg CO_2-eq/kg$_{SA}$), while 30.4% reduction is observed for ADP (Table 6.4). Likewise, AP and EP of Case 1 are 26.9% and 35.9% lower than Case 2. However, the HTP of Case 1 is 16% higher than Case 2 due to the high impact of construction material and utilities used for photovoltaics production (e.g. electricity, heavy metals).

Figure 6.4 presents the distribution of each bioprocessing stage in Cases 1 and 2 (OFMSW hydrolysis, fermentation, DSP) on individual environmental indicators. When grid electricity mix is considered, the contribution of OFMSW hydrolysis of Case 2 to the five indicators (15.9-27.7%) is higher than the corresponding contribution of OFMSW hydrolysis of Case 1 (11.5-20.9%) due to the lower yield of Case 2 that leads to higher OFMSW requirements.

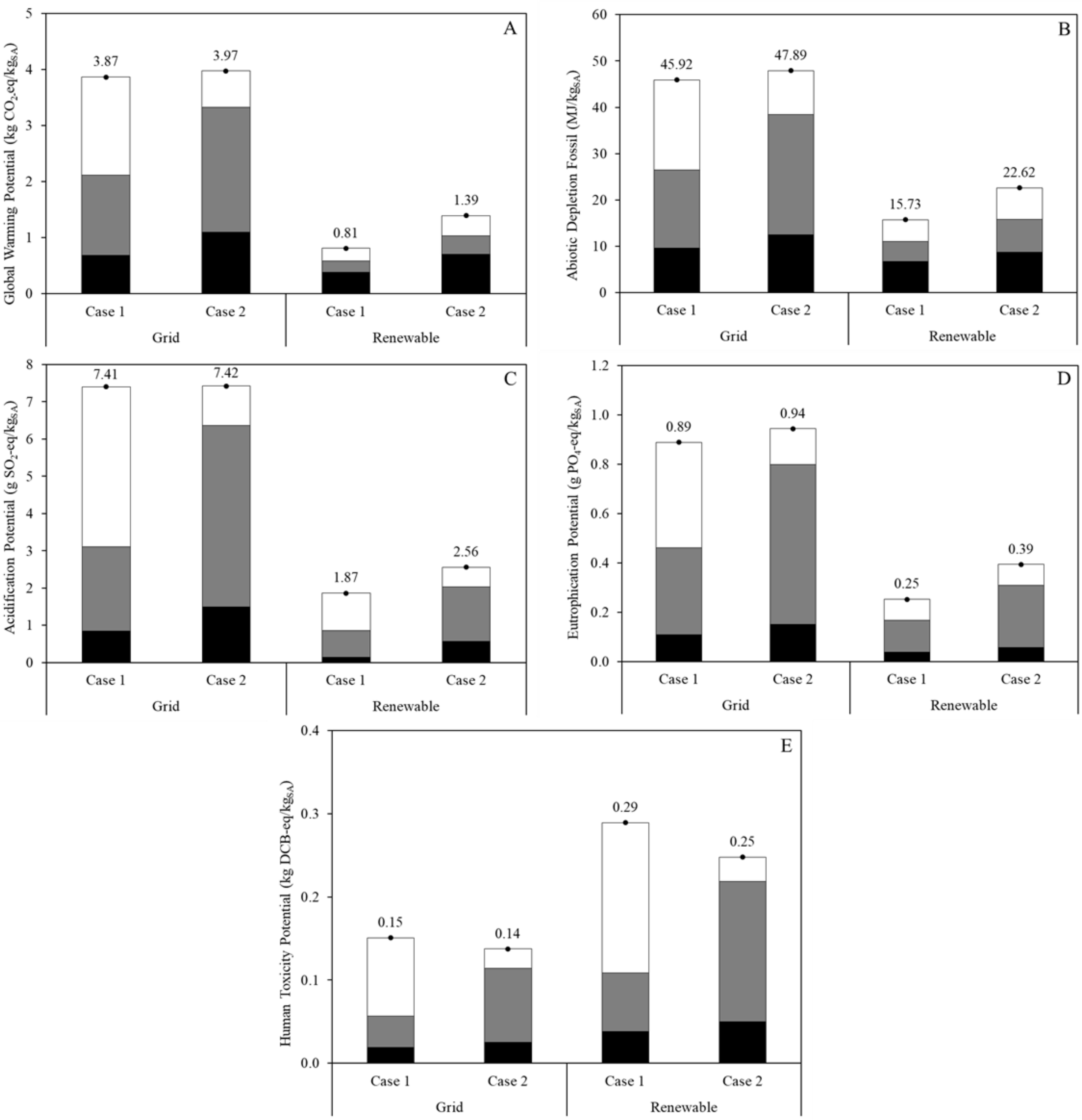


Figure 6.4 Global Warming Potential (A), Abiotic Depletion (B), Acidification Potential (C), Eutrophication Potential (D) and Human Toxicity Potential (E) for succinic acid production using the EMB-based process (Case 1) and the conventional bioprocess (Case 2). The contribution of each bioprocessing stage on individual environmental indicators is presented. (■) OFMSW hydrolysis stage, (■) Fermentation stage, (□) DSP stage.

The impact of the fermentation stage is mainly attributed to NaOH usage for fermentation pH regulation and utilities consumption. Given the lower NaOH requirements in Case 1 due to the EMB system, the contribution of the fermentation stage of Case 1 to all indicators (25-39.6%) is significantly lower than Case 2 (54.3-68.7%) when grid electricity mix is considered. The DSP stage of Case 1 contributes higher environmental impacts (42.5-62.3%) than Case 2 (14.3-19.6%) as the environmental impacts of electricity consumption in the electrolysis cell in Case 1 are higher than the environmental impacts of HCl consumption in Case 2 for resin regeneration that is employed after acidification of succinate salts.

When renewable electricity is used, the contribution of DSP of Case 1 to GWP, ADP and EP (28.1-33.5%) is significantly lower than the respective DSP contribution of Case 1 when grid electricity mix is used (42.5-48.1%). However, the DSP contribution of Case 1 remains high in the case of AP (53.8%) and HTP (62.4%). Thus, the EMB system and renewable electricity (photovoltaics) contribute variable effects on individual indicators, but in most cases, except for HTP, lead to lower environmental impacts than the conventional bioprocess. Lower environmental impacts could be achieved through integration of electricity production via combined heat and power (CHP) by exploiting the lignin content of OFMSW (5.6-12.1%) that remains after polysaccharide hydrolysis and proteins/lipids extraction (Ioannidou et al. 2020) and biogas production via anaerobic digestion of residual bioprocessing streams (e.g. fermentation broth).

Cok et al. (2014) reported the GWP and ADP of SA production from corn-derived glucose via (i) low pH yeast fermentation with direct crystallization-based SA purification (0.88 kg CO_2-eq/kg_{SA}, 32.7 MJ/kg_{SA}), and (ii) anaerobic bacterial fermentation to succinate salt at pH 7 with SA purification via an electrodialysis-based process (1.7 kg CO_2-eq/kg_{SA}, 49.4 MJ/kg_{SA}), using a European electricity production mix. The main difference in the GWP estimated in this study for Case 1 using grid electricity mix (3.87 kg CO_2-eq/kg_{SA}) and the GWP reported by Cok et al. (2014) for the electrodialysis-based process is mainly attributed to the carbon uptake during corn cultivation (ca. 1.5 kg CO_2-eq/kg_{SA}). The GWP of Case 1 using renewable electricity (0.81 kg CO_2-eq/kg_{SA}) is lower than either process reported by Cok et al. (2014). The ADP of Case 1 using grid electricity mix (45.92 MJ/kg_{SA}) is 8.5% lower than the electrodialysis-based process reported by Cok et al. (2014), while the ADP of Case 1 using renewable electricity (15.73 MJ/kg_{SA}) is 51.9% lower than the low pH yeast fermentation reported by Cok et al. (2014). The GWP (1.94 kg CO_2-eq/kg_{SA}) and ADP (59.2 MJ/kg_{SA}) for petroleum-derived SA production using maleic anhydride as feedstock are significantly higher than Case 1 when renewable electricity is used Cok et al. (2014). Moussa et al. (2016) presented the environmental performance of SA production from sorghum using the process developed by Myriant Corporation (i.e. *Escherichia coli* fermentation with NH_3 usage for pH regulation, salt separation with continuous ion exchange, evaporation and crystallization) with simultaneous production of ammonium phosphate as co-product fertiliser. The GWP (0.87 kg CO_2-eq/kg$_{SA}$) and ADP (6.89 MJ/kg$_{SA}$) reported by Moussa et al. (2016) (considering -4.02 kg CO_2-eq/kg$_{SA}$ and -62.5 MJ/kg$_{SA}$ avoided impacts due to ammonium phosphate production) are 7.5% higher and 56.2% lower than the respective values of Case 1 when renewable electricity is used. Further reduction of NaOH requirements during fermentation and the integration of CHP for renewable electricity production could further reduce the ADP of Case 1.

Chapter 7 Biorefinery development and sustainability assessment for the conversion of OFMSW into succinic acid and value-added fractions

7.1 Introduction

In the EU, the organic fraction of municipal solid waste (OFMSW) contains the park and garden organic waste as well as food waste from processing, retail and consumption stages of food supply chains (Stylianou et al., 2020). The composition of OFMSW varies depending on regional, seasonal and socioeconomic factors. The OFMSW contains 30 – 60 % carbohydrates, which are suitable as carbon sources for the production of bio-based chemicals, polymers and fuels via fermentation. OFMSW-based processes have been evaluated for bio-based lactic acid, succinic acid, hydrogen, butanol, biopolymers and biogas production (Babaei et al., 2019; Bernat et al., 2019; López-Gómez et al., 2019; Meng et al., 2019; Stylianou et al., 2021).

Stylianou et al. (2020) reported the production of succinic acid via *A. succinogenes* cultures using OFMSW-derived hydrolysates produced with commercial enzymes. Crude enzymes could be produced on-site via solid state fermentation (SSF) using OFMSW as substrate. Using the whole SSF solids in OFMSW hydrolysis could eliminate enzyme purification stages and enhance nutrient release due to fungal biomass autolysis (Koutinas et al., 2005) and the presence of mycelium-bound enzymes (Farinas, 2018). The fungal strain *Aspergillus awamori* could be used in OFMSW hydrolysis due to its ability to produce amylolytic, proteolytic and cellulolytic enzymes via SSF in various crude feedstocks (Efthymiou et al., 2021; Koutinas et al., 2004; Wang et al., 2009). Integrating SSF of *A. awamori* in OFMSW-based biorefineries for on-site production of crude enzymes could lead to reduced processing costs improving the profitability of bio-based succinic acid production.

The exploitation of the oils/fats and protein fractions extracted from OFMSW for the production of bio-based chemicals and fuels could lead to a novel biorefinery concept. Waste vegetable oils and animal fats could be employed for biodiesel or green diesel production (Hájek et al., 2021). The protein-rich fraction could be used for bio-based adhesive production to replace formaldehyde-based adhesives as has been demonstrated with proteinaceous slaughterhouse waste and vegetable proteins (Adhikari et al., 2018). Furthermore, the PERCAL BBI-JU research project (www.percal-project.eu) has demonstrated that chemical and/or enzymatic modification of oil/fats and proteins extracted from OFMSW could be employed for the production of biosurfactants that could replace conventional surfactants used in European detergents.

This chapter presents the development of a novel OFMSW-based biorefinery integrating the extraction of oils/fats and proteins as well as on-site enzyme production via SSF for the hydrolysis of OFMSW polysaccharides. The crude hydrolysate has been employed as fermentation medium for succinic acid production. Process design, techno-economic assessment and estimation of Global Warming Potential (GWP 100 years) and Abiotic Depletion Potential (ADP) have been carried out to show the sustainability potential of the proposed biorefinery focusing also on the cost-competitiveness of succinic acid production.

7.2 Description of the process

Figure 7.1 illustrates the OFMSW-based biorefinery starting with OFMSW fractionation into oil/fats and protein fractions followed by the production of a nutrient-rich hydrolysate that is subsequently employed as fermentation medium. The OFMSW stream (75% moisture content) is initially dried (DR-101) and subsequently mixed with hexane (V-101) at a solid to liquid ratio of 1:2 (w/v) for lipid extraction. The evaporator EV-101 is employed for the recovery of the solvent leading to 100% oil/fats recovery. The oil/fats free solids separated via centrifugation (stream 102) are mixed with water and NaOH (0.1 $kg/kg_{protein}$) to solubilise the protein fraction. Successive filtrations are employed for the separation of the remaining solids (F-201) and the recovery of the protein fraction (F-202, retentate). The protein-rich fraction contains ca. 68% (w/w) of the initial protein content in OFMSW and 90% (w/w) protein purity. The protein-rich fraction is dried in DR-201. The permeate stream from F-202 (steam 203) contains the liquid stream with a low protein content (3.8% losses) and free sugars (35% of the initial content in OFMSW). The permeate stream is considered as waste due to the low sugar concentration and high pH.

The OFMSW is also used as solid substrate in SSF (TF-301) with the produced enzymes subsequently used in the hydrolysis stage (V-302). The SSF duration is 81 h that resulted in the highest glucoamylase activity (38.8 U/g_{OFMSW}), the highest maltase activity (24.2 U/g_{OFMSW}) and the highest cellulase activity (1.84 U/g_{OFMSW}), while invertase, protease and phytase activities were 15.7, 119.5 and 125 U/g_{OFMSW}, respectively. The remaining OFMSW solids after the extraction of oil/fats- and proteins (stream 202) are mixed with the SSF solids and hydrolysis is performed for 20 h. The centrifugal separator CF-301 removes the remaining solids. The sugar- and nutrient-rich hydrolysate is used as fermentation medium.

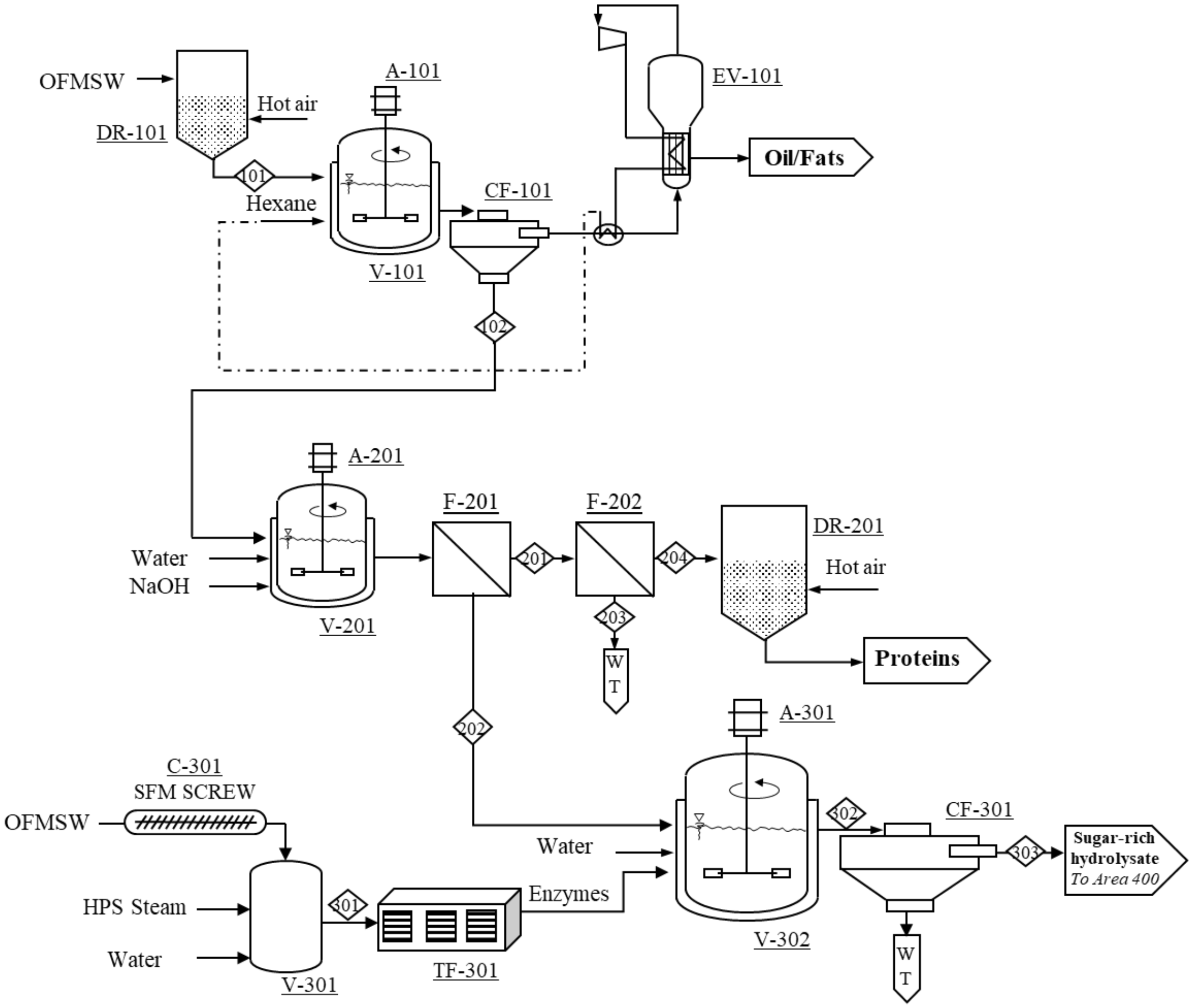


Figure 7.1 Process flow diagram of the OFMSW-based biorefinery including oil/fats extraction (Area 100), protein extraction (Area 200) and enzyme production (Area 300)

The bioprocessing section can be divided into two sections, namely bioconversion and downstream separation and purification (DSP). A continuous sterilisation system (E-401, E-402, E-403) is firstly employed and then the sterilized stream 401 enters the bioreactor F-403. The fermentation is performed by *A. succinogenes* leading to 31.7 g/L succinic acid, 0.68 g/g yield and 0.67 g/(L·h) productivity. The inoculation bioreactor train (F-401, F-402) is used for inoculum preparation. The methodology presented by Dheskali et al. (2017) has been employed for designing, sizing and scheduling the bioconversion stage (E-401-403, F-403, F-401/402) using the experimental fermentation efficiency. Table 5.1 presents the optimal bioreactor design parameters at various SA production capacity.

Table 7.1 Optimal bioreactor parameters for succinic acid production at various annual production capacities (estimated based on the methodology presented by Dheskali et al., 2017)

Annual capacity (t)	**10,000**	**20,000**	**30,000**	**40,000**	**60,000**	**80,000**
Uploading time τ_{ul} (h)	13	6	4	3	3	3
Loading time τ_{l} (h)	3	5	3	5	5	5
Number of batches (N_b)	605	1,311	1,967	2,622	2,622	2,622
Number of bioreactors (N_f)	5	10	14	19	19	19
Working volume of bioreactor V_b (m^3)	521.25	481.10	480.97	481.10	721.64	962.19

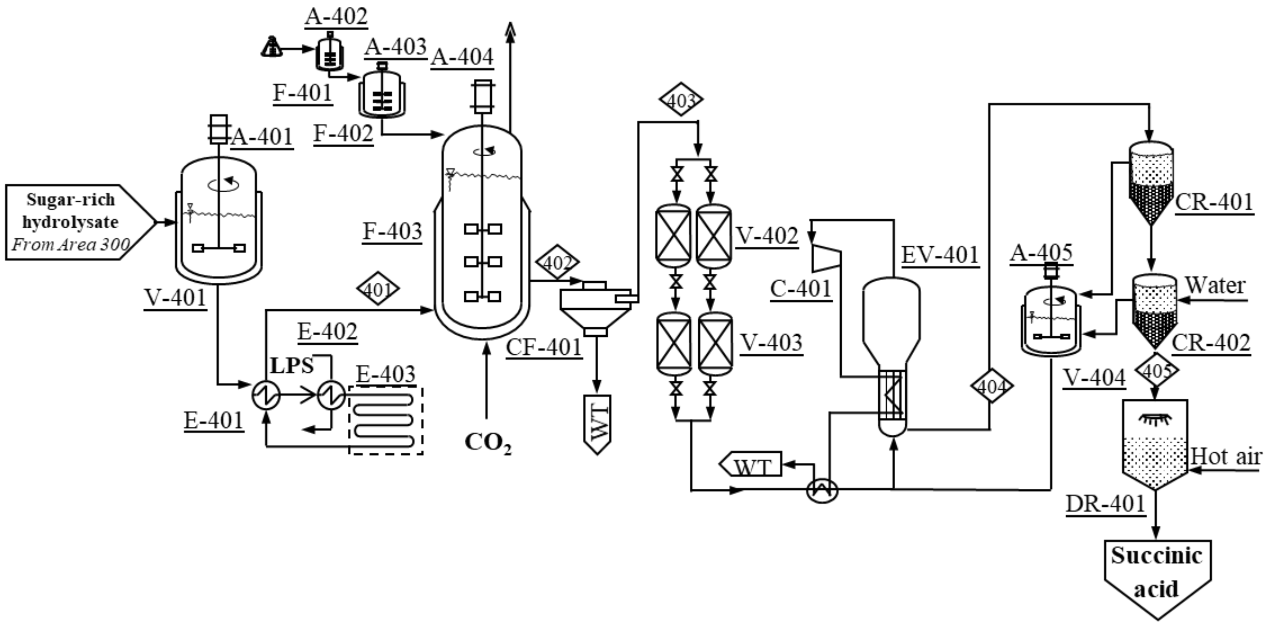


Figure 7.2 Process flow diagram of the OFMSW-based biorefinery including succinic acid production via fermentation followed by DSP (Area 400)

After the bioconversion section, succinic acid crystals are purified employing the DSP reported by Alexandri et al. (2019). Stream 402 is centrifuged (CF-401) to remove the bacterial biomass. The biomass-free fermentation broth is then fed to the activated carbon columns (V-402) for decolorization and impurity removal. The decolorized effluent is fed to the cationic resin columns (V-403) in order to transform organic acid salts into their corresponding organic acids. The acidified liquid stream is then mixed with the recirculated stream that comes from the crystallizers (CR-401, CR-402) via V-404 and the resulting stream is concentrated using the mechanical vapor recompression MVR-forced circulation evaporator system (EV-401). Stream 404 is subsequently treated via crystallization in continuous crystallizers (CR-401, CR-402) at 4°C. Dried succinic acid crystals are produced using a spray dryer (DR-401). The remaining liquid is recycled at the evaporation stage as mentioned above. The SA crystal purity achieved is higher than 99.5%, while the overall succinic acid recovery yield in the DSP is ca. 95% (w/w).

7.3 Techno-economic assessment

The process design and TEA were carried out using the fermentation efficiency achieved at 47.5 h where the highest productivity (0.67 g/(L·h)) was observed, with 31.7 g_{SA}/L and 0.68 g/g yield, in order to minimize the FCI and COM related to the fermentation stage. The FCI and COM expressed per kg SA were estimated, considering the unit operations presented in Figure 7.2, at various plant capacities (10,000-100,000 t/year) to evaluate the effect of economies of scale on capital investment and SA production cost (Figure 7.3). The FCI (\$6.45/kg_{SA}) and COM (\$2.79/kg_{SA}) reach a plateau at 60,000 t_{SA}/year. The FCI is high as it includes all equipment used in Areas 100-400 (Figures 7.1 and 7.2). The COM is also high considering that the market price of bio-based SA is \$2.94/kg_{SA} (E4tech et al., 2015), which occurred because no co-product revenue and OFMSW management fees were considered. The succinic acid production stage (Figure 7.2) contributes 69% to the total COM.

Table 7.2 presents the free-on-board (FOB) purchase equipment cost (C_p) at 2018, FCI, operating labour, C_{OL}, utility requirements and C_{UT} for the proposed OFMSW biorefinery (Areas 100-400, Figure 1) producing 60,000 t_{SA}/year that is derived from 1,163,300 t wet OFMSW.

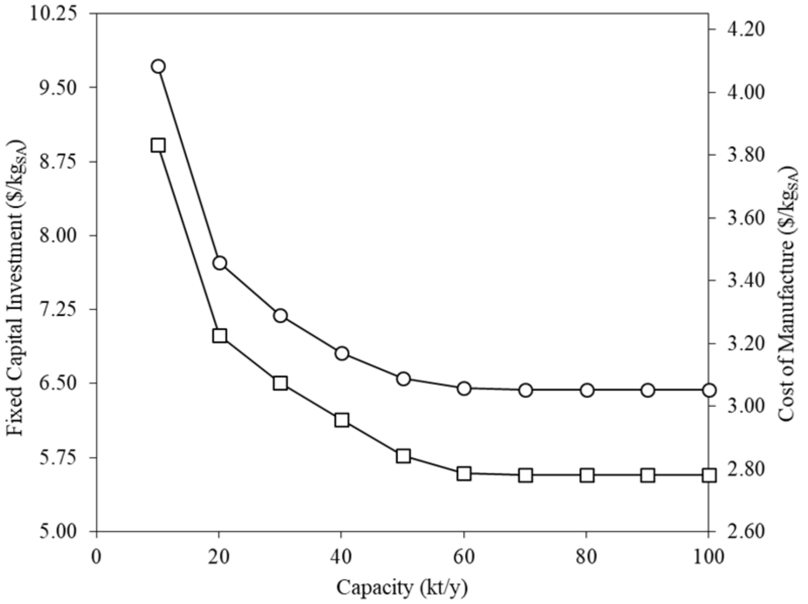


Figure 7.3 FCI (○) and COM (□) expressed per kgSA estimated at varying production capacities (10,000-100,000 t_{SA}/year)

Table 7.2 FOB purchase equipment cost (Cp), FCI, workers, COL, utility requirements and CUT of the proposed OFMSW biorefinery (Areas 100-400, Figures 7.1 and 7.2) with 60,000 t/year succinic acid production capacity and annual wet OFMSW treatment capacity of 1,163,300 t/y

Unit	Unit operation	No of units & workers	CEPCI$_{t0}$[d]	Characteristic size (X_t)[e]	C_p@2018 (M$)	Electricity (kWh/year)	Steam (t/year)	Process water (t/year)	Natural gas (GJ/year)
Area 100									
DR-101	Dryer[a]	4	525.4	A=888.91 m^2	4.680				2,392,973.1
V-101	Mixing tank[a]	1	521.9	V=21.67 m^3	0.236				
A-101	Agitator[b]	1	521.9	P=2.32 hp	0.006	13,732.3			
CF-101	Centrifugal separator[c]	1	444.2	Q=98.25 m^3/h	0.091	237,600.0			
EV-101	Evaporator[a]	1	521.9	A=43.38 m^2	0.293		54,576.8		
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t	$3.16/GJ
Workers A100		2							
Total C_p A100 (M$)					5.305				
FCI A100 (M$)				**5 × Total C_p =**	**26.52**	**C_{UT} A100 (M$/y)**	**8.077**		
Area 200									
V-201	Mixing tank[b]	1	521.9	V=459.14 m^3	0.524				
A-201	Agitator[b]	1	521.9	P=49.22 hp	0.052	290,910.7			
FL-201	Filtration[c]	1	344.0	Q=367.31 m^3/h	2.068	1,011,363.6			
FL-202	Filtration[c]	1	344.0	Q=293.85 m^3/h	3.832	6,435,950.1			
DR-201	Dryer[a]	3	525.4	A=18.56 m^2	2.586				49,962.7
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t	$3.16/GJ
Workers A200		3							
Total C_p A200 (M$)					9.062				
FCI A200 (M$)				**5 × Total C_p =**	**45.310**	**C_{UT} A200 (M$/y)**	**0.622**		
Area 300									
C-301	Screw conveyor[a]	1	390.4		1.658	2,154,428.1			
V-301	Mixing tank[b]	6	521.9	V=893.12 m^3	3.176		470.4		
TF-301	Tray SS bioreactors[c]	1	390.4	A=2,143.48 m^2	2.462				
V-302	Mixing tank[a]	1	521.9	V=3,969.41 m^3	1.023		60,778.5		
A-301	Agitator[b]	1	521.9	P=29.39 hp	0.031	167,668.0			
CF-301	Centrifugal separator[c]	2	444.2	Q=132.31 m^3/h	1.341	736,560.0			
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t	$3.16/GJ
Workers A300		2							
Total C_p A300 (M$)					9.691				

FCI A300 (M$)				**5 × Total C_p =**	**48.45**	**C_{UT} A300 (M$/y)**	**0.784**		
Area 400									
E-401	Heat exchanger[b]	1	444.2	A=920.53 m^2	0.358				
E-402	Heat exchanger[b]	1	444.2	A=48.21 m^2	0.040		38,024.9		
E-403	Holding tube[b]	1	500	l=0.12 m	0.122				
F-403	Bioreactor[b]	19	521.9	V=751.71 m^3	18.203			12,551,300	
A-404	Agitator[b]	19	521.9	P=896.04 hp	19.457	100,914,538.0			
F-401/402	Seed bioreactor[b]	1	521.9	V=75.17 m^3	0.223				
A-401/402	Seed agitator[b]	1	521.9	P=89.60 hp	0.093				
CF-401	Disc stack centrifuge[c]	3	444.2	Q=246.30 m^3/h	2.369	2,021,1			
V-402/V-403	Ion exchange resins[c]	4	521.9	V=110.78 m^3	3.117				
EV-401	Evaporator[a]	3	521.9	A=931.40 m^2	2.798	56,983,832.8	17,321.9		
CR-401	Crystalizer[a]	1	525.4	M=48,626 kg/h	1.026	12,821,168.7			
CR-402	Crystalizer[a]	1	525.4	M=18,030.3 kg/h	0.805	3,487,887.0			
DR-401	Dryer[a]	1	525.4	M=841.75 kg/h	4.865	35,790,000.0			
Unitary utility cost						\$0.0674/kWh	\$9.45/t	\$0.0154/t	\$3.16/GJ
Workers A400		20							
Total C_p A400 (M$)					53.476				
FCI A400 (M$)				**5 × Total C_p =**	**267.38**	**C_{UT} A400 (M$/y)**	**12.596**		
Total FCI A100-400 (M$)						**387.16**			
Total C_{OL} A100-400 (M$)		**5.054**							
						Total C_{UT} A100-400 (M$/y)	**22.079**		

FOB purchase equipment cost (C_p) estimation: [a] Turton et al., 2018; [b] Dheskali et al., 2017; [c] Peters et al., 2003; [d] $CEPCI_{t0}$: Chemical Engineering Plant Cost Index at the year where the purchase equipment cost (C_{p,t_0}) is available considering a characteristic size X_{t_0}; [e] X_t: is the characteristic size of each unit operation estimated in this study via process design and used for the estimation of the FOB purchase equipment cost at 2018 as follows $C_{p,2018} = \frac{CEPCI_{2018}}{CEPCI_{t_0}} C_{p,t_0} \left(\frac{X_t}{X_{t_0}}\right)^n$

In Area 100, ca. 88% of the $C_{p,A100}$ is attributed to the dryers (DR-101) used to reduce the OFMSW moisture content from 75% to 10% (w/w). Significant energy consumption (39,882 kJ/kg_{SA} or 2,057,05 kJ/$kg_{wet\ OFMSW}$) is also required during drying using natural gas as fuel (Table 7.2). The hexane make-up for oil/fats extraction (V-101), considering also the hexane recycled after evaporation (EV-101), has been taken as 10% corresponding to 3,398 t/year for a biorefinery producing 60,000 t_{SA}/year (Table 7.3). In Area 200, the filtration equipment (FL-201 and FL-202) contribute ca 65% of the total $C_{p,A200}$ and the highest utility consumption (446.84 kJ/kg_{SA}). Electricity consumption (290,910.7 kWh/year) is also required for agitation of V-201 corresponding to 17.45 kJ/kg_{SA} (Table 7.2).

In Area 300, the mixing tanks and the tray solid state (SS) bioreactors contribute ca. 58% of the total $C_{p,A300}$, while steam consumption (2,107 kJ/kg_{SA}) in V-302 contributes the highest utility cost. The overall cost of utilities in A300 (0.784 M$/year) is similar to the one estimated in Area 200 (0.622 M$/year). In the SA production stage (Area 400), ca. 70% of the total $C_{p,A400}$ is attributed to the bioreactor vessels (F-403, 19 units with 751.71 m^3 each) and the agitators (A-404, 19 units with 896.04 hp each), while the energy consumption for agitation in the fermentation stage is similar to the energy required for the whole DSP section (6,054.78 kJ/kg_{SA}) producing dry SA crystals. Table 7.3 presents the C_{RM} for the reference annual capacity. The COM_{SA} of 60,000 t_{SA}/year has been estimated using the FCI, C_{UT} and C_{OL} presented in Table 3 and the C_{RM} presented as supplementary data. Figure 7.3 shows that 60,000 t_{SA}/year is the OPC from which capacity upwards constant FCI and COM are achieved for the proposed biorefinery.

Table 7.3 Raw materials cost (CRM) for 60,000 t annual succinic acid production capacity using 1,163,300 t/year wet OFMSW

Material	**Amount (t/year)**	**Cost (M$/year)**
Water	306,882	0.131
Hexane	3,398	3.398
NaOH	42,264	13.906
HCl	40,000	2.600
Yeast extract	9,461	14.191
$MgCO_3$	9,461	14.191
Total		**48.417**

As a next step, DCF analysis was carried out at the OPC for the estimation of NPV, MSP and DPP considering 10% interest rate, 30 years plant lifetime, 35% corporate tax rate, 3 years plant construction duration and other DCF parameters taken from Humbird et al. (2011). OFMSW management fees were included in the DCF analysis as revenues. The OFMSW management fees vary ($35-118/t) depending on the country and the region (Hogg, 2002). Three different OFMSW management fees were considered depending on the country where the fee is applied, namely Spain ($35/t), the Netherlands ($70/t) and Germany ($100/t). The revenues from co-product sales used in the DCF analysis were estimated by considering indicative market prices for oil/fats and proteins depending on their potential industrial application. Oils/fats could be used for biofuel production with market price in the range of $0.6-0.9/kg (Smith et al., 2013). The proteins could be used as bio-based adhesives for wood panel applications with market price in the range of $1.0-1.4/kg (Alibaba.com).

Considering the lowest market prices for oil/fats ($0.6/kg) and proteins ($1.0/kg), the estimated MSP_{SA} at the OPC is $2.39/$kg_{SA}$ in Spain, $1.71/$kg_{SA}$ in the Netherlands and $1.13/$kg_{SA}$ in Germany (Table 7.4). All MSPs are lower than the current market price of bio-based SA ($2.94/$kg_{SA}$). The respective NPV is 207.1 M$ in Spain, 456.7 M$ in the Netherlands and 670.6 M$ in Germany. The respective DPP is 12 years in Spain, 8 years in the Netherlands and 7 years in Germany.

Table 7.4 TEA indicators for the proposed biorefinery estimated at the optimum plant capacity (60,000 tSA/year) using 1,163,300 t/year wet OFMSW considering three different OFMSW management fees

Parameter / Indicator	**Spain**	**Netherlands**	**Germany**
OFMSW management fee ($/t)	35.0	70.0	100.0
Oil/fats market price ($/kg)	0.6	0.6	0.6
Protein market price ($/kg)	1.0	1.0	1.0
OPC (t_{SA}/year)	60,000	60,000	60,000
FCI ($/kg)	6.45	6.45	6.45
COM ($/kg)	2.79	2.79	2.79
NPV (M$)	207.1	456.7	670.6
MSP ($/kg)	2.39	1.71	1.13
DPP (years)	12	8	7

The MFR indicator describes the minimum feedstock quantity (1,163,300 t/year wet OFMSW), corresponding to 98,929 t/year fermentable sugars, that is required for the production of the OPC (60,000 t_{SA}/year). The MFR could be used in order to assess the potential construction of an OFMSW biorefinery in a country or region considering the feedstock availability in the respective area. Ioannidou et al. (2020) presented the OFMSW-derived fermentable sugars that are available in EU countries considering OFMSW statistical data. According to Ioannidou et al. (2020), the estimated MFR (98,929 t/year OFMSW-derived fermentable sugars) is available in Spain (738,505 t/year), the Netherlands (303,248 t/year), Germany (1,786,000 t/year) and many other EU countries.

Figure 7.4 presents the MSP_{SA} at three different market prices for oils/fats ($0.6/kg, $0.75/kg, $0.9/kg) and proteins ($1.0/kg, $1.2/kg, $1.4/kg) as well as the lowest OFMSW management fee ($35/t). The line in Figure 7.4 represents the MSP_{SA} ($2.38/$kg_{SA}$) estimated without oil/fats and proteins extraction (no biorefinery development case) and considering the lowest OFMSW management fee ($35/t). The same hydrolysis and fermentation efficiency achieved in the experimental work presented in this study were used in all cases. The MSP_{SA} varies from $2.39/$kg_{SA}$ when the lowest co-product market prices are assumed to $2.1/$kg_{SA}$ when the highest co-product prices are considered.

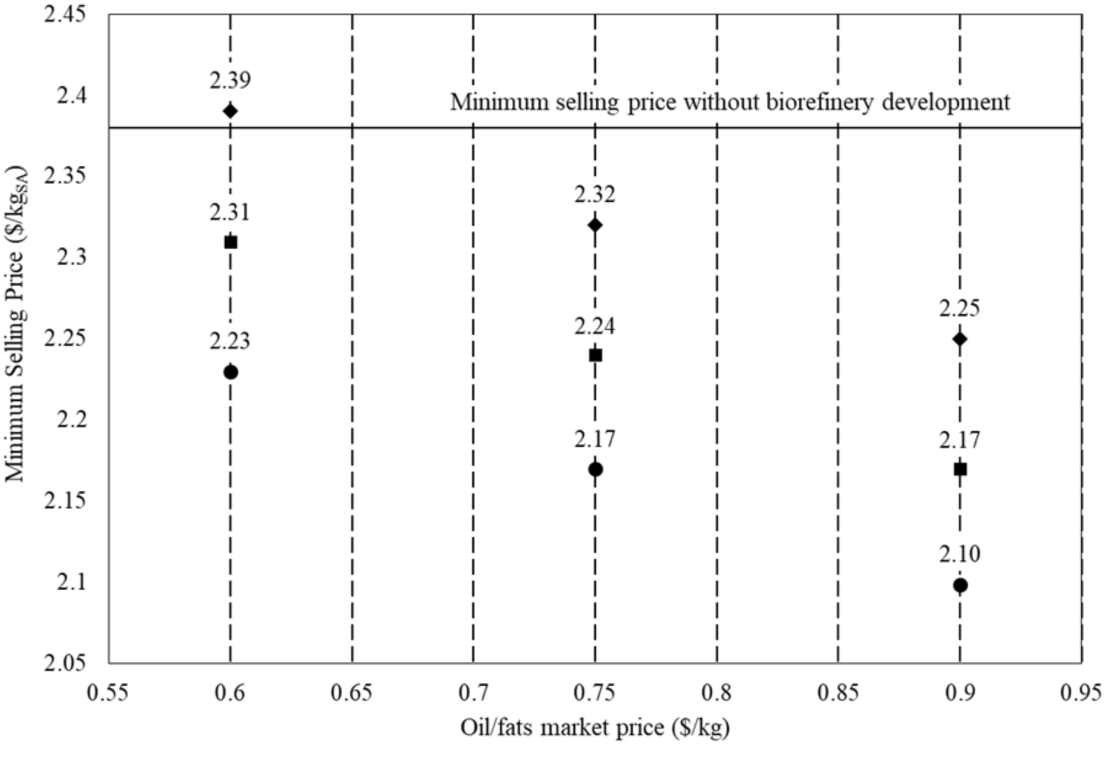


Figure 7.4 MSPSA at varying market prices for oil/fats ($0.6/kg, $0.75/kg, $0.9/kg) and proteins ($1/kg, $1.2/kg, $1.4/kg) as compared to the MSPSA produced from OFMSW without any co-product stream extraction (no biorefinery development) (B). Protein market price: $1/kg (♦), $1.2/kg (■), $1.4/kg (●).

Figure 7.4 shows that the proposed biorefinery leads up to 11.7% lower MSP_{SA} than the case where the SA is produced from OFMSW without any co-product extraction (no biorefinery development case). Producing higher value bio-based chemicals and polymers from the oil/fats and protein fractions could enhance further process profitability. For instance, used cooking oils could be considered as feedstock for oleochemical production (e.g. fatty alcohols, epoxidized oils, plasticizers, surfactants, lubricants) with bulk prices higher than \$1.3/kg (Rincón et al., 2019).

7.4 Life Cycle Assessment

7.4.1 Goal and scope

The main goal of this study is the assessment of the environmental performance of an OFMSW-based biorefinery for the production of succinic acid and value-added fractions. The functional unit was selected as 1 kg dry OFMSW in order to avoid impact allocation among co-products and facilitate comparison with alternative OFMSW management (e.g. landfilling) and valorisation (e.g. levulinic acid production) options. The system boundaries for the environmental assessment include OFMSW pretreatment for oil/fats and protein extraction, SSF and hydrolysate production, and succinic acid production, separation and purification (Figure 7.1). A "cradle-to-gate" LCA approach has been considered.

7.4.2 Life Cycle Inventory

The mass and energy input and output data have been estimated for each stage of the OFMSW-based biorefinery using the selected system boundaries and the process flow diagram presented in Figure 7.1 (Table 7.5). The life cycle inventory for the whole OFMSW-based biorefinery is presented as supplementary data considering input that corresponds to 1 kg dry OFMSW. Raw materials and utilities required in each stage of the proposed biorefinery are referred as inputs, while outputs correspond to the products and the remaining streams of each stage. Steam generation from natural gas and electricity production from grid and have been considered.

7.4.3 Life Cycle Impact Assessment

The environmental impacts of the whole OFMSW-based biorefinery has been evaluated and compared to OFMSW landfilling and alternative production processes for succinic acid and the other co-products. The two selected environmental impact indicators are GWP 100 years and ADP fossil as the most representative and frequently used indicators in the literature.

Table 7.5 Life cycle inventory for each life-cycle stage of the OFMSW biorefinery (Functional unit: 1 kg dry OFMSW)

Olis/fats extraction		**Protein extraction**		**SSF & Hydrolysis**		**Succinic acid production**	
Material	**Value**	**Material**	**Value**	**Material**	**Value**	**Material**	**Value**
Inputs							
OFMSW (75% moisture, kg)	4.002	Solid residue (kg)	0.895	Solid residue (kg)	0.817	Sugars (kg)	0.304
Hexane (kg)	0.012	NaOH (kg)	0.008	Steam (lps, kg)	0.212	Water (kg)	1.056
Steam (lps, kg)	0.188	Electricity (kWh)	0.027	Electricity (kWh)	0.007	NaOH (kg)	1.444
Natural gas (kg)	0.158	Natural gas (kg)	0.003			CO_2 (kg)	0.116
Electricity (kWh)	$4.72 \cdot 10^{-5}$					Yeast extract (kg)	0.033
						$MgCO_3$ (kg)	0.033
						HCl (kg)	0.144
						Steam (lps, kg)	0.190
						Electricity (kWh)	0.721
Outputs							
Solid residue (kg)	0.895	Solid residue (kg)	0.817	Solid residue (kg)	0.514	Succinic acid (kg)	0.206
Lipids (kg)	0.105	Protein (kg)	0.078	Sugars (kg)	0.304		

The GWP (1.15 kg CO_2-eq per kg dry OFMSW) and ADP fossil (22.88 MJ per kg dry OFMSW) (Figure 7.5) were estimated for the biorefinery using the mass and energy inventory presented in Table 7.5. The oil/fats extraction stage (Area 100, Figure 7.1) contributes 56% of the GWP of the whole biorefinery due to the high natural gas requirements in OFMSW drying. The oil/fats extraction (Area 100) and succinic acid production (Area 400) stages contribute ca. 47% each of the ADP of the whole biorefinery. The protein extraction (Area 200) and hydrolysate production (Area 300) stages contribute the lowest GWP and ADP values (Figure 7.5) to the total respective impacts due to the relatively lower energy requirements and CO_2 emissions.

Scenario 1 in Figure 7.6 presents the CO_2 emissions (3,110.9 kg CO_2-eq/t_{OFMSW}) from the proposed biorefinery using 1000 kg dry OFMSW for the production of 105 kg oil/fats, 87 kg proteins and 206.4 kg SA, including the CO_2 emissions (1,964.9 kg CO_2-eq) produced via landfilling of the remaining solids (467.8 kg). Scenario 2 in Figure 7.6 presents the CO_2 emissions (4,790.9 kg CO_2-eq/t_{OFMSW}) derived from landfilling of 1000 kg dry OFMSW (4,200 kg CO_2-eq) as well as the production of 105 kg sunflower oil (-234.2 kg CO_2-eq), 87 kg soy protein isolate (390.1 kg CO_2-eq) and 206.4 kg SA (435 kg CO_2-eq) produced from fossil resources. Scenario 2 represents the conventional production of end-products and OFMSW management.

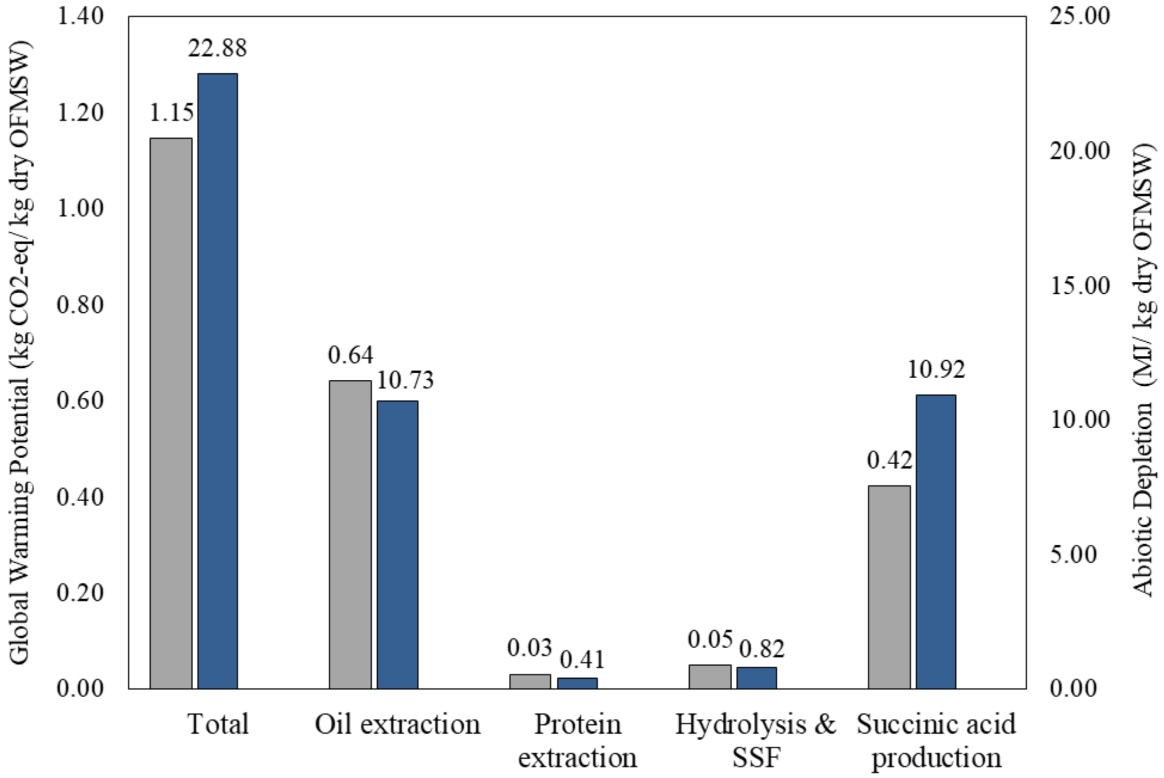


Figure 7.5 GWP (grey bars) and ADP (blue bars) expressed per kg dry OFMSW of the whole biorefinery and individual Areas 100-400

The CO_2 emissions for dry OFMSW landfilling (4.2 kg CO_2-eq/kg$_{OFMSW}$) were estimated using the Solid Waste Emissions Estimation Tool (SWEET) developed by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 2021). It has been assumed that the dry OFMSW contains food waste (50%), prunings (30%) and paper (20%). The impact of transportation is not considered in neither scenario. The CO_2 emissions for sunflower oil production (-2.23 kg CO_2-eq/kg$_{oil}$) were taken from Kachrimanidou et al. (2021) considering sunflower seeds cultivation, oil and SFM production from the seeds (mass allocation has been considered to oil and SFM) and oil refining. The negative CO_2 emissions for oil production is attributed to the CO_2 uptake (2.82 kg CO_2-eq/kg$_{oil}$) from the atmosphere due to sunflower cultivation. The CO_2 emissions for soy protein isolate production (ca. 5 kg CO_2-eq/kg$_{protein}$) has been taken from Arias et al. (2021), considering soybean cultivation and soy protein extraction (mass allocation has been considered among protein, whey and spent flour). The emissions for fossil derived SA (1.89 kg CO_2-eq/kg$_{SA}$) were taken from Smidt et al. (2015). The total CO_2 emissions of scenario 1 are 35% lower, corresponding to 1,680 kg CO_2-eq/t$_{OFMSW}$ savings, than the respective CO_2 emissions of scenario 2.

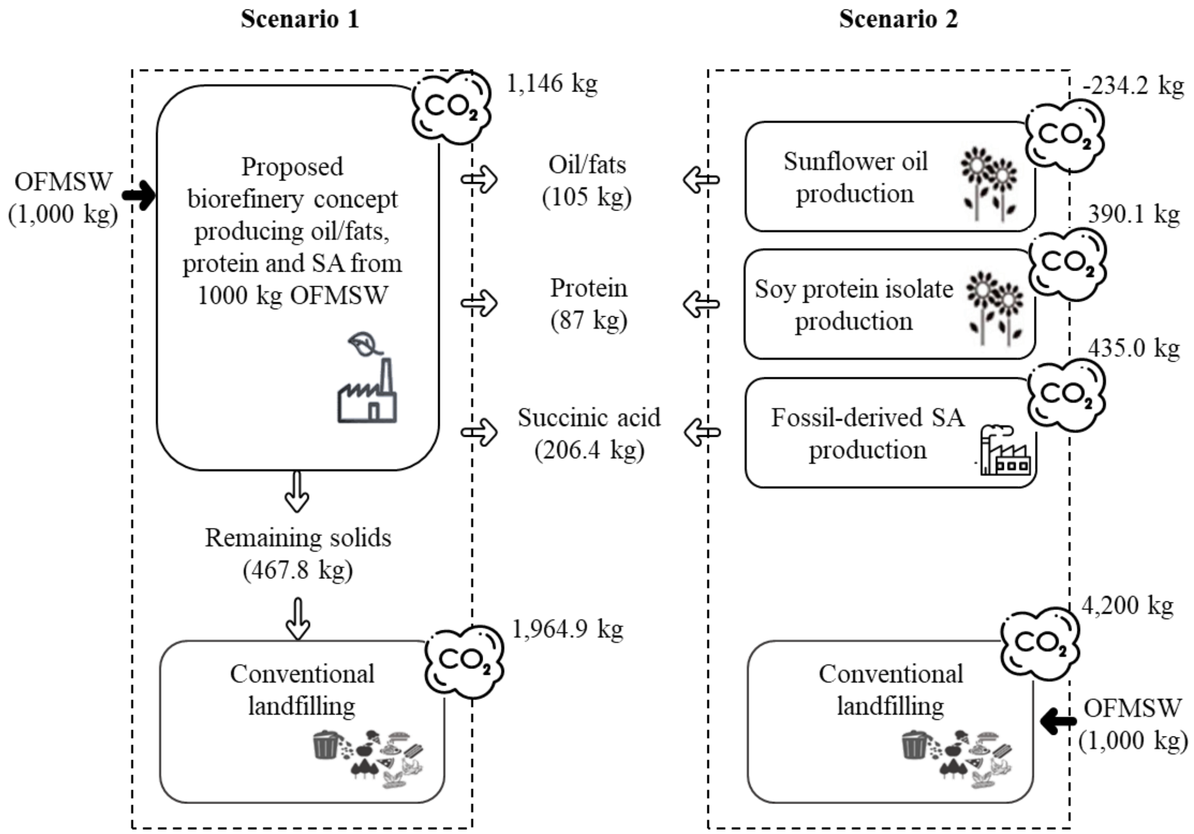


Figure 7.6 CO_2 emissions of the proposed biorefinery including landfilling of the remaining solids (scenario 1) as compared to CO_2 emissions derived from conventional processes for sunflower oil production, soy protein isolate production, fossil SA production and OFMSW landfilling (scenario 2)

Khoshnevisan et al. (2020) reported 73 kg CO_2-eq per t OFMSW-derived biopulp savings (compared to conventional processes producing equivalent end-products) when 1000 kg OFMSW-derived biopulp (18.3% total solids content) was converted into 13.3 kg bio-based SA, 1.52 kg bio-methane, biofertilizer containing 4.93 kg N, 0.5 kg P and 1.67 kg K, and 78.68 kg biogas (60% CH_4) for combined heat and power generation. It could be pointed out that converting the remaining solids in scenario 1 (Figure 7.6) into biogas and biofertilizer would improve further the environmental impact of the proposed biorefinery.

Escamilla-Alvarado et al. (2017) reported that a four-stage OFMSW biorefinery for the production of hydrogen, methane, enzymes and hydrolysates for further processing could lead to lower global warming (-128 kg CO_2-eq/t_{OFMSW} considering 20% total solids content in OFMSW) when compared to OFMSW landfilling. Escamilla-Alvarado et al. (2017) also reported that their proposed biorefinery was self-sustainable considering power requirements and partially independent considering heat requirements when the wastes from the bioproducts stage were digested.

Sadhukhan and Martinez-Hernandez (2017) pressented the exploitation of all possible fractions of MSW for biorefinery development via a mechanical biological chemical treatment system where the OFMSW (ca. 46.1% of the total MSW) is mainly processed via chemical conversion, effluent treatment and anaerobic digestion for the production of levulinic acid (7.4%), char (14.7%), biogas (3.5%), fertilizer (8.3%) and recyclable water (14.7%). The environmental impact potential benefit for the whole process is 294 kg CO_2-eq/t_{MSW} for GWP and 6.14 GJ/t_{MSW} for fossil energy saving. When the savings were expressed on individual product basis, the GWP savings were 2.4 kg CO_2-eq per kg of levulinic acid and 1.3 kg CO_2-eq per kg fertilizer.

Chen et al. (2017) reported the environmental impact of caproic acid production from mixed organic waste employing biological acidification, chain elongation, liquid-solid separation, chemical acidification, liquid-liquid extraction and distillation as process stages. The GWP of this process was 14.9 kg CO_2-eq per kg caproic acid.

The environmental impact of OFMSW-based biorefineries could be reported on per product or feedstock basis. Reporting the environmental impacts using the feedstock as functional unit facilitates the comparison of different alternative biorefinery scenarios. Future studies should focus on life cycle costing in order to combine techno-economic production costs with monetized environmental impacts.

Chapter 8 Sustainability assessment of the development of OFMSW biorefinery for the production of market products

8.1 Introduction

In 2019, ca. 225 million t of municipal solid wastes (MSW) were generated in EU with the organic fraction (OFMSW) constituting 30-40% of the total MSW (European Environment Agency, 2013; Eurostat, 2021a). According to the EU Directive 2018/851, OFMSW includes biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises and comparable waste from food processing plants (Stylianou et al., 2020). The OFMSW is rich in lipids (1.5-11.5%), proteins (7.0-11.8%), free sugars (0.7-7.4%), starch (14.2-22.1%), cellulose (8.5-15.4%), hemicellulose (4.2-11.5%) and lignin (5.6-12.1%). The OFMSW could support the development of sustainable biorefineries as it is widely available, while particularly in EU countries the highest production capacities in 2018 were observed in Germany (ca. 15.6 million t/y, wb) and France (ca. 10.43 million t/y).

A novel biorefinery concept has been developed focusing on the utilisation of OFMSW for the development of two alternative value chains, one focusing on the production of lactic acid (LA) and biosurfactants and the other on the production of succinic acid (SA) and biosurfactants. The OFMSW was initially treated via enzymatic hydrolysis for the production of a C5/C6 sugar-rich hydrolysate that was used for fermentative production of either lactic acid or succinic acid. The poly(lactic acid) (PLA) produced from lactic acid was employed as ingredient in hot melt adhesives (HMAs). Succinic acid has been evaluated as substitute for adipic acid or commercial succinic acid for the production of polyester polyols (PP) that were used for the production of polyurethane urea dispersions (PUDs). The lipid and protein rich fraction that remained after enzymatic hydrolysis of polysaccharides was used for the production of biosurfactants.

HMAs offer the advantages of being solids at room temperature and liquids with adhesive properties when heated that bond rapidly to the substrate at subsequent cooling. HMAs have superior processing advantages to solvent- and water-based adhesives due to no solvent/water requirements, low volatile organic compounds, fast drying, bonding versatility and quick set time (Vineeth and Gadhave, 2020). The global market for HMAs was valued at \$6.74 billion in 2019 and it is expected to grow at a CAGR of 6.7% until 2027, owing to their increasing applications (Global Market Insights, 2016). As their utilisation in packaging is intensified, the replacement of petroleum-derived HMAs by bio-based, biodegradable and 100% recyclable counterparts is of high importance. PLA has been used for HMA production with versatile bonding applications (Kadoma et al., 2015). In this study, the lactic acid produced via fermentation of OFMSW-derived hydrolysate has been used for the production of bio-based HMAs.

The SA market is projected to grow from $131.7 million in 2018 to $237.8 million by 2027 considering both petro-based and bio-based SA (Markets and Markets, 2019). The petro-based SA segment dominates the market due to its cost-competitiveness with the major industrial application being the production of polyester polyols for polyurethane manufacturing. PUDs are mainly used in construction, automotive, furniture, leather and textile industries, while the PUDs market growth is projected to grow from $1.9 billion in 2020 to $2.7 billion by 2025 (Markets and Markets, 2021a). The PUDs produced in the PERCAL project are suitable for the production of coating compositions for flexible substrates, such as textiles, leather, paper, glass fibres, plastics fibres and graphite fibres (Grablowitz et al., 2012). The substitution of petro-based SA or adipic acid by OFMSW-derived bio-based SA for polyester polyol and PUDs production could increase process sustainability. For instance, the bio-based SA produced from corn-derived glucose via fermentation leads to 90% and 54.6% less greenhouse gas emissions (GHG) than petro-based adipic acid (AA) and petro-based SA, respectively (Cok et al., 2014).

The surfactants market is expected to reach $52.4 billion by 2025 from $42.1 billion in 2020, with home care products (e.g. detergents, cleaners) leading the market (Markets and Markets, 2020). The biosurfactants market is expected to reach $6.04 billion by 2029 from $4.18 billion in 2022 with household cleaners dominating the market (46.8% of the total) (Fortune Business Insights, 2021). The production of surfactants from amino acids and vegetable oils is well-known (Infante et al., 2004). High surface activity can be achieved from amphiphilic structures produced from polar amino acids/peptides (hydrophilic moiety) and non-polar long-chain compounds (hydrophobic moiety). The surfactant type (e.g. cationic, anionic, non-ionic, amphoteric) and properties (e.g. adsorption, aggregation, biological activity) is dependent on the amino acid or peptide moieties. The PERCAL project produced biosurfactants from OFMSW-derived lipids and proteins for non-food applications (e.g. detergents) as substitute for petroleum-derived surfactants, such as linear alkylbenzene sulphonates, that dominate the market.

Process design, techno-economic evaluation and life cycle assessment (LCA) have been employed in this study for the evaluation of four biorefinery concepts using OFMSW for the production of biosurfactants and one of the following end-products (Figure 1): LA (Biorefinery 1, B1), SA (Biorefinery 2, B2), HMAs (Biorefinery 3, B3) and PUDs (Biorefinery 4, B4). The main novelty of this study lies on the assessment of the proposed technologies for the utilisation of OFMSW as industrial feedstock in the bioeconomy era as a sustainable alternative to conventional OFMSW management practices. The production of multiple products from OFMSW is essential in order to reach process viability and profitability. Thus, the protein and lipid fractions should be used for the production of non-food products as the nature of the feedstock prohibits food and feed applications. For this reason, four biorefinery concepts have been evaluated with biosurfactants being the common end-product derived from lipids, proteins and bacterial biomass (Figure 8.1). Lipids and proteins have been separated from the solids remaining after enzymatic hydrolysis of OFMSW to avoid drying of OFMSW for lipid separation, loss of free sugars present in OFMSW and high unit operation capacity requirement for the extraction of lipids/proteins from the initial untreated OFMSW. Ladakis et al. (2022) presented a biorefinery concept for SA production from OFMSW where lipids and proteins were removed before enzymatic hydrolysis of polysaccharides. OFMSW drying is required for hexane extraction of lipids leading to 2.057 GJ/t_{OFMSW} with major contribution in the environmental impact, while free sugars are lost (ca. 25% of the total sugars available in OFMSW). To illustrate the importance of biorefinery development, the production of LA, SA, HMAs and PUDs has been evaluated either individually or in combination with biosurfactants production.

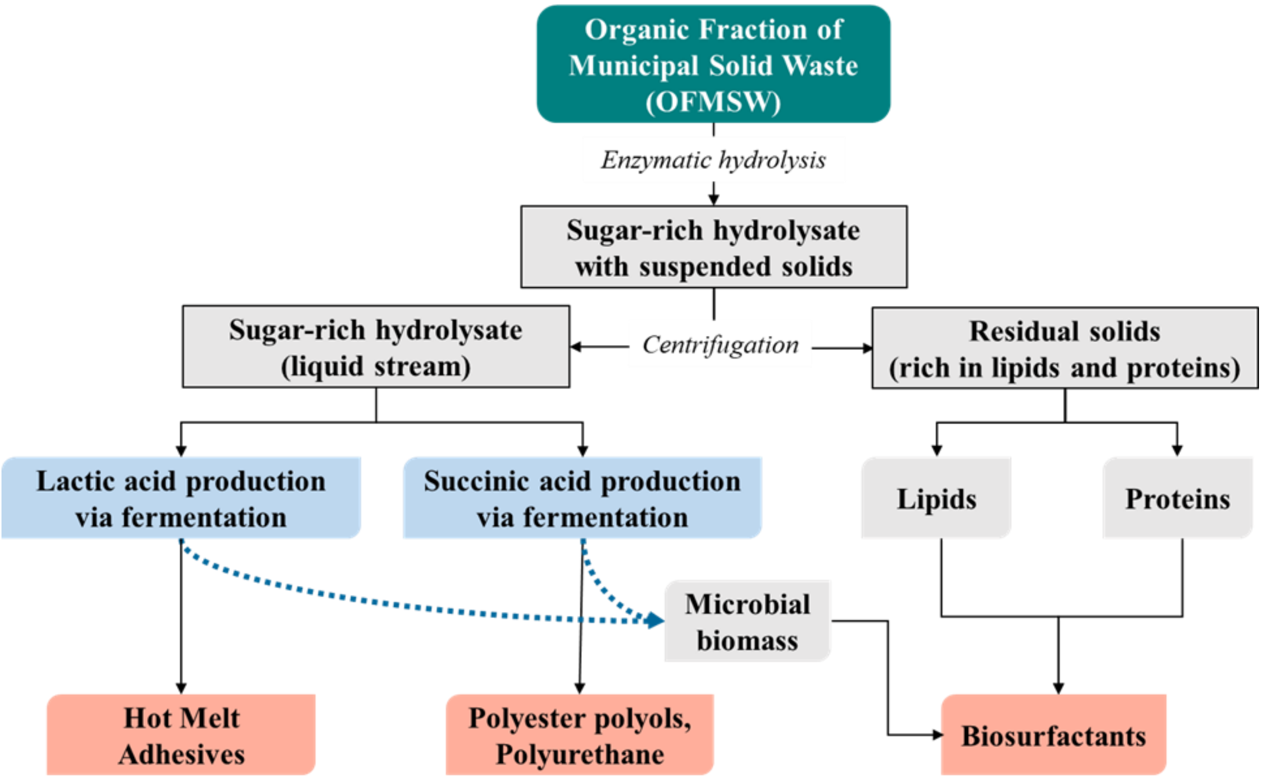


Figure 8.1 Utilisation of OFMSW for the development of four biorefinery concepts producing biosurfactants and one of the following products: LA (B1), SA (B2), HMAs (B3) and PUDs (B4)

8.2 Description of the processes

8.2.1 OFMSW hydrolysis

The OFMSW used in this study contains 4.71% starch, 39.64% cellulose, 0.2% hemicellulose, 9.47% lignin, 10.15% protein, 1.57% lipids and 15.87% pectin on a dry basis, while 75% moisture content was considered (Stylianou et al., 2020). Enzymatic hydrolysis of OFMSW (Figure 8.2) was carried out in agitated tank V-101 at 50^{o}C for 72 h using a tailor-made enzymatic cocktail the enzyme activities of which cannot be disclosed due to confidentiality reasons. The enzyme cocktail cost (\$4.24/kg$_{enzyme}$) was taken from Humbird et al. (2011) that considered the cost for cellulase, which was close to the cost of the enzymatic cocktail used in this study. The enzyme cocktail quantity used in each hydrolysis was approx. 0.01 kg enzyme cocktail/kg OFMSW. After hydrolysis, stream 101 is centrifuged (CF-101) to separate the solid residues that are rich in lipid and protein fractions (stream 102) from the sugar-rich hydrolysate (stream 103).

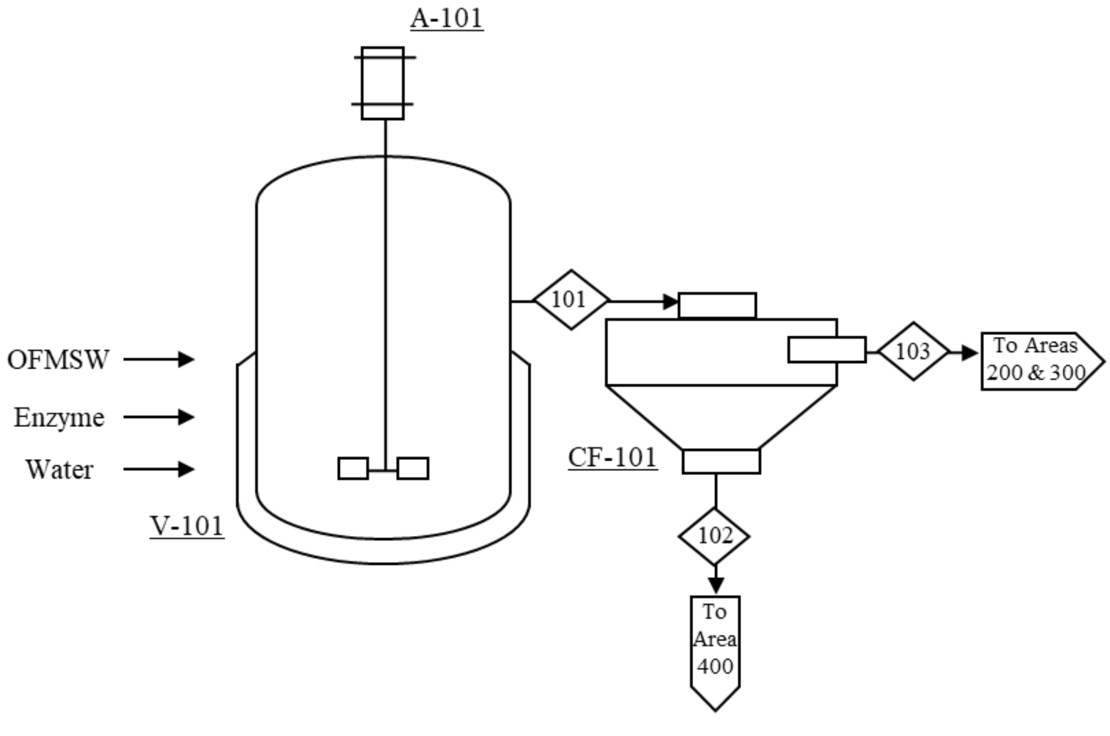


Figure 8.2 Process flow diagram for OFMSW pretreatment (Area 100).

8.2.2 Lactic acid production

The sugar-rich hydrolysate is sterilized in continuous mode using three heat exchangers (E-201, E-202, E-203). LA production is subsequently carried out in the bioreactor (Figure 8.3, F-203) leading to 60 g$_{LA}$/L with 0.7 g$_{LA}$/g$_{sugars}$ yield and 2.68 g$_{LA}$/(L·h) productivity (López-Gómez et al., 2019)

These fermentation efficiency parameters have been used in the optimization of bioreactor design (i.e. loading time, uploading time, number of batches per year, number of bioreactors per batch and working volume of each bioreactor) via the mathematical software GAMS following the methodology described by Dheskali et al. (2017). The optimal parameters for bioreactor design in various annual capacities are presented in Table 8.1. In the downstream separation and purification (DSP) section, the bioreactor outflow stream 202 is centrifuged (CF-201) and then filtered (NF-201) to remove bacterial cells and any salt residues. The liquid stream goes through a softening process (SF-201) followed by lactic acid recovery using monopolar (ME-201) and bipolar (BE-201) electrodialysis, during which a LA-rich stream is separated from the base and salt fractions. The evaporator EV-201 is employed for the concentration of the retentate stream from monopolar electrodialysis to reduce LA losses by recycling the concentrated stream though monopolar electrodialysis. After bipolar electrodialysis, stream 206 is treated through a series of resin columns (V-203, V-204, V-205) for decolourisation followed by evaporation (EV-202) to produce a LA-rich stream with 99.9% purity and 97.7% recovery yield. Recycling of processing streams has been considered to reduce water requirements. NaOH is recycled (stream 205) from bipolar electrodialysis to the bioreactor.

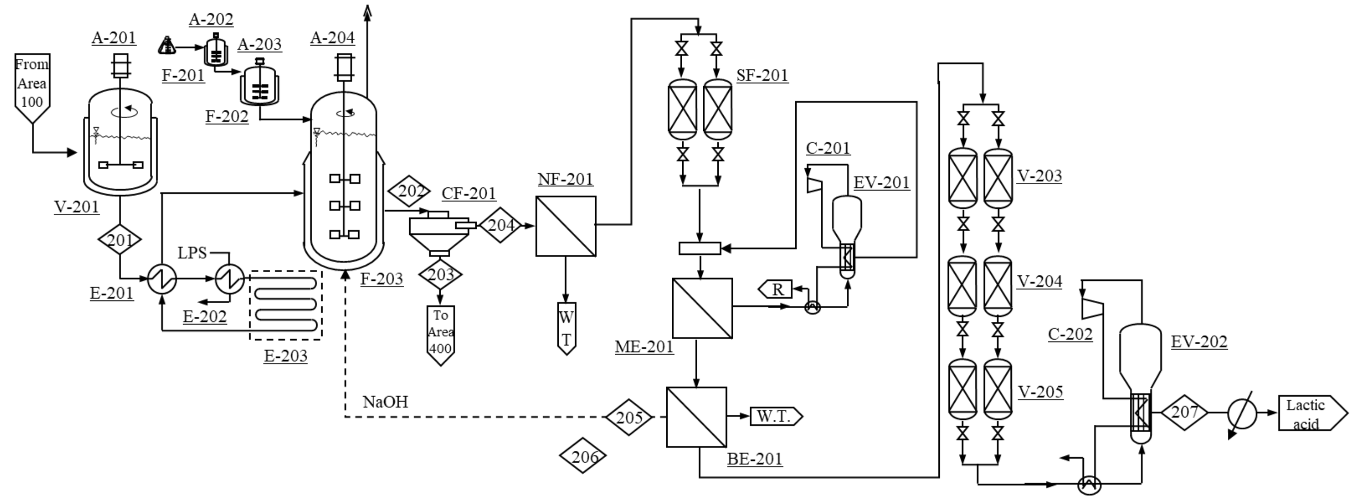


Figure 8.3 Process flow diagram for lactic acid production (Area 200)

Table 8.1 Optimal bioreactor design parameters for lactic acid production in various annual capacities. The bioreactor design optimization was based on the methodology developed by Dheskali et al.

Annual capacity (t)	**10,000**	**20,000**	**40,000**	**50,000**	**60,000**
Loading time, τ_l (h)	2	2	2	4	4
Uploading time, τ_{ul} (h)	5	5	5	3	3
Number of batches per year, N_b	1579	1579	1579	2631	2631
Number of bioreactors per batch, N_f	6	6	6	10	10
Working volume of each bioreactor V_b (m^3)	105.5	211.1	422.2	316.7	380.1

8.2.3 Succinic acid production

The OFMSW hydrolysate is sterilized (E-301, E-302, E-303) using the same continuous system as in the case of lactic acid. SA production is subsequently carried out in the bioreactor (F-303, Figure 8.4) with inoculum preparation bioreactors (F-301, F-302) using the bacterial strain *Actinobacillus succinogenes* to produce 29.4 g_{SA}/L with 0.56 g_{SA}/g_{sugars} yield and 0.89 g_{SA}/(L·h) productivity (Stylianou et al., 2020). The optimal bioreactor design and scheduling parameters (i.e. loading time, uploading time, number of batches per year, number of bioreactors per batch and working volume of each bioreactor) have been identified (Table 8.2) using the fermentation efficiency parameters presented above and using the mathematical software GAMS following the methodology described by Dheskali et al. (2017). The DSP of SA is carried out according to the methodology described by Alexandri et al. (2019b). Centrifugation of the fermentation broth (CF-301) is carried out to remove the bacterial biomass followed by treatment of stream 304 via activated carbon columns (V-302) for decolourisation and impurity removal. The decolourised effluent is fed to the cationic resin columns (V-303) to convert organic acid salts into their corresponding organic acids. The acidified liquid stream is then mixed with the recycled stream from the crystallisers (CR-301, CR-302) followed by concentration using the mechanical vapour recompression (MVR) - forced circulation evaporator system (EV-301). The concentrated liquid is subsequently treated via crystallisation in continuous crystallisers (CR-301, CR-302) at 4°C. The wet succinic acid crystals are dried in a spray dryer (DR-301). The SA crystal purity and recovery yield are ca. 99.9% and 95%, respectively.

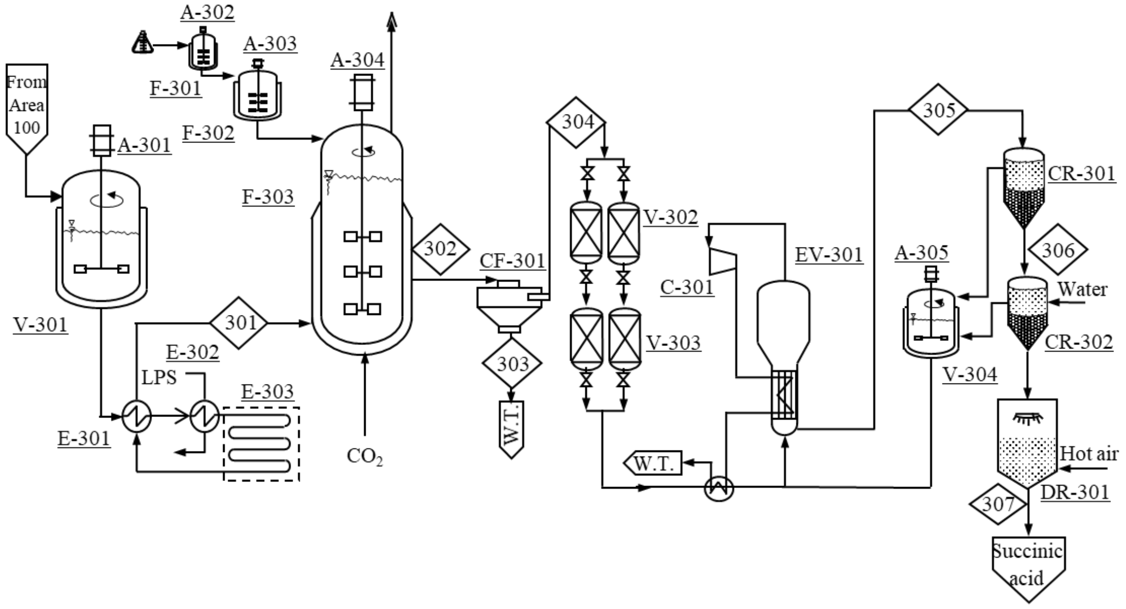


Figure 8.4 Process flow diagram for succinic acid production (Area 300)

Table 8.2 Optimal bioreactor design parameters for succinic acid production in various annual capacities. The bioreactor design optimization was based on the methodology developed by Dheskali et al.

Annual capacity (t)	**10,000**	**20,000**	**40,000**	**50,000**	**60,000**
Loading time, τ_l (h)	2	2	2	2	4
Uploading time, τ_{ul} (h)	6	4	2	2	2
Number of batches per year, N_b	1314	1971	3942	3942	3942
Number of bioreactors per batch, N_f	7	10	19	19	20
Working volume of each bioreactor, V_b (m^3)	258.8	345.1	345.1	431.4	517.7

8.2.4 Biosurfactants production

Biosurfactants production is based on data provided by the company CENER and Kester (1949) using clorated lipids and proteins separated from the remaining solids after OFMSW hydrolysis (stream 102) along with bacterial cells from LA (stream 203) and SA (stream 303) production (Figure 8.5). Around 50% of the aforementioned solid streams are dried (DR-401) followed by lipid extraction (V-401) using a mixture of ethanol and ethyl-acetate (1:1 ratio, 16% w/v). The solvents are recycled via evaporation (EV-401), while the lipids are clorated with HCl (37%, 100% w/w). The remaining solids (50% of the total) are enzymatically hydrolysed (V-402) for protein extraction using protease (0.12 kg_{enzyme}/kg_{solids}) at 50°C for 24 h. After centrifugation (CF-401), the liquid stream is concentrated via evaporation (EV-402). Streams 404 and 407 are mixed and condensated (V-403) in the presence of KOH (85%, 11% w/v) and the intermediate product is then precipitated (V-404) with the use of HCl (37%, 12% v/v). After centrifugation (CF-402), the stream 409 is mixed with petroleum ether and water (1:2 ratio, 77% v/v) (V-405, V-406) and then with ethanol (V-407). Stream 412 is purified (EV-403) at 50°C and the final biosurfactants are recovered. Recovery of solvents (ethanol, petroleum ether and water) has been considered in all stages when required. Thus, the amounts of solvents for the inventory analysis are calculated considering 10% losses for each solvent.

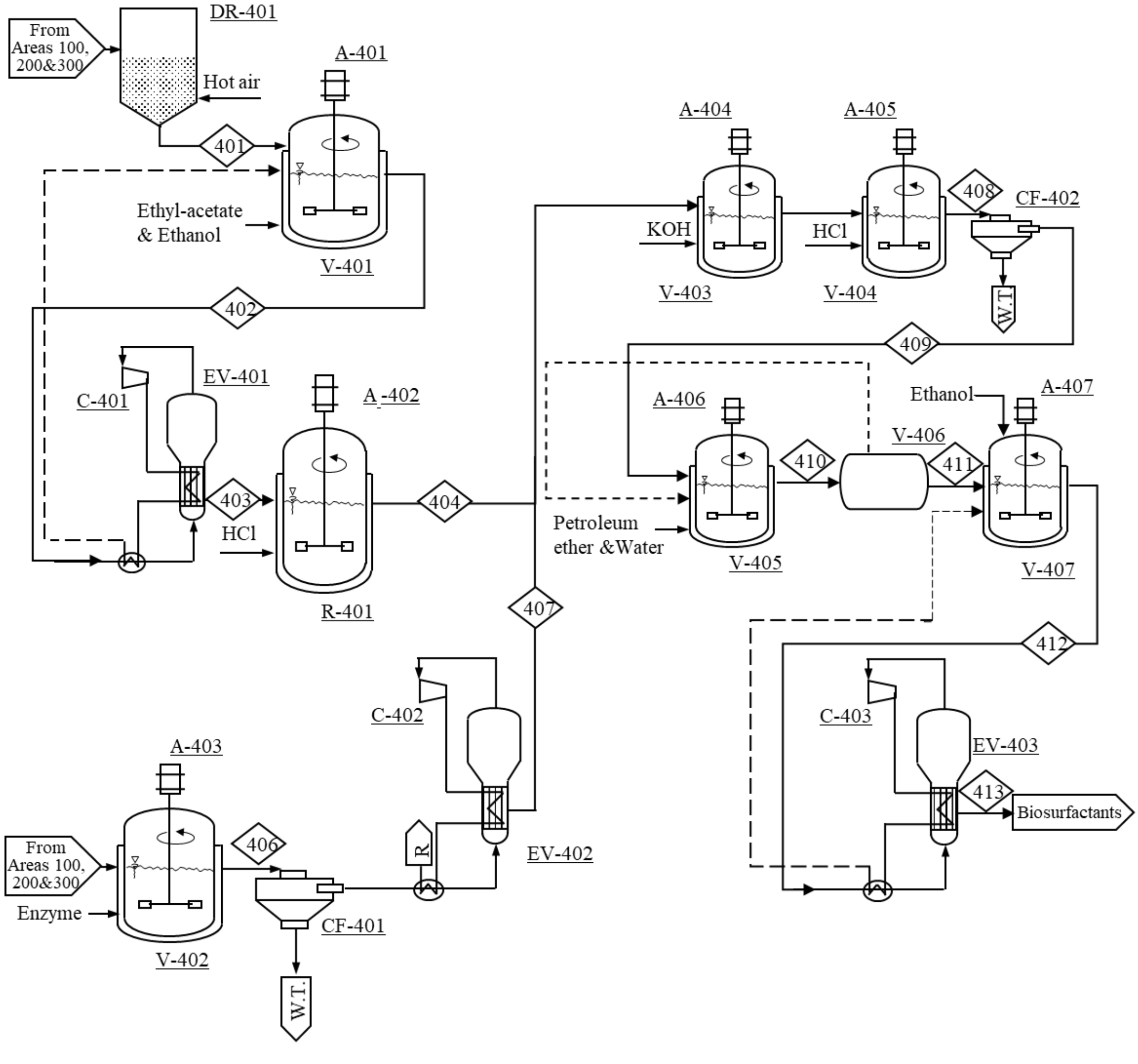


Figure 8.5 Process flow diagram for biosurfactants production (Area 400)

8.2.5 Hot Melt Adhesives production

LA polycondensation (R-501) is carried out at 190^{o}C for 5 h and low MW PLA is produced with simultaneous water removal via aqueous distillation (T-501). Then, depolymerisation of PLA takes place (R-502) with simultaneous lactide oligomer distillation (T-502) at 250^{o}C for 12 h in the presence of catalyst (zinc acetate) so as to yield lactide. The lactide stream is cooled (E-505), recrystallised at 56^{o}C in acetone (V-501) and collected via thermal crystallisation (CR-501) and drying (DR-501). The acetone is fully recovered through DR-501 and reused for lactide purification (Figure 8.6).

Lactide is mixed (V-502) with polycaprolactone (PCL) diol, catalyst (stannous octoate) and stabilisers (triphenylphosphine, Songnox 1135) at 0.3 bar. Reactive extrusion is carried out (EX-501) via ring-opening polymerisation of lactide and e-caprolactone, initiated with PCL diol, added in the previous step, to yield PLA-co-PCL (copolymer). The copolymer is finally compounded (EX-502) with tackifier and antioxidant at 170^{o}C to produce HMAs. The energy requirements for lactide production have been estimated based on lab-scale experiments. Lower utility requirements are expected on industrial scale.

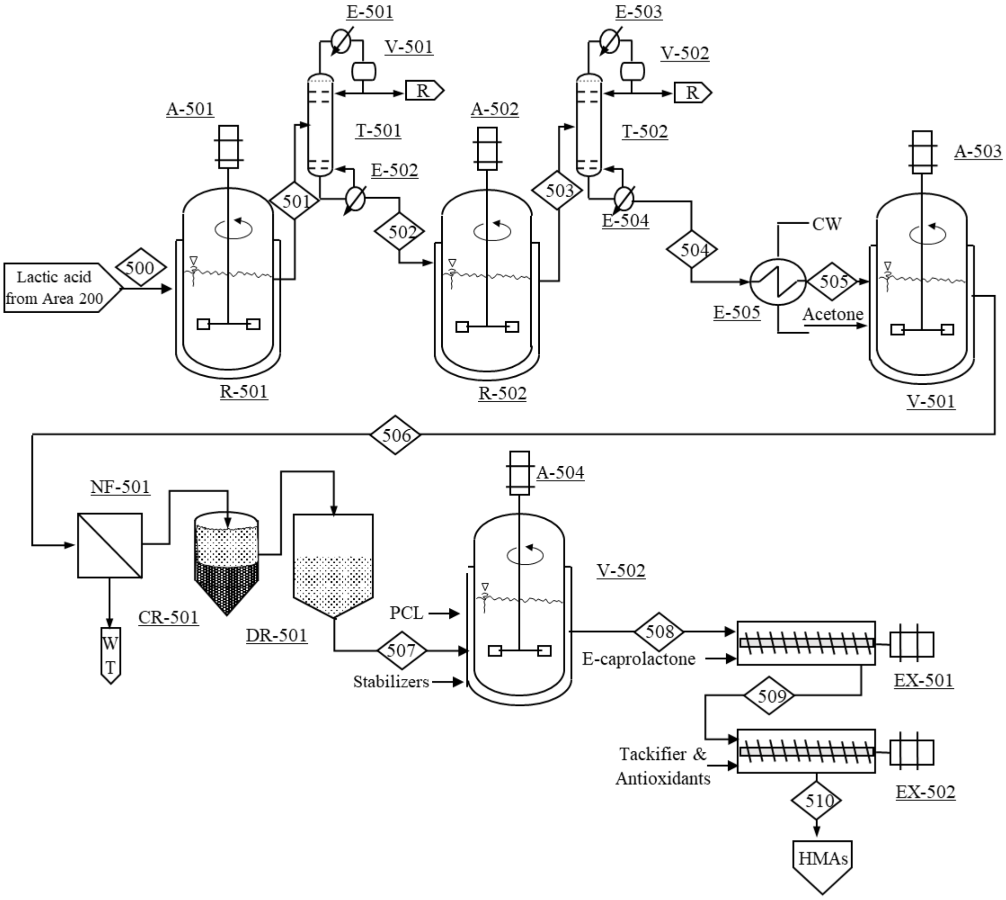


Figure 8.6 Process flow diagram for HMAs production (Area 500)

8.2.6 Polyurethane Urea Dispersions production

PUDs production, containing 42 wt.% solid polyurethane, has been simulated according to the patent of Grablowitz et al. (2012) where two main stages are considered, polyester polyol formation and then the reaction with isocyanates to create PUDs (Figure 8.7).

Polyester polyol production begins with mixing of 1,6-hexanediol (HXDO) and neopentyl glycol (NPG) with $SnCl_2$ (V-601) at 100°C. Then, the liquid outflow is heated to 220°C and added into the reactor (R-601) along with SA using the following ratio 0.7 HXDO:0.4 NPG:1 SA. After the monomer (ester) formation, the stream enters the second reactor (R-602) for polymerisation. The total reaction time (considering both monomer and polymer production) is about 13 h and the final product has a MW of about 1,730.

In the second stage, isophorone diisocyanate (IPDI), 1,6 hexamethylene diisocyanate (HDI), the monofunctional hydrophilising agent LB25 and polyester polyol produced in Area 600 are heated to 50°C (E-701) and then reacted at 100°C (R-701) to produce the prepolymer. Acetone is then added at 80°C (E-702), the total outflow of the reactor is cooled to 40°C (E-703) and the prepolymer is dissolved. After that, a chain-extending solution of isophorone diamine (IPDA), diaminosulfonate (AAS) and hydrazine hydrate (HyHy) (1:0.35:0.3 ratio) is added along with the prepolymer to the second reactor (R-702) for 5 min at 40°C. The product is dispersed in water at 1.46:1 water to solid ratio. Finally, the acetone is distilled off at 120 mbar and 40°C (T-701). Aqueous PUDs having a solids content of 41.9 wt.% with MW of 100,000 g/mol and a density of 1,000 kg/m^3 is obtained.

The simulation is performed in Honeywell UniSim that has a limited capability as far as polymerisation reactions are concerned. Thus, some assumptions have been made. The first assumption is related to the thermodynamic data of IPDI, HDI, LB25, IPDA, AAS, polyester polyol and polyurethane. These components had to be registered in the software as hypothetical components and their properties have been determined by estimation methods. As the prepolymer in R-701 could not be determined, the reactions in R-701 and R-702 are assumed as one total reaction taking place in the first reactor. The reactants are IPDI, HDI, LB25, polyester polyol and the mixture of the chain extending solution and the final product is the polyurethane. The duration for the entire reaction is about 10 h. Owing to the lack of data about the specific reaction rate, a stoichiometry reaction for polymerisation is assumed. The energy of the reaction at 100°C is estimated considering that 352 kJ per kg solid polyurethane is required.

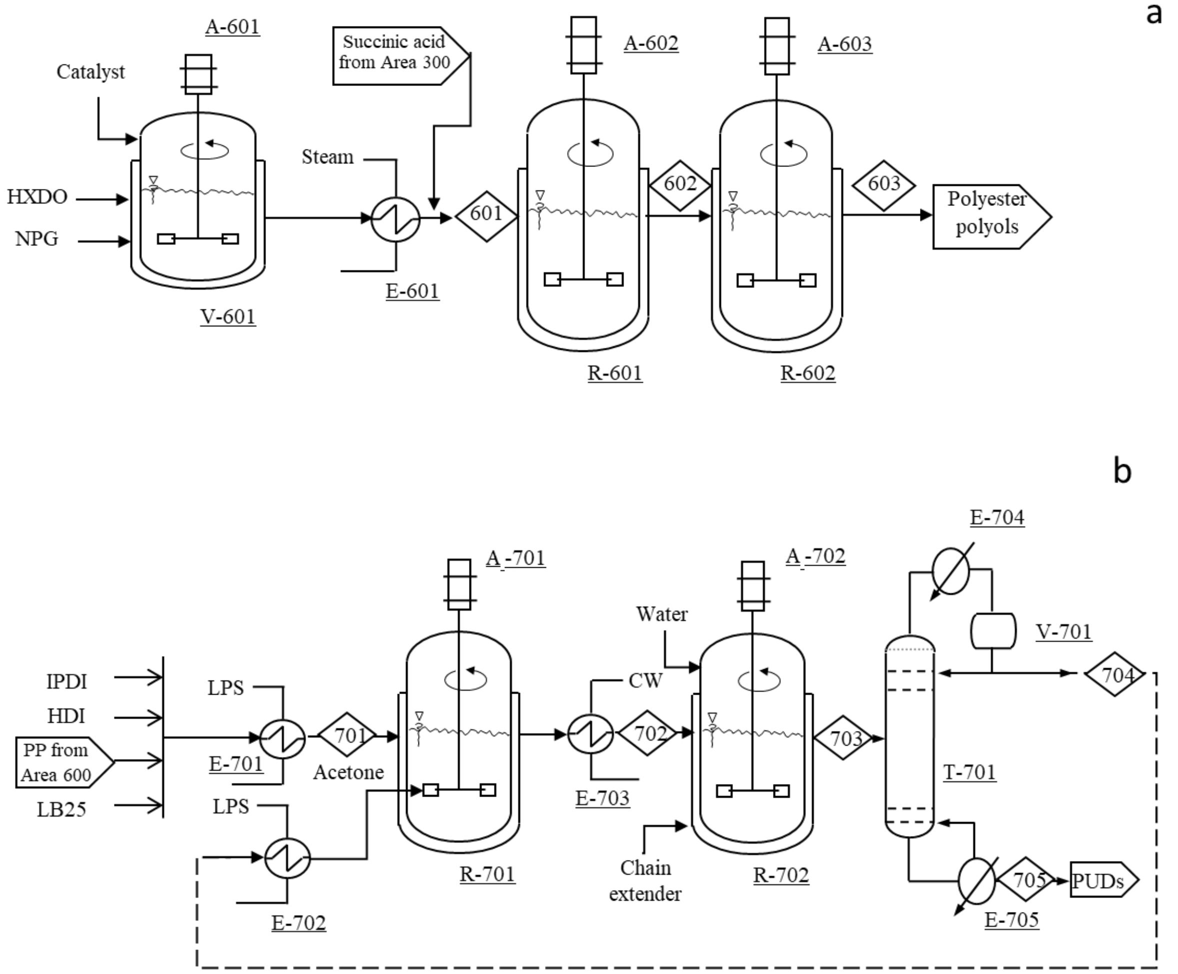


Figure 8.7 Process flow diagram for polyester polyols (Area 600, a) and PUDs (Area 700, b) production.

8.3 Techno-economic assessment

8.3.1 OFMSW hydrolysis and biosurfactants

All biorefinery concepts begin with enzymatic hydrolysis of starch, cellulose and hemicellulose contained in the OFMSW resulting in a nutrient-rich hydrolysate containing ca. 100 g/L total sugars, 630 mg/L free amino nitrogen and 553 mg/L inorganic phosphorus. Table 8.3 presents the FCI (M\$53.67) of Area 100 for the hydrolysis of 1,197,261 t OFMSW (on wet basis, wb) that is required for the production of 50,000 t_{SA}. The respective COM (M\$30.08) of the hydrolysis section for 50,000 t_{SA} production has been estimated using the C_{UT} (M\$2.9), the C_{OL} (M\$0.39) and the C_{RM} (M\$12.82). The FCI (M\$66.11) and COM (M\$36.96) of Area 100 have been also estimated for the production of 76,500 t_{LA} from 1,465,400 t_{OFMSW} (wb) (see section 8.3.5). The lowest sugar production cost is \$205/t_{sugars} at OFMSW capacity of 718,597 t, when economy of scale has been achieved. It should be mentioned that OFMSW management fees have been included in the DCF analysis as revenues. These fees vary ($35-118/t) depending on the country and region (Hogg, 2002). In this study, the most conservative scenario has been used ($35/$t_{OFMSW}$). The cost of glucose syrup from corn is ca. $230/t (USDA, 2018), which is higher than the sugar production cost from OFMSW. The techno-economic cost of OFMSW hydrolysis (Area 100) has been combined with those of LA (Areas 200) and SA (Area 300) production.

Table 8.4 presents the FCI (M$144.43) of Area 400 for the production of 25,000 t biosurfactants, which is the capacity produced from 1,197,261 t_{OFMSW} that is used for the production of 50,000 t_{SA}. The evaporators (EV-401, EV-402 and EV-403) employed for solvents recirculation, concentration of protein stream and biosurfactants purification contribute the highest purchase equipment cost (ca. 88%) for Area 400. The COM (M$69.35) for the production of 25,000 t biosurfactants is estimated using the C_{UT} (M$5.62), C_{OL} (M$3.65) and C_{RM} (M$21.52), corresponding to a biosurfactants unitary production cost of $2.77/kg (see section 8.3.5). The respective techno-economic data for the production of 31,000 t biosurfactants, produced when 76,500 t_{LA} is evaluated, is presented in section 8.3.3. The current market price of biosurfactants is $4.1/kg (Alibaba.com), which is 32.4% higher than the unitary production cost estimated in this study, showing the profitability potential of biosurfactants production from OFMSW.

Table 8.3 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for enzymatic hydrolysis of 1,197,261 t OFMSW (Area 100).

Unit	**Description**	**Unit number**	**$CEPCI_{t0}$ [c]**	**Characteristic size (X_t) [d]**	**FOB Cost (C_p@2018, M$)**	**Electricity (kWh/y)**	**Steam (t/y)**	**Cooling water (t/y)**
V-101	Mixing tank[a]	3	521.9	V=4,737 m^3	4.096		72,005	
A-101	Agitator[a]	7	521.9	P=725.93 hp	4.672	32,194,489		
CF-101	Centrifugal separator[b]	2	444.2	Q=78.95 m^3/h	1.966	736,560		
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A100 (N_{OL})		2						
Total Ceq.fob (M$)					10.734			
FCI A100 (M$)			**5 × Total Ceq.fob A100 =**		**53.670**			
C_{OL} A100 (M$)					**0.390**	**C_{UT} A100 (M$/y) =**	**2.9**	

FOB purchase equipment cost (C_p) estimation: [a] Dheskali et al.[17]; [b] Peters, Timmerhaus and West[21]; [c] $CEPCI_{t0}$: Chemical Engineering Plant Cost Index at the year where the purchase equipment cost (C_{p,t_0}) is available considering a characteristic size (X_{t_0}); [d] X_t: is the characteristic size of each unit operation estimated in this study via process design and used for the estimation of the FOB purchase equipment cost at 2018 as follows $C_{p,2018} = \frac{CEPCI_{2018}}{CEPCI_{t_0}} C_{p,t_0} \left(\frac{X_t}{X_{t_0}}\right)^n$

Table 8.4 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 25,000 t biosurfactants (Area 400)

Unit	**Description**	**Unit number**	**$CEPCI_{t0}$**	**Characteristic size (X_t)**	**FOB Cost (Cp@2018, M$)**	**Electricity (kWh/y)**	**Steam (t/y)**	**Cooling water (t/y)**
DR-401	Dryer[c]	1	397.0	A=24.24 m^2	1.298	50,317,596	19,324	
V-401	Mixing tank[c]	1	521.9	V=576.58 m^3	0.397			
A-401	Agitator[a]	1	521.9	P=687.29 hp	0.571	4,059,143		
EV-401	Evaporator[a,c]	29	521.9	A=976.75 m^2	12.529	1,060,194		
R-401	Reactor[c]	2	397.0	V=20.81 m^3	0.194	293,053		164,084
V-402	Mixing tank[a]	3	521.9	V=790.77 m^3	1.459		30,395	
A-403	Agitator[a]	4	521.9	P=706.95 hp	2.355	16,701,173		
CF-401	Centrifugal separator[b]	1	444.2	Q=79.08 m^3/h	0.767	736,560		
EV-402	Evaporator[a,c]	2	521.9	A=897.97 m^2	2.167	789,659	2,835	
V-403	Mixing tank[a]	1	521.9	V=35.89 m^3	0.202			528,283
A-404	Agitator[a]	1	521.9	P=42.79 hp	0.043	252,735		
V-404	Mixing tank[a]	1	521.9	V=54.25 m^3	0.202			
A-405	Agitator[a]	1	521.9	P=64.69 hp	0.061	382,096		
CF-402	Centrifugal separator[b]	1	444.2	Q=21.71 m^3/h	0.339	237,600		
V-405	Mixing tank[a]	1	521.9	V=13.33 m^3	0.202			
A-406	Agitator[a]	1	521.9	P=15.89 hp	0.021	93,870		
V-406	Decanter[c]	1	521.9	V=53.33 m^3	0.046			
V-407	Mixing tank[a]	1	521.9	V=14.99 m^3	0.202			
A-407	Agitator[a]	1	521.9	P=17.87 hp	0.022	105,538		
EV-403	Evaporator[a,c]	11	521.9	A=942.48 m^2	5.807	767,852		
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A400 (N_{OL})		20						
Total Ceq.fob (M$)					28.886			
FCI A400 (M$)				**5 × Total Ceq.fob A400 =**	**144.431**			
C_{OL} A400 (M$)					**3.650**		**C_{UT} A400 (M$/y) =**	**5.616**

[a] Dheskali et al; [b] Peters, Timmerhaus and West; [c] Turton et al.;

8.3.2 Lactic acid

Table 8.6 presents the characteristic size of each unit operation in Area 200, the total Ceq.fob, the FCI (M$283.1) and the C_{UT} (M$19.97/year) for an annual production capacity of 76,500 t_{LA}. This LA production capacity has been considered to satisfy the 5% of current HMAs production. The bioreactors (F-203/A-204) contribute the highest FCI (ca. 31%) followed by the monopolar electrodialysis membrane (ME-201, ca. 22%) and evaporation (EV-201, ca. 20%). The C_{UT} is mainly affected by energy consumption for both electrodialysis membrane unit operations, agitation and the steam used in the evaporator. The COM (M$89.38) of LA production has been estimated using the CUT, the C_{OL} (M$4.55) and the C_{RM} (M$1.17) presented in Table 8.5.

The FCI and COM have also been estimated at various plant capacities (10-100 kt/y) (Figure 8.8) considering both OFMSW enzymatic hydrolysis (Area 100) and LA production (Area 200) stages. The OPC in which economy of scale is achieved is 50,000 t_{LA}. The lowest unitary LA production cost is \$1.74/kg_{LA} (Figure 8.8). Kwan et al. (2018) reported a higher LA production cost (\$2.47/kg_{LA}) when food waste was used at annual capacity of ca. 25,000 t_{LA}.

DCF analysis showed that the MSP at the OPC is \$1.78/kg_{LA} with the current LA market price being \$1.45/kg_{LA} (E4tech et al., 2015) When the biorefinery concept B1 is considered, including the production of both LA and biosurfactants, the MSP is reduced to \$1.58/kg_{LA}. The MSP_{LA} when the biorefinery concept B1 is considered is close to the current market price of lactic acid. Increasing the fermentation efficiency of lactic acid production is essential in order to reduce further the MSP_{LA}. Li et al. (2021) reported a MPS range of \$1.09-1.91/kg_{LA} that depends on the selection of key technological parameters (e.g. yiesld, technology used in DSP and process parameter sensitivities). The MFR for 50,000 t lactic acid production is 952.38 kt_{OFMSW}/year (wb), which is available in many EU countries, including Germany and France.

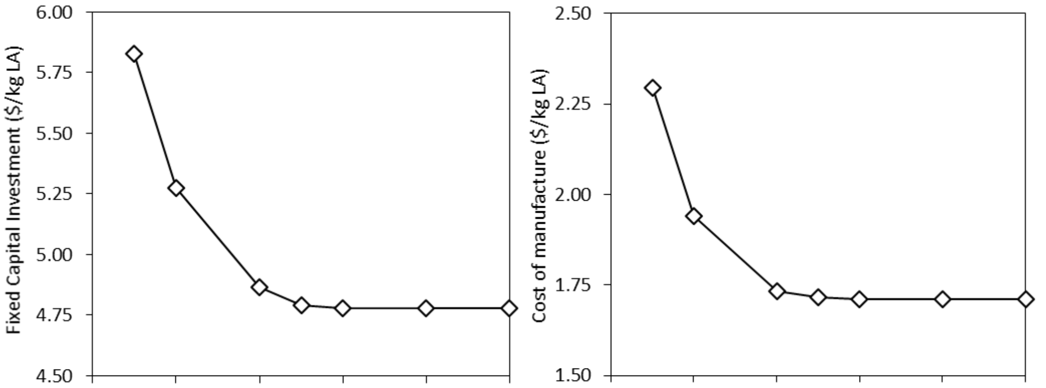


Figure 8.8 Fixed capital investment (a), cost of manufacture (b) per kg lactic acid as a function of lactic acid annual production capacity.

8.3.3 Hot Melt Adhesives

Table 8.7 presents the characteristic size and Ceq.fob of each unit operation in Area 500, the FCI (M$54.91) and the C_{UT} (M$15.13/year) for annual production of 80,000 t HMAs (ca. 5% of global annual production). At this production capacity, economy of scale has been achieved for LA production (Figure 8.8). The COM is M$136.5 when only Area 500 is considered (Table 8.5). When OFMSW hydrolysis, LA production and HMAs production are considered, the respective COM for HMAs production is M$262.84 or $3.28/$kg_{HMAs}$ (Table 8.5). The HMAs production stage (Area 500) contributes the highest cost in the COM of the process starting from OFMSW hydrolysis due to the high cost of raw materials used in this stage.

When only HMAs production is considered from OFMSW, then the MSP_{HMAs} is $3.37/$kg_{HMAs}$. When the biorefinery B3 is considered, the MSP_{HMAs} is estimated at $2.92/$kg_{HMAs}$ when biosurfactants are sold at their current market price ($4.1/kg). The current market price of HMAs is ca. $4.7/$kg_{HMAs}$ (Alibaba.com) that is 37.8% higher than the MSP estimated either with or without biosurfactants production. The payback period for biorefinery B3 is estimated at 7 years.

Table 8.5 Summary of individual costs for the production process of 80,000 t HMAs.

	OFMSW pretreatment	**Lactic acid**	**HMAs production**	**Biosurfactants**
Capacity (t/y)	1,465,400	76,500	80,000	31,000
FCI (M$)	66.11	283.11	54.91	177.7
C_{UT} (M$)	3.54	19.97	15.13	6.95
C_{RM} (M$) [a]	15.69	1.17	62.11	26.69
C_{OL} (M$) [b]	0.51	4.55	11.58	4.35
COM (M$)	36.96	89.38	136.5	85.25

[a] C_{RM}= Unitary raw material costs (Table 4.6) × mass balances (Table 8.12);

[b] C_{OL}= N_{OL} (Tables 8.3,8.4,8.6,8.7) × number of workers required (4.5) × working time of each worker (2080 h/year) × average labour cost ($20/h)

Table 8.6 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 76,500 t lactic acid (Area 200).

Unit	Description	Unit number	$CEPCI_{t0}$	Characteristic size (X_t)	FOB Cost (Cp@2018, M$)	Electricity (kWh/y)	Steam (t/y)	Cooling water (t/y)
E-201	Heat exchanger[a]	1	444.2	A=772.71 m^2	0.299			
E-202	Heat exchanger[a]	1	444.2	A=40.47 m^2	0.037		25,622.5	
E-203	Holding tube[a]	1	500.0	l=0.12 m	0.126			
F-203	Bioreactor[a]	10	521.9	V=605.76 m^3	6.064			3,051,191
A-204	Agitator[a]	10	521.9	P=722.06 hp	5.985	31,166,667		
F-201/202	Seed bioreactor[a]	1	521.9	V=60.57 m^3	0.181			
A-202/203	Seed agitator[a]	1	521.9	P=72.21 hp	0.066			
CF-201	Centrifugal separator[b]	4	444.2	Q=86.47 m^3/h	3.289	736,560.0		
NF-201	Nanofiltration[d]	1	342.5	A=9,163 m^2	5.239			
SF-201	Softening[b]	2	395.6	V=3.18 m^3	0.003			
ME-201	Monopolar electr.[d]	1	342.5	A=13,705 m^2	12.237	62,118,000		
EV-201	Evaporator[a,c]	28	521.9	A=981.89 m^2	11.493	6,071,078	155,268	
BE-201	Bipolar electr. [d]	1	342.5	A=8,721 m^2	8.680	159,885,000		
V-203-V-205	I.E. resins[b]	6	521.9	V=1.72 m^3	0.007	3,213,000		
EV-202	Evaporator[a,c]	6	521.9	A=839.93 m^2	2.915	6,024,565		
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A200 (N_{OL})		25						
Total Ceq.fob (M$)					56.621			
FCI A200 (M$)				**5 × Total Ceq.fob A200 =**	**283.107**			
C_{OL} A200 (M$)					**4.550**		**C_{UT} A200(M$/y) =**	**19.968**

[a] Dheskali et al; [b] Peters, Timmerhaus and West; [c] Turton et al; [d] Blanch and Clark;

Table 8.7 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 80,000 t HMAs (Area 500).

Unit	Description	Unit number	CEPCI$_{t0}$	Characteristic size (X_t)	FOB Cost (C_p@2018, M$)	Electricity (kWh/y)	Steam (t/y)	Cooling water (t/y)
R-501	Reactor[b]	2	397.0	V=25.05 m^3	0.214	352,757	20,407	
T-501	Distillation column[b]	1	239.0	N=9	0.079			
E-501	Heat exchanger[a]	1	444.2	A=20.66 m^2	0.025			747,929
E-502	Heat exchanger[a]	1	444.2	A=0.35 m^2	0.041		479	
R-502	Reactor[b]	3	397.0	V=32.07 m^3	0.366	677,293	5,563	
T-502	Distillation column[b]	1	239.0	N=9	0.077			
E-503	Heat exchanger[a]	1	444.2	A=4.28 m^2	0.021			191,733
E-504	Heat exchanger[a]	1	444.2	A=0.42 m^2	0.043		33	
E-505	Heat exchanger[a]	1	444.2	A=4.83 m^2	0.025			333,355
V-501	Mixing tank[a]	1	521.9	V=9.38 m^3	0.016			
A-503	Agitator[a]	1	521.9	P=11.18 hp	0.016	330,059		
NF-201	Nanofiltration[c]	1	342.5	A=1,216 m^2	0.868			
CR-502	Crystalizer[b]	1	525.4	A=4.49 m^2	0.538		6,408	
DR-501	Dryer[b]	1	525.4	M=624.49 kg/h	0.860	64,803	45	12,266
V-502	Mixing tank[b]	1	397.0	V=1.05 m^3	0.005			
A-504	Agitator[a]	1	521.9	P=1.26 hp	0.013	37,071		
EX-501	Extruder[b]	24	397.0	M=0.11 kg/s	3.529	128,547,336		
EX-502	Extruder[b]	29	397.0	M=0.11 kg/s	4.246	8,949,337		
Unitary utility cost						\$0.0674/kWh	\$9.45/t	\$0.0154/t
Workers A500 (N_{OL})		62						
Total Ceq.fob (M$)					10.982			
FCI A500 (M$)				**5 × Total Ceq.fob A500 =**	**54.909**			
C_{OL} A500 (M$)					**11.580**		**C_{UT} A500 (M$/y) =**	**15.125**

[a] Dheskali et al.; [b] Turton et al; [c] Blanch and Clark;

8.3.4 Succinic acid

Table 8.9 presents the characteristic size of each unit operation in Area 300, the total Ceq.fob, the FCI (M$164.3) and the C_{UT} (M$8.59/year) for annual production capacity of 50,000 t_{SA}, which has been considered as the OPC of SA production. The bioreactors (F-303/A-304) contribute the highest FCI (ca. 60%) followed by the dryer (DR-301, ca. 13%) and the evaporator (EV-301, ca. 8%). The C_{UT} is mainly affected by energy consumption for agitation and evaporation, and the steam used in the evaporator. The COM_{SA} (M$99.98) has been estimated using the C_{UT}, the C_{OL} (M$3.0) and the C_{RM} (M$42.0) presented in Table 8.8.

The lowest unitary SA production cost is \$2.6/kg_{SA} (Figure 8.9) has been estimated considering varying plant capacities (10-100 kt/y) including both OFMSW hydrolysis (Area 100) and SA production (Area 300) stages. The MSP_{SA} (\$2.39/kg_{SA}) estimated at the OPC is lower than the current bio-based SA (\$2.94/kg_{SA}) and fossil-based SA (\$2.50/kg_{SA}) market prices (E4tech et al., 2015) The revenue from OFMSW management fees ($35/t) has been considered in the estimation of the MSP. When the production of both SA and biosurfactants is considered (biorefinery B2), the MSP_{SA} is reduced to \$2.14/kg_{SA}, which shows enhanced profitability potential. The MFR for 50,000 t_{SA} production is 1,197 kt_{OFMSW}/year (wb).

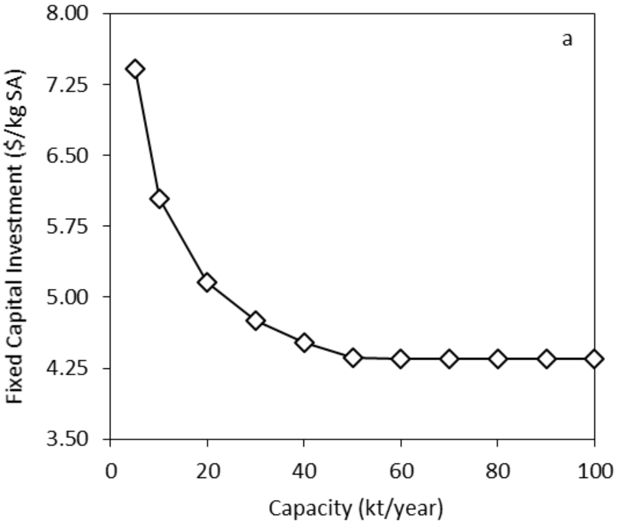


Figure 8.9 Fixed capital investment (a) and cost of manufacture (b) per kg succinic acid as a function of succinic acid annual production capacity.

8.3.5 Polyurethane Urea Dispersions

Tables 8.10 and 8.11 present techno-economic data on the production of 79,711 t polyester polyols (Area 600) and 284,000 t PUDs (Area 700), where 50,000 t_{SA} are required. Table 8.8 summarises the FCI (M\$3.23 and M\$8.26), C_{UT} (M\$2.79/year and M\$1.58/year), C_{RM} (M\$153.24/year and M\$221.15/year) and C_{OL} (M \$1.12/year and M \$1.25/year) for Areas 600 and 700. When OFMSW hydrolysis, SA production, PP production and PUDs production are taken into the account, the COM_{PUDs} is M\$604.49 or \$2.13/kg_{PUDs} (Table 8.8). The PUDs production stage (Area 700) contributes the highest cost in the COM of the whole process starting from OFMSW hydrolysis due to the high cost of raw materials used in this stage.

When only PUDs production is considered from OFMSW (Areas 100-300-600-700), the MSP_{PUDs} is \$2.10/kgPUDs. When the biorefinery B4 is considered where PUDs production is combined with biosurfactants production, the MSP_{PUDs} is estimated at \$1.95/kg_{PUDs} when biosurfactants are sold at their current market price (\$4.1/kg). The current market price of PUDs is ca. \$3.5/kg_{PUDs} (Alibaba.com) that is ca. 44.2% higher than the MSP_{PUDs} estimated when the biorefinery B4 is considered. The payback period for biorefinery B4 is estimated at 4 years.

Table 8.8 Summary of individual costs for the production of 284,000 t PUD

	OFMSW pretreatment	**Succinic acid**	**PP**	**PUD**	**Biosurfactants**
Capacity (t/y)	1,197,261	50,000.00	79,711.00	283,691.45	25,000.00
FCI (M\$)	53.67	164.29	3.23	8.26	144.43
C_{UT} (M\$)	2.90	8.59	2.79	1.58	5.62
C_{RM} (M\$) [a]	12.82	42.00	153.24	221.15	21.52
C_{OL} (M\$) [b]	0.39	3.00	1.12	1.25	3.65
COM (M\$)	30.08	99.98	195.57	278.86	69.35

[a] C_{RM}= Unitary raw material costs (Table 4.6) × mass balances (Table 8.12);

[b] C_{OL}= N_{OL} (Tables 8.3,8.4,8.8,8.9) × number of workers required (4.5) × working time of each worker (2080 h/year) × average labour cost (\$20/h)

Table 8.9 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 50,000 t succinic acid (Area 300).

Unit	**Description**	**Unit number**	**$CEPCI_{t0}$**	**Characteristic size (X_t)**	**FOB Cost (Cp@2018, M$)**	**Electricity (kWh/y)**	**Steam (t/y)**	**Cooling water (t/y)**
E-301	Heat exchanger[a]	1	444.2	A=917.22 m^2	0.336		34,177	
E-302	Heat exchanger[a]	1	444.2	A=72.05 m^2	0.046			
E-303	Holding tube[a]	1	500.0	l=0.12 m	0.154			
F-303	Bioreactor[a]	19	521.9	V=539.28 m^3	10.200			8,587,316
A-304	Agitator[a]	19	521.9	P=642.82 hp	9.468	62,358,277		
F-301/302	Seed bioreactor[a]	1	521.9	V=53.93 m^3	0.160			
A-302/303	Seed agitator[a]	1	521.9	P=64.28 hp	0.057			
CF-301	Centrifugal separator[b]	1	444.2	Q=73.79 m^3/h	2.051	736,560		
V-302/V-303	I.E. resins[b]	4	521.9	V=94.67 m^3	2.183			
EV-301	Evaporator[a,c]	3	521.9	A=838.59 m^2	2.512	31,320,607	12,571	
CR-301	Crystalizer[c]	1	525.4	M=40,522 kg/h	1.070	6,688,575		
CR-302	Crystalizer[c]	1	525.4	M=15,025 kg/h	0.451	406,732		
DR-301	Dryer[c]	1	525.4	M=4,208 kg/h	4.170	17,435,807		
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A300 (N_{OL})		16						
Total Ceq.fob (M$)					32.858			
FCI A300 (M$)				**5 × Total Ceq.fob A300 =**	**164.290**			
C_{OL} A300 (M$)					**3.000**		**C_{UT} A300(M$/y) =**	**8.591**

[a] Dheskali et al.; [b] Peters, Timmerhaus and West; [c] Turton et al.;

Table 8.10 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 79,711 t polyester polyols (Area 600)

Unit	Description	Unit number	CEPCI$_{t0}$	Characteristic size (X_t)	FOB Cost (Cp@2018, M$)	Electricity (kWh/y)	Steam (t/y)	Cooling water (t/y)
V-601	Mixing tank[a]	1	397.0	V=28.58 m^3	0.115	201,178	19,423	
R-601	Reactor[a]	1	397.0	V=17.14 m^3	0.088	120,687	8,662	
R-602	Reactor[a]	4	397.0	V=26.67 m^3	0.443	751,017	255,514	
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A600 (N_{OL})		6						
Total Ceq.fob (M$)					0.646			
FCI A600 (M$)				**5 × Total Ceq.fob A600 =**	**3.228**			
C_{OL} A600 (M$)					**1.120**		**C_{UT} A600 (M$/y) =**	**2.793**

[a] Turton et al.[22]

Table 8.11 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for an annual production capacity of 284,000 t PUDs (Area 700)

Unit	Description	Unit number	CEPCI$_{t0}$	Characteristic size (X_t)	FOB Cost (C_p@2018, M$)	Electricity (kWh/y)	Steam (t/y)	Cooling water (t/y)
E-701	Heat exchanger[a]	1	444.2	A=27.57 m^2	0.032		4,613	
E-702	Heat exchanger[a]	1	444.2	A=383.63 m^2	0.156		55,276	
R-701/ R-702	Reactor[b]	6	397.0	V=32.41 m^3	0.737	1,369,134	20,131	
E-703	Heat exchanger[a]	2	444.2	A=566.91 m^2	0.444			3,302,520
T-701	Distillation column[b]	1	240.0	N=32	0.213			
E-704	Heat exchanger[a]	1	444.2	A=56.37 m^2	0.036			3,095,215
E-705	Heat exchanger[a]	1	444.2	A=43.98 m^2	0.034		66,790	
Unitary utility cost						$0.0674/kWh	$9.45/t	$0.0154/t
Workers A700 (N_{OL})		7						
Total Ceq.fob (M$)					1.652			
FCI A700 (M$)				**5 × Total Ceq.fob A700 =**	**8.260**			
C_{OL} A600 (M$)					**1.250**		**C_{UT} A700 (M$/y) =**	**1.578**

[a] Dheskali et al.; [b] Turton et al.;

8.4 Life Cycle Assessment

8.4.1 Goal and scope

The LCA will assess the environmental impact of LA, SA, biosurfactants, HMAs and PUDs production from OFMSW. The system boundaries for the evaluation are determined as a "cradle-to-gate" approach, namely 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). The production of 1 kg end-product has been considered as functional unit. The LCA system boundaries enclose the OFMSW hydrolysis, fermentation and DSP stages, and biosurfactants HMAs and PUDs production.

8.4.2 Life Cycle Inventories

Mass and energy inputs and outputs (inventories) have been estimated via process design of Areas 100-700. Table 8.12 presents the inventories of mass end energy balances for the individual Areas 200-700. LCA was conducted using the CML 2001 (Jan. 2016) methodology (Guinée et al., 2002). Global Warming Potential (GWP 100 years), Abiotic Depletion (ADP fossil), Acidification Potential (AP), Eutrophication Potential (EP) and Human Toxicity Potential (HTP) are estimated as environmental indicators. It should be mentioned that two electricity sources have been considered, namely grid-derived electricity and renewable-sourced electricity. Photovoltaics are selected as the renewable energy source, constituting one of the best-case scenarios of the renewable resources regarding their environmental performance. The high energy requirements of many unit operation deems necessary the assessment of alternative renewable energy sources for chemical production from OFMSW.

Table 8.12 Summary of the mass and energy balances inventory for all processes

	Unit	SA	LA	Biosurfactants	HMAs	PP	PUD
Sugars	kg/$kg_{product}$	1.78	1.43	-	-	-	-
Solid residues (dry)	kg/$kg_{product}$	-	-	11.9	-	-	-
1,6-hexanediol	kg/$kg_{product}$	-	-	-	-	0.44	-
Neopentyl glycol	kg/$kg_{product}$	-	-	-	-	0.26	-
Succinic acid	kg/$kg_{product}$	-	-	-	-	0.63	-
Lactic acid	kg/$kg_{product}$	-	-	-	0.96	-	-
Additives	kg/$kg_{product}$	-	-	-	0.41	-	0.14
Nutrients	kg/$kg_{product}$	0.29	-	-	-	-	-
HCl	kg/$kg_{product}$	1.34	-	1.84	-	-	-
NaOH	kg/$kg_{product}$	1.20	0.04	0.23	-	-	-
KOH (85%)	kg/$kg_{product}$	-	-	0.82	-	-	-

Table 8.12 Summary of the mass and energy balances inventory for all processes (continue)

	Unit	SA	LA	Biosurfactants	HMAs	PP	PUD
Ethanol	kg/kg$_{product}$	-	-	0.23	-	-	-
Petroleum ether	kg/kg$_{product}$	-	-	0.17	-	-	-
Acetone	kg/kg$_{product}$	-	-	-	-	-	0.67
Enzyme	kg/kg$_{product}$	-	-	0.048	-	-	-
Water	kg/kg$_{product}$	2.05	6.4	-	-	-	0.61
Electricity	kWh/kg$_{product}$	3.93	3.97	3.02	2.82	0.01	0.01
Steam	kg/kg$_{product}$	0.89	2.36	1.32	0.41	3.56	0.52
Cooling water	kg/kg$_{product}$	171.74	39.9	27.70	16.07	-	22.55

8.4.3 Life Cycle Impact Assessment

Table 8.13 presents the five LCA indicators for all processes under study, estimated by considering conventional electricity (grid) or renewable electricity derived from photovoltaics. In the next subsections, a discussion is held for the environmental performance of each process and the main contributors in the final environmental impacts. Figure 8.10 illustrates the distribution of individual environmental impacts to different sections. In the final subsection, a more holistic approach is presented by comparing the biorefinery development with the base case scenario and estimating the GHG emissions savings.

Table 8.13 Environmental assessment for the production of 1 kg of each product from OFMSW. The absolute values of the environmental impact of PUDs have not been included due to confidentiality reasons

		GWP 100 years (kg CO_2-eq)	ADP fossil (MJ)	AP (kg SO_2-eq)	EP (kg PO_4-eq)	HTP (kg DCB-eq)
Lactic acid	Grid	2.95	38.30	5.78	1.23	0.11
	Renewable	1.25	21.54	2.64	0.85	0.19
HMAs	Grid	5.91	88.00	9.98	1.80	0.21
	Renewable	3.18	61.00	5.06	1.21	0.33
Succinic acid	Grid	3.18	47.70	7.43	1.67	0.13
	Renewable	1.15	27.58	3.70	1.24	0.21
Biosurfactants	Grid	4.01	66.78	16.30	3.49	0.77
	Renewable	2.71	53.86	14.00	3.22	0.82

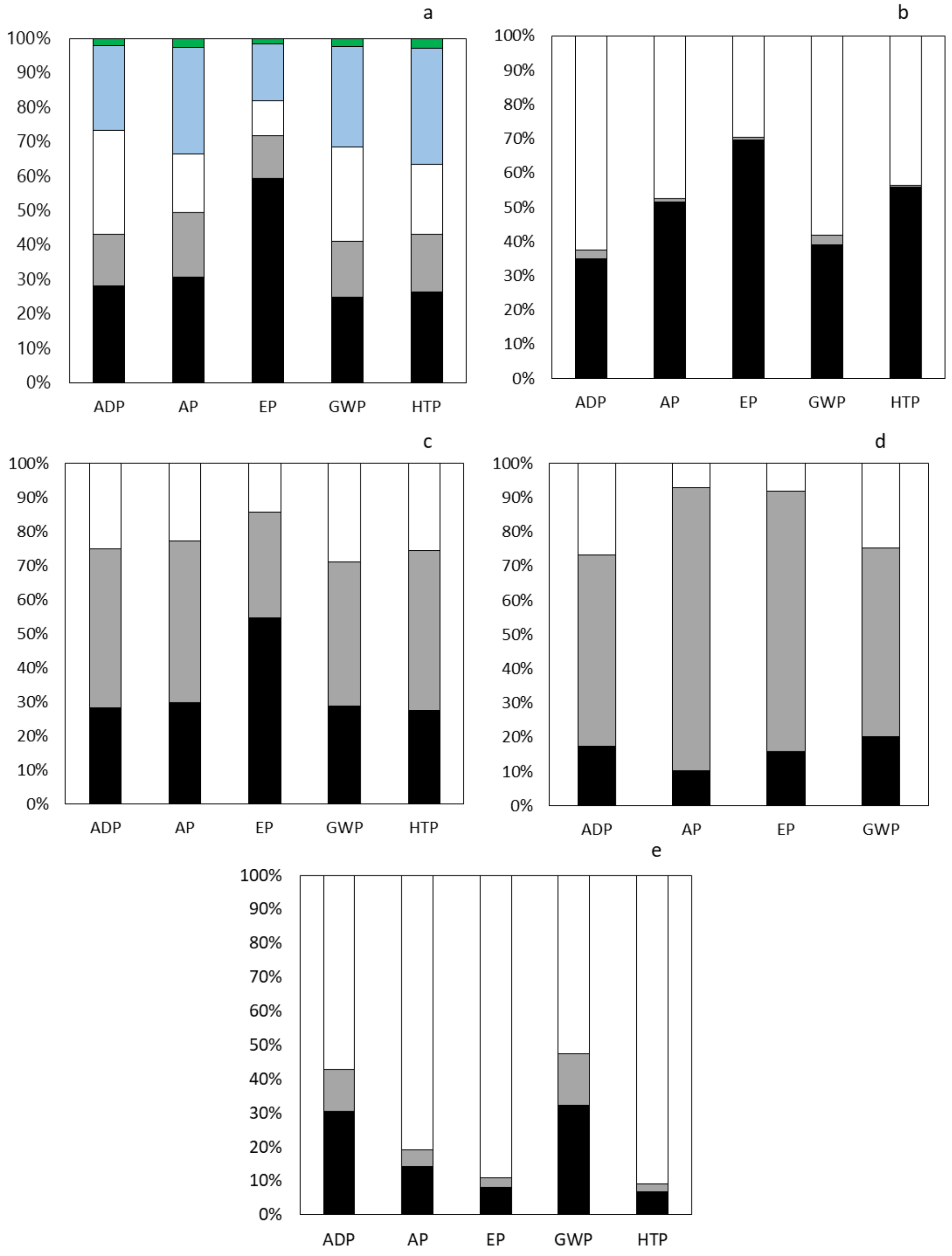


Figure 8.10 Distribution of individual environmental impacts to different sections in: Areas 100-200 including OFMSW hydrolysis and LA production (a), Areas 100-200-500 including OFMSW hydrolysis, LA and HMAs production (b), Areas 100-300 including OFMSW hydrolysis and SA production (c), Areas 100-300-600-700 including OFMSW hydrolysis, SA, PP and PUDs production (d), and biosurfactants production (e). In all cases electricity from grid has been considered. The different coloured bar sections stand for: (a) black – OFMSW hydrolysis, grey – LA production, white – monopolar electrodialysis, blue – bipolar electrodialysis, green – other stages in LA production; (b) black – LA in HMAs production (integrated with OFMSW hydrolysis), grey – lactide production, white – HMAs formulation; (c) black – OFMSW hydrolysis, grey – SA production, white – DSP of SA; (d) black – SA in PUD production (integrated with OFMSW hydrolysis), grey – PP production, white – PUDs formation; (e) black – lipids production, grey – protein production, white – biosurfactants formulation.

Lactic acid

Table 8.13 presents the five LCA indicators for LA production (Area 300) including OFMSW hydrolysis (Area 100) and considering utilisation of conventional electricity (grid) or renewable electricity derived from photovoltaics. GWP (1.25 kg CO_2-eq), ADP fossil (21.54 MJ), AP (5.78 kg SO_2-eq) and EP (1.23 kg PO_4-eq) are 30.9-57.6% lower when renewable electricity is employed, except for HTP (0.19 kg DCB-eq) that is 42% higher due to heavy metals usage as photovoltaics construction materials. Figure 8.10a shows that OFMSW hydrolysis, fermentation and electrodialysis membrane units contribute the highest environmental impact due to the high steam and electricity requirements in these stages. OFMSW hydrolysis shows the highest contribution (59%) in the EP mainly due to production of the enzymatic cocktail using glucose derived from agricultural crops. The fermentation stage has moderate contribution in all indicators (17% to GWP, 15% to ADP, 19% to AP, 13% to EP and 17% to HTP) due to the relatively low utility requirements.

Lower GWP than the one estimated in this study has been reported for lactic acid production using agricultural crops and residues. The cradle-to-Corbion plant LA produced from sugarcane results to a GWP of -0.22 kg CO_2-eq/kg_{LA}, having taken into account the CO_2 uptake from cultivation (1.47 kg CO_2/kg_{LA}) (Morão and de Bie, 2019). Similarly, De Matos et al. (2015) reported a range of GWP and ADP fossil when corn (0.3-1.2 kg CO_2/kg_{LA} and 21.8-37.5 MJ/kg_{LA}), sugarcane (-0.6-0.2 kg CO_2/kg_{LA} and 9.0-15.7 MJ/kg_{LA}) and corn stover (-0.2-0.6 kg CO_2/kg_{LA} and 16.4-25.4 MJ/kg_{LA}) are used as feedstocks. The lower GWP values reported when agricultural crops and residues are used is attributed to the CO_2 uptake due to the cultivation. The environmental benefits of the OFMSW-derived LA should be evaluated when compared to the current management practise of OFMSW where significant environmental savings are achieved.

Hot Melt Adhesives

Table 8.13 presents the five LCA indicators for HMAs production including LA production (integrated with OFMSW hydrolysis), lactide production and HMAs formulation, considering utilisation of either conventional electricity (grid) or renewable electricity (photovoltaics). GWP (3.18 kg CO_2-eq/kg_{HMAs}), ADP fossil (61 MJ/kg_{HMAs}) AP (5.06 g SO2-eq/kg_{HMAs}) and EP (1.21 g PO_4-eq/kg_{HMAs}) are 30.6-49.4% lower when renewable electricity is used, while HTP (0.33 kg DCB-eq/kg_{HMAs}) is 36.3% higher due to the reason mentioned above. Figure 8.10b shows that LA production integrated with OFMSW hydrolysis (39% to GWP, 35% to

ADP, 52% to AP, 70% to EP and 56% to HTP) and HMAs formulation (58% for GWP, 62% for ADP, 47% for AP, 30% for EP and 43% to HTP) contribute the highest environmental impacts. The e-caprolactone that is used for the production of PLA-co-PCL contributes the highest environmental impact in HMAs formulation stage.

Succinic acid

When integrated OFMSW hydrolysis and SA production is considered, the GWP (1.15 kg CO_2-eq/kg_{SA}), ADP fossil (27.58 MJ/kg_{SA}) AP (3.7 g SO_2-eq/kg_{SA}) and EP (1.24 g PO_4-eq/kg_{SA}) are 25.7%-63.8% lower when renewable electricity is used (Table 8.13). As in previous products, HTP (0.21 kg DCB-eq/kg_{SA}) is 38.1% higher when renewable electricity is used.

Figure 8.10c shows that OFMSW hydrolysis contributes similar environmental impact in all categories, besides EP where 54% contribution is estimated due to the environmental impact of enzyme production from agricultural crops. The fermentation stage contributes the highest environmental impact in GWP (42%), ADP (47%), AP (47%) and HTP (47%) mainly due to NaOH requirements during fermentation. The contribution of DSP ranges from 14% in the case of EP to 29% in the case of GWP.

Cok et al. (2014) reported the GWP_{SA} and ADP_{SA} from corn-derived glucose via (i) low pH yeast fermentation with direct crystallization-based SA purification (0.88 kg CO_2-eq/kg_{SA} and 32.7 MJ/kg_{SA}), and (ii) anaerobic bacterial fermentation to succinate salt at pH 7 with SA purification via an electrodialysis-based process (1.7 kg CO_2-eq/kg_{SA} and 49.4 MJ/kg_{SA}), using a European electricity production mix. The main difference in the GWP_{SA} (1.15-3.18 kg CO_2-eq/kg_{SA}) estimated in this study using OFMSW and the values reported by Cok et al. is mainly attributed to the carbon uptake during corn cultivation (ca. 1.5 kg CO_2-eq/kg_{SA}) and the electricity production mix used. The ADP_{SA} from OFMSW (27.58-47.7 MJ/kg_{SA}) is comparable to the values reported by Cok et al. (2014). The GWP_{SA} and ADP_{SA} for petroleum-derived SA production using maleic anhydride as feedstock are 1.94 kg CO_2-eq/kg_{SA} and 59.2 MJ/kg_{SA}, respectively (Cok et al., 2014). Patel et al. (2018) reported the GWP and ADP of 1G (0.77 kg CO_2-eq/kg_{SA} and 32.0 MJ/kg_{SA}) and 2G (-0.01 kg CO_2-eq/kg_{SA} and 18.0 MJ/kg_{SA}) succinic acid from corn-derived glucose and corn stover, respectively. The reported environmental performance of 1G SA is re-estimated from the results reported by Cok et al. with consideration of updated yields in the process.

Polyurethane Urea Dispersions

The absolute figures of environmental metrics of PUDs production cannot be reported due to confidentiality reasons. The environmental metrics estimated are 3.7-12.9% lower when renewable electricity is used (Table 8.13). Figure 8.10d presents the contribution of OFMSW hydrolysis, SA production, PP production and PUDs production to the environmental impacts under study when electricity from the grid is employed. The contribution of SA production to the overall metrics is 25% for GWP, 19% for ADP, 12% for AP and 18% for EP. PP production has the highest environmental impact (74% to GWP, 54% to ADP, 81% to AP and 74% to EP) due to the high impact of the two diols used for PP production. Moreover, considerable steam consumption is employed for both reaction and distillation stages.

Biosurfactants

The GWP (2.71 kg CO_2-eq), ADP fossil (53.86 MJ), AP (14 kg SO_2-eq) and EP (3.22 kg PO_4-eq) estimated when renewable electricity is used are up to 32.4% lower (in the case of GWP) than the respective values when grid electricity is used. However, the HTP (0.82 kg DCB-eq) is 6% higher when renewable electricity is used due to the heavy metals used as construction materials for photovoltaics. Area 400 can be divided into lipid extraction, protein extraction and biosurfactants formulation sections, with the latter contributing the highest impact in all five environmental indicators (Figure 8.10e). For instance, the biosurfactants formulation section contributes from 53% in GWP up to 91% in HTP (Figure 8.10e). The KOH used in biosurfactants formulation contributes the highest environmental impact in this section.

8.4.4 GHG emissions savings

Table 8.14 presents the unitary GHG emissions of the respective fossil- and bio-based counterparts of LA, SA, biosurfactants, HMAs and PUDs produced from OFMSW (Cok et al., 2014; De Matos et al., 2015; Dewulf et al., 2015; EPDLA, 2012; McDevitt and Grigsby, 2014; Schowanek et al., 2018). The GWP of LA (1.25-2.95 kg CO_2-eq/kg_{LA}) and biosurfactants (2.71-4.01 kg CO_2-eq/kg) produced from OFMSW are higher than the respective values of their counterparts (Table 8.13) even when renewable electricity is used. The GWP of fossil-based SA is within the range of GWP (1.15-3.18 kg CO_2-eq/kg_{SA}) of SA produced from OFMSW. However, the GWP of bio-based SA produced from corn is always lower than the respective value from OFMSW even in the case that renewable electricity is used. The GWP of fossil-based adhesives is within the range of GWP (3.18-5.91 kg CO_2-eq/kg_{LA}) of HMAs produced from OFMSW.

Table 8.14 Greenhouse gas emission of the fossil- and bio-based counterparts of the end-products derived from OFMSW

Fossil- and bio-based counterpart	**GHG (kg CO_2-eq/kg$_{product}$)**	**Reference**
Bio-based LA from corn-derived glucose	0.3-1.2	(De Matos et al., 2015)
Fossil-based SA	1.89	(Dewulf et al., 2015)
Bio-based SA from corn-derived glucose	0.88	(Cok et al., 2014)
Fossil-based surfactants	2.1	(Schowanek et al., 2018)
Fossil adhesives	5.0	(McDevitt et al., 2014)
Adipic acid based PUDs	3.4	(EPDLA,2012)

Only the SA-based PUDs derived from OFMSW has a GWP value (absolute values are not presented due to confidentiality reasons) that is 18.2-28.8% lower than the GWP of the adipic acid based PUDs depending on the electricity production mix used. The GWP and ADP of fossil-based adipic acid is 8.82 kg CO_2-eq/kg$_{AA}$ and 124.3 MJ/kg$_{AA}$, respectively (Cok et al., 2014). However, these comparisons do not take into consideration the current OFMSW management practices that contribute significantly to GWP.

To account for current OFMSW management practices, two scenarios have been considered for comparison purposes: (1) 100% landfilling of OFMSW and (2) 37.45% composting and 62.55% landfilling of OFMSW. The second scenario has been based on the average OFMSW management practice in EU-27 where 83 kg$_{OFMSW}$/capita (out of 221.66 kg$_{OFMSW}$/capita in total) was recycled in 2018 (Eurostat, 2019b; Favoino and Giavini, 2020) The environmental impact for landfilling of OFMSW is considered at 4.2 kg CO_2-eq/kg$_{OFMSW}$ (U.S. Environmental Protection Agency, 2021) (on dry basis), while the impact for the recycling via composting of OFMSW is considered at 2.3 kg CO_2-eq/kg$_{OFMSW}$ (db) (taken from the Gabi software). Figure 8.11 illustrates the processes that are compared, namely the four alternative OFMSW-based biorefineries B1-B4 and the respective current production routes to the fossil-based or bio-based counterparts, considering also that either the whole OFMSW (current practice) or the OFMSW solids remaining in the four biorefineries are processed through the two OFMSW management scenarios. The basis for the comparison is the production of 1 kg LA, SA, HMAs or PUDs (designated as main product) in each OFMSW-based biorefinery considering conventional electricity use (grid) (Tables 8.15 and 8.16).

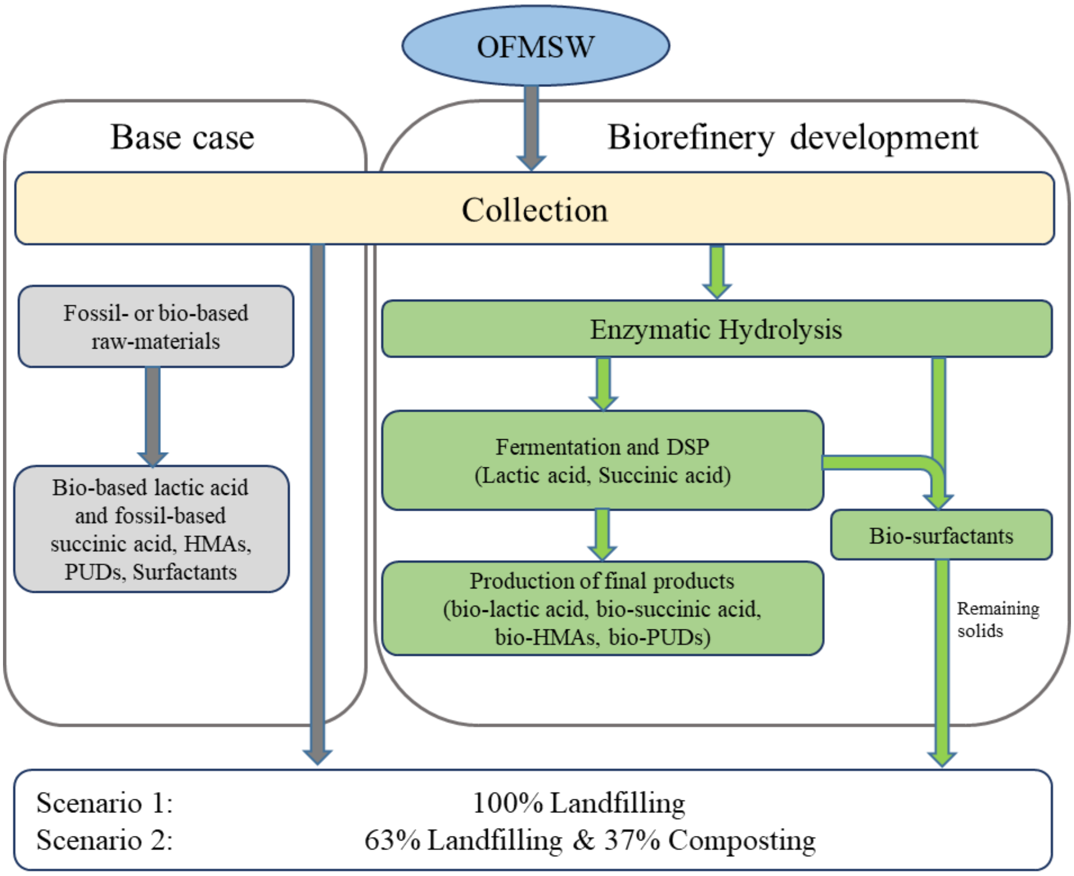


Figure 8.11 Illustrative description of current practices (base case) and alternative OFMSW-based biorefineries

Table 8.15 Estimation of GHG emissions savings for each OFMSW-based biorefinery considering landfilling as OFMSW management practice

	Lactic acid		**Succinic acid**		**HMAs**		**PUDs**	
	Base Case	**B1**	**Base Case**	**B2**	**Base Case**	**B3**	**Base Case**	**B4**
OFMSW requirements (kg)	-	4.76	-	5.95	-	4.58	-	2.51
Main product (kg)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fossil- or bio-surfactant (kg)	0.41	0.41	0.50	0.50	0.39	0.39	0.21	0.21
OFMSW or remaining solids landfilled (kg)	4.76	2.62	5.95	3.27	4.58	2.52	2.51	1.38
GHG of main product (kg CO_2-eq)	0.80	2.95	1.89	3.18	5.00	5.91	3.40	2.78
GHG of surfactant (kg CO_2-eq)	0.86	1.64	1.05	2.01	0.82	1.56	0.44	0.84
GHG of landfilling (kg CO_2-eq)	19.99	11.00	24.99	13.74	19.24	10.58	10.54	5.80
Total GHG (kg CO_2-eq per kg product)	21.65	15.59	27.93	18.93	25.06	18.05	14.38	9.42
Savings (kg CO_2-eq per kg product)	6.06		9.00		7.00		4.96	
Savings (kg CO_2-eq per kg dry OFMSW)	1.27		1.51		1.53		2.06	

Table 8.16 Estimation of GHG emissions savings for each OFMSW-based biorefinery considering OFMSW management via 37.45% composting and 62.55% landfilling.

	Lactic acid		**Succinic acid**		**HMAs**		**PUDs**	
	Base Case	**B1**	**Base Case**	**B2**	**Base Case**	**B3**	**Base Case**	**B4**
OFMSW requirements (kg)	-	4.76	-	5.95	-	4.58	-	2.51
Main product (kg)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fossil- or bio-surfactant (kg)	0.41	0.41	0.50	0.50	0.39	0.39	0.21	0.21
OFMSW or remaining solids landfilled (kg)	4.76	2.62	5.95	3.27	4.58	2.52	2.51	1.38
GHG of main product (kg CO_2-eq)	0.80	2.95	1.89	3.18	5.00	5.91	3.40	2.78
GHG of surfactant (kg CO_2-eq)	0.86	1.64	1.05	2.01	0.82	1.56	0.44	0.84
GHG of landfilling (kg CO_2-eq)	16.61	9.13	20.76	11.42	15.98	8.79	8.76	4.82
Total GHG (kg CO_2-eq per kg product)	18.27	13.73	23.70	16.60	21.80	16.26	12.60	8.44
Savings (kg CO_2-eq/$kg_{product}$)	4.54		7.10		5.53		4.16	
Savings (kg CO_2-eq/kg $_{OFMSW,dry}$)	0.95		1.19		1.21		1.74	

The quantity of OFMSW used in each biorefinery for the production of 1 kg main product is subsequently estimated using the mass balances presented in this study. The estimation of biosurfactants production is based on the OFMSW used in each scenario. The respective quantities of conventional counterparts (i.e. main product and fossil surfactants) are considered in each scenario. Tables 8.15 and 8.16 present the GHG emissions savings attributed to each biorefinery as compared to the two OFMSW management practices. Figures 8.12 illustrate the environmental performance of all production processes under study. It can be observed that savings in GHG emissions (25-35%) are achieved in all cases. Further processing improvements (e.g. higher fermentation and OFMSW hydrolysis efficiency, improved DSP for fermentation products based on low pH cultures) could lead to improved environmental impact.

Khoshnevisan et al. (2020) reported the production of 13.3 kg bio-based SA, 1.52 kg bio-methane, biofertilizer containing 4.93 kg N, 0.5 kg P and 1.67 kg K, and 78.68 kg biogas (60% CH_4) for combined heat and power generation from 1 t biopulp derived from OFMSW (18.3% total solids content) from which 73 kg CO_2-eq/$t_{biopulp}$ savings are achieved when compared to conventional processes producing the respective counterparts. In this study, 1 t OFMSW leads to the production of 168 kg SA and 84 kg biosurfactants corresponding to GWP of 2,790 kg CO_2-eq/t_{OFMSW} (on a dry basis) and 1,190 kg CO_2-eq/t_{OFMSW} savings when compared to conventional production of fossil-based SA, fossil surfactants and OFMSW management scenario 2. Escamilla-Alvarado et al. (2017) reported 128 kg CO_2-eq/t_{OFMSW} (20% total solids content) savings, as related to OFMSW landfilling, for OFMSW refining to methane, hydrogen, enzymes and hydrolysates.

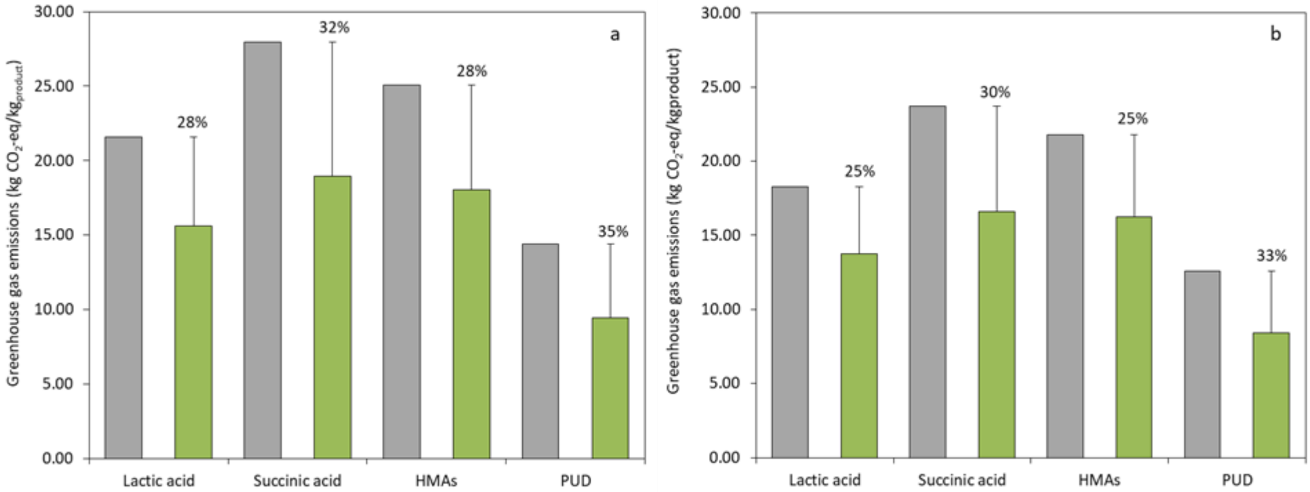


Figure 8.12 Environmental performance of all processes in GHG emissions for base case scenario and alternative approach having as OFMSW management 100% landfilling (a) and 37.45% recycling/62.55% landfilling (b).

8.5 Social Assessment

The analysis of the social impacts for the two biorefineries of the final products (HMAs-B3 and PUDs-B4) is based on data inputs derived from the simulation, economic and environmental assessment of the biorefineries. A set of 8 indicators related to workers and local community stakeholders are evaluated as analyzed in section 4.6. Table 8.17 presents the simulation and assessment results per stage of HMAs and PUDs production, while Table 8.18 summarizes the required data for the estimation of the social indicators for each biorefinery. C_{OL} and salaries have been expressed in € for comparison purposes with wages in EU-27 countries. In order to estimate the indicators, Table 8.19 presents the industrial water withdrawal, total water withdrawal, net living wage, net salary and CO_2 emissions of each country of EU-27. Finally, Table 8.20 illustrates the ratios of selected indicators.

Table 8.17 Simulation and assessment results used to calculate social indicators for B3 and B4 biorefineries.

	Capacity (t/y)	Employees per shift	C_{OL} (€)	Cooling water (kg/y)	Process water (kg/y)
OFMSW pretreatment	1,465,400	3	440,885	-	4.91E+09
Lactic acid	76,500	25	3,895,820	3.05E+09	-
HMAs production	80,000	63	9,917,344	1.29E+09	-
Biosurfactants	31,000	24	3,727,482	8.59E+08	2.30E+07
OFMSW pretreatment	1,197,261	3	334,004	-	4.91E+09
Succinic acid	50,000	21	2,569,260	8.59E+09	-
PP	79,711	8	959,190	-	-
PUDs	283,692	9	1,070,525	6.40E+09	1.74E+08
Biosurfactants	25,000	23	3,125,933	1.66E+08	1.85E+07

Table 8.18 Required data for the estimation of the social indicators for each biorefinery

	HMAs	PUD
Child labour in the industry	0	0
Salary (€/month)	1,396.17	1,396.17
Number of employees	518	64
Working hours total (h/week)	37	37
Water process (m^3/y)	4.94E+06	5.11E+06
Water cooling (m^3/y)	1.12E+05	3.37E+05
CO_2-eq (kg/capita)	12.44	19.04

Table 8.19 Industrial water withdrawal, total water withdrawal, net living wage, net salary and CO_2 emissions of each country of EU-27

	Industrial water withdrawal (m^3/y)	Total water withdrawal (m^3/y)	Net Living Wage (€/month)	Net minimum wage (€/month)	Working hours (h/week)	CO_2 emissions (kg/capita)
Austria	2.70E+09	3.49E+09	983.50	N.A.	36.5	6,870
Belgium	3.21E+09	3.99E+09	957.00	1,216	37.2	8,330
Bulgaria	3.94E+09	5.66E+09	662.00	202	40.7	5,870
Croatia	1.84E+08	7.15E+08	703.04	370	39.6	3,970
Cyprus	1.70E+07	3.11E+08	841.00	N.A.	39.3	5,260
Czech Republic	9.67E+08	1.63E+09	498.64	408	40.1	9,170
Denmark	3.29E+07	7.41E+08	N.A.	N.A.	33.5	5,940
Estonia	1.72E+09	1.79E+09	571.50	482	38.2	14,850
Finland	1.42E+09	6.56E+09	1,064.50	N.A.	36.8	8,660
France	1.82E+10	2.64E+10	1,273.50	1,386.00	37.3	4,570
Germany	1.98E+10	2.44E+10	1,116.50	1,102.00	34.9	8,890
Greece	2.08E+08	1.12E+10	703.00	578	42.0	6,180
Hungary	3.36E+09	4.50E+09	399.93	296	39.6	4,270
Ireland	5.10E+07	7.57E+08	1,589.00	1,509.00	36.5	7,310
Italy	7.70E+09	3.42E+10	896.50	N.A.	37.2	5,270
Latvia	2.52E+07	1.81E+08	653.50	314	38.9	3,450
Lithuania	6.97E+07	2.59E+08	589.00	361	38.6	4,380
Luxembourg	1.60E+06	4.56E+07	1,592.00	1,687.00	37.6	17,360
Malta	1.00E+06	6.38E+07	1,017.00	571	38.9	5,400
Netherlands	1.47E+10	1.61E+10	985.50	1,430.00	30.4	9,920
Poland	7.04E+09	1.01E+10	402.71	353	40.4	7,520
Portugal	1.50E+09	9.15E+09	711.50	587	39.5	4,330
Romania	4.23E+09	6.77E+09	324.35	251	39.6	3,520
Slovakia	2.31E+08	5.56E+08	449.00	397	40.0	5,660
Slovenia	7.58E+08	9.31E+08	783.50	642	39.2	6,210
Spain	5.97E+09	3.12E+10	821.00	733	37.7	5,030
Sweden	1.35E+09	2.38E+09	1,304.55	N.A.	36.4	4,480
Average	**3.68E+09**	**7.56E+09**	**842**	**732**	**37.1**	**6,766**

The monthly salary that is considered for the evaluation is estimated by taking into consideration the median hourly gross earnings that Eurostat reports and then the removal of taxes in order to estimate the net salary. More specifically, the median hourly gross earnings of EU-27 countries are €13.54/h (Eurostat, 2021b), but in this study the hourly gross earnings are €15.72/h, as this value is the average hourly gross earning of the countries with the highest industrial activity in Europe (Germany, Italy, France, Spain and Poland) (Eurostat, 2022). Then, the estimated net salary is estimated by removing the amount of taxes which is assumed to be

40% of the gross salary. Moreover, it should be mentioned that the lack of values in the minimum wage of Austria, Denmark, Finland, Cyprus, Italy and Sweden occurs because these countries do not have a minimum wage set by the government (collective bargaining agreements effective, instead of minimum wage) (Reinis Fischer, 2018).

Table 8.20 Indicators of living wage (LW), minimum wage (MW), level of facility water use (FWU) in industrial sector and in total and relative contribution of gaseous emissions (RCGE) for the developed biorefineries.

	All biorefineries		HMAs			PUD		
	LW	MW	FWU sector	FWU total	RCGE	FWU sector	FWU total	RCGE
Austria	1.42	N.A.	0.187%	0.145%	0.181%	0.202%	0.156%	0.277%
Belgium	1.46	1.15	0.157%	0.126%	0.149%	0.170%	0.136%	0.229%
Bulgaria	2.11	6.91	0.128%	0.089%	0.212%	0.138%	0.096%	0.324%
Croatia	1.99	3.77	2.743%	0.706%	0.313%	2.958%	0.761%	0.480%
Cyprus	1.66	3.42	29.689%	1.623%	0.237%	32.015%	1.750%	0.362%
Czech Republic	2.80	N.A.	0.522%	0.310%	0.136%	0.563%	0.334%	0.208%
Denmark	N.A.	N.A.	15.341%	0.681%	0.209%	16.542%	0.734%	0.320%
Estonia	2.44	2.90	0.293%	0.283%	0.084%	0.316%	0.305%	0.128%
Finland	1.31	1.01	0.356%	0.077%	0.144%	0.384%	0.083%	0.220%
France	1.10	N.A.	0.028%	0.019%	0.272%	0.030%	0.021%	0.417%
Germany	1.25	1.27	0.026%	0.021%	0.140%	0.028%	0.022%	0.214%
Greece	1.99	2.42	2.423%	0.045%	0.201%	2.613%	0.048%	0.308%
Hungary	3.49	4.72	0.150%	0.112%	0.291%	0.162%	0.121%	0.446%
Ireland	0.88	0.93	9.896%	0.667%	0.170%	10.672%	0.719%	0.260%
Italy	1.56	N.A.	0.066%	0.015%	0.236%	0.071%	0.016%	0.361%
Latvia	2.14	4.45	20.028%	2.787%	0.361%	21.597%	3.005%	0.552%
Lithuania	2.37	3.87	7.241%	1.949%	0.284%	7.808%	2.101%	0.435%
Luxembourg	0.88	0.83	315.447%	11.068%	0.072%	340.155%	11.935%	0.110%
Malta	1.37	2.45	504.715%	7.911%	0.230%	544.248%	8.531%	0.353%
Netherlands	1.42	0.98	0.034%	0.031%	0.125%	0.037%	0.034%	0.192%
Poland	3.47	3.96	0.072%	0.050%	0.165%	0.077%	0.054%	0.253%
Portugal	1.96	2.38	0.337%	0.055%	0.287%	0.364%	0.059%	0.440%
Romania	4.30	5.56	0.119%	0.075%	0.353%	0.129%	0.080%	0.541%
Slovakia	3.11	3.52	2.183%	0.907%	0.220%	2.354%	0.978%	0.336%
Slovenia	1.78	2.17	0.666%	0.542%	0.200%	0.718%	0.584%	0.307%
Spain	1.70	1.90	0.085%	0.016%	0.247%	0.091%	0.017%	0.378%
Sweden	1.07	N.A.	0.375%	0.213%	0.278%	0.405%	0.229%	0.425%
Average	**1.38**	**1.91**	**33.83%**	**1.13%**	**0.21%**	**36.48%**	**1.22%**	**0.33%**

After the estimation of all indicators, the following conclusions can be drawn for each indicator:

1. As child labour is forbidden in the European Union, this indicator is considered zero for all selected biorefineries.
2. Regarding the subcategory fair salary, the indicators of living wage and minimum wage are evaluated by comparing the salary considered for the operating labour of biorefineries (€1,162.88/month) to the living wage and minimum wage of the countries of EU-27 as well as to the average wages. As Figure 8.13 illustrates, the ratios of 24 out of 26 for the living wage and 18 out of 21 for the minimum wage are above 1, which means that the considered salary is above the living and minimum wage in these countries. Moreover, the same trend is observed when the salary is compared to the average wages of EU-27.
3. Considering the working time in the selected biorefineries, the hours per week are estimated to be 37 for each employee. This value is similar to the average working hours in the counties of EU-27 (Table 8.18).
4. The developed biorefineries could contribute to the job generation in EU-27 by creating 518 and 95 working positions for HMAs and PUD production, respectively.

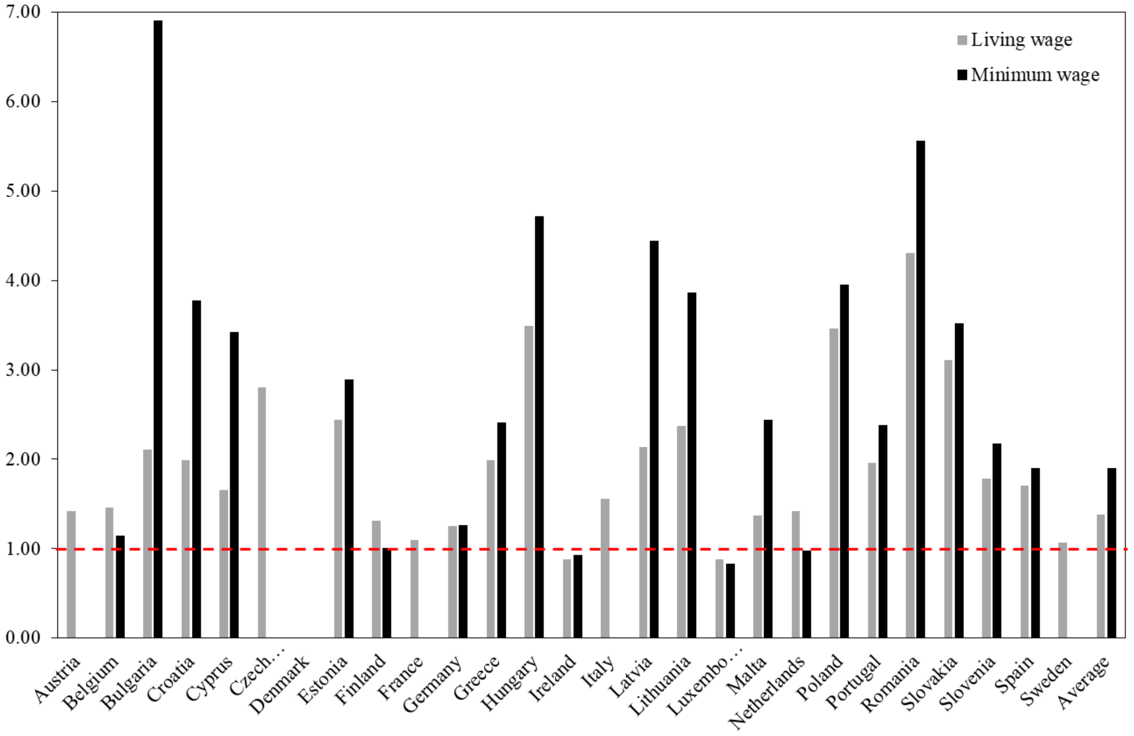


Figure 8.13 Ratios of living wage and minimum wage with the assumed salary for biorefineries' operation.

5. As far as access to material resources is concerned, the level of facility water use is evaluated, compared to the water use of the industrial sector and the total available water of the countries of EU-27. As Table 8.20 presents, the percentages for HMAs and PUD production are 33.83% and 36.48%, respectively, regarding the industrial sector and 1.13% and 1.229%, respectively, regarding the total water available in each country. Luxembourg and Malta indicate very low industrial activity and therefore the percentages of these countries are quite high if compared to the required water for the developed biorefineries. On the other hand, in countries that present high industrial activity (Germany 28% of the EU total, Italy 16%, France 12%, Spain 8% and Poland 5%), the percentages of the industrial sector are equal or below 0.1% (Eurostat, 2022).
6. Finally, the relative contribution of GHG emissions in the average GHG emissions of EU-27 countries is 0.21% in the case of HMAs and 0.33% in the case of PUD. Moreover, another remarkable result for GHG emissions is the estimated savings per capita for the biorefineries. According to the results presented in Section 8.4.4 (Table 8.15), when comparing the most common scenario (OFMSW management with landfill with simultaneous production of fossil-derived products) to the biorefinery development approach, savings equal to 7.00 kg CO_2-eq/ kg HMAs and 4.96 kg CO_2-eq/ kg PUD can be achieved. These savings can also be expressed as kg CO_2-eq/capita in EU-27 countries and are equal to 11.99 and 30.14 for HMAs and PUDs production, respectively.

Chapter 9 Sustainability assessment of a biorefinery using winery waste streams for the production of succinic acid and value-added co-products

9.1 Introduction

The global production of wine in 2018 was 29.2 million m^3 (OIV, 2019). The production of 0.7 L wine requires approximately 1 kg of grapes. Wineries generate significant quantities of waste streams. According to Galanakis (2017), the production of 1000 m^3 of wine generates 82.5 t grape pomace (includes skins and seeds) on a dry basis (db), 35.7 t grape stalks (db) and 85.7 t wine lees. Wine-making is a seasonal process and for this reason the residues produced should be processed in a short time. The disposal of such a large amount of waste causes environmental pollution problems because winery wastes are rich in phenolic compounds with a high organic load (Ahmad et al., 2020). Moreover, wineries may have to pay for waste disposal, while in many cases the cost is expended indirectly through the community (De Iseppi et al., 2020). In particular, wine lees disposal to the environment constitutes a major problem due to its high content in organic compounds at a low pH (De Iseppi et al., 2020). Biorefinery development is the only sustainable alternative for the valorisation of winery waste streams leading to the production of various bio-based products (Chowdhary et al., 2021; Sirohi et al., 2020).

Grape pomaces are usually discarded at a disposal cost, fermented to produce alcoholic beverages, employed in livestock feed production or used as fertiliser (Williams et al., 2019). Grape pomaces have been used for the production of various value-added products including enzymes, biogas, bioethanol, biopolymers, biochar and bio-active compounds among others (Chowdhary et al., 2021). Grape pomaces have been used for the extraction of bioactive compounds and grape seed oil with applications in animal feed, pharmaceuticals, cosmetics and the food industry (Beres et al., 2017; Sirohi et al., 2020). The solids remaining after the extraction of bioactive compounds contain carbohydrates that could be used as carbon sources for the production of bio-based chemicals and polymers, such as polyhydroxyalkanoates (Martinez et al., 2016) and succinic acid (SA) (Filippi et al., 2021). Grape stalks have a low market value and are either discarded or used as fertilizers, while they could be used as carbon sources in fermentation processes (Filippi et al., 2021). The wine lees produced in the clarification process could be used for the extraction of bioactive compounds, ethanol, calcium tartrate and yeast cells that could be converted into a nitrogen-rich fermentation supplement (Dimou et al., 2016).

Literature-cited studies on biorefinery development have mainly used individual winery waste streams (Dimou et al., 2016; Ahmad et al., 2020). Filippi et al. (2022) proposed the utilization of all major winery waste streams for the production of multiple end-products. In this way, conventional wineries could be restructured into sustainable biorefineries. The integration of bio-based chemical production in such biorefineries is the only way to achieve their sustainable production that cannot be achieved by conventional bioprocesses. For instance, bio-based succinic acid production in industrial facilities is currently carried out by Myriant, Reverdia, Succinity and LCY Biosciences. The production of bio-based succinic acid is not cost-competitive as compared to petro-based succinic acid due to high capital investment requirements, technology issues, economies of scale requirements, adequate supply of raw materials and demanding R&D to deliver a sustainable product (Markets and Markets, 2021b). The main carbon sources used for bio-based succinic acid production are glucose syrup and glycerol using engineered bacterial or yeast strains (e.g. *Actinobacillus succinogenes*, *Basfia succiniciproducens*, *Escherichia coli*). The integration of bio-based succinic acid production in novel biorefineries using crude renewable resources could lead to process sustainability as compared to petro-based succinic acid (Babaei et al., 2019; Li et al., 2019; Stylianou et al., 2021). Filippi et al. (2022) showed that grape pomace, grape stalks and wine lees could be employed in a novel biorefinery concept for the production of both high value – low volume products (e.g. polyphenols) and low value – high volume products (e.g. succinic acid).

This study focuses on the techno-economic evaluation (TEA) and life cycle assessment (LCA) of the novel biorefinery presented by Filippi et al. (2022) using winery waste for the production of bio-based succinic acid and value-added co-products, namely crude phenolic-rich extract (CPE), grape seed oil (GO), calcium tartrate (CaT) and crude tannin-rich extract (CTE). Previous studies have carried out techno-economic analysis to evaluate the profitability potential of either single product generation from winery waste or the valorisation of a single winery waste stream. Dimou et al. (2016) carried out a techno-economic evaluation of wine lees valorisation to produce ethanol, calcium tartrate, antioxidants and yeast cells as animal feed. Jin et al. (2021) presented a techno-economic evaluation for the production of grape-seed oil, polyphenols and biochar from grape pomace. Todd and Baroutian (2017) presented a techno-economic evaluation for the extraction of bioactive compounds from grape pomace utilising different extraction techniques. Duba and Fiori (2019) evaluated the economic feasibility of grape-seed oil extraction. This study assesses the holistic valorisation of all major winery waste streams and the potential reduction in succinic acid production cost through integrated biorefinery development.

9.2 Description of the biorefinery development

The proposed biorefinery involves three different winery waste streams, namely grape pomaces, which include skins and seeds, grape stalks and wine lees generated after the winemaking process. All design parameters (e.g. processing conditions, extraction yields, pretreatment and hydrolysis yields, fermentation efficiency, material balances) for the proposed biorefinery have been taken from Filippi et al. (2022). All process flowsheets described below have been developed using the experimental results presented by Filippi et al. (2022). Succinic acid is produced via fermentation using the carbohydrate content of waste streams after the extraction of value-added fractions. The process design software UniSim (Honeywell) has been used to carry out all simulations.

In order to determine the annual waste utilization and co-product generation of the biorefinery, the annual production of succinic acid was set at around 30,250 t/y. This value is a common annual production quantity of a platform chemical at which economies of scale can be achieved (Bonatsos et al., 2020; Stylianou et al., 2021). Given the succinic acid production capacity mentioned above, the carbohydrate content of winery wastes and the conversion yields and fermentation efficiency reported by Filippi et al. (2022), the required quantity of grapes (2.48 million t/y) and the resulting wine production capacity (1.73 million t/y) were estimated. Based on these quantities, the generated winery wastes were estimated as 805,536 t/y containing 77% grape pomace, 12% grape stalks and 11% wine lees. Grape pomace and stalks have moisture contents of 75% and 50%, respectively, while the solid content of wine lees is 20.8% (w/w) (Galanakis, 2017; Ioannidou et al., 2020). Figure 9.1 presents the material balances of the proposed biorefinery concept using the experimental results presented by Filippi et al. (2022) and the quantities of individual waste streams and succinic acid production presented above.

Due to seasonal production of wine, it is assumed that the wastes are stored so that they can be used throughout the year to ensure the continuous operation of the plant. After extraction of free sugars, the grape pomace is dried prior to storage until further processing.

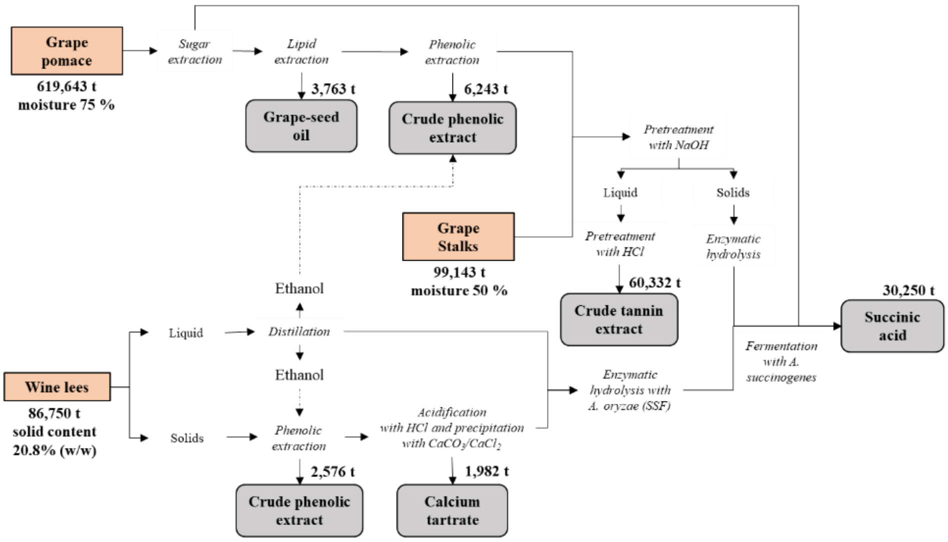


Figure 9.1 Mass balances in the proposed biorefinery using winery waste streams for the extraction of value-added fractions and the production of bio-based succinic acid via fermentation

9.2.1 Grape pomace processing (Area 100)

As illustrated in Figure 9.2, soluble sugars contained in grape pomace (skin and seeds) are initially extracted with water at 40°C for 2 h (V-101) under continuous stirring (A-101). The solid residue is separated from the slurry via centrifugation (CF-101), and the obtained liquid stream is fed to a mechanical vapour recompression MVR-forced circulation evaporator system (EV-103, C-103, E-103) to concentrate the free sugar fraction to 500 g/L. The concentration of the free sugars stream facilitates storage for longer periods until the free sugars are used as carbon sources for succinic acid production in Area 400. The solid stream after centrifugation (stream 102) is dried (DR-101) and stored to facilitate storage for longer periods until further processing. The dried solids (stream 103) are fed into the vessel V-102 for GO extraction with ethyl lactate under continuous agitation (A-102) for 2 h at ambient temperature. The suspension is centrifuged (CF-102) to separate the solid from the liquid fraction. The GO is isolated by evaporation (EV-101) under vacuum at 70°C. The recovered ethyl lactate is recycled in the GO extraction vessel (V-102), while 5% ethyl lactate is added to replace the losses of the solvent during processing. The phenolic compounds contained in the remaining solid fraction (stream 105) are extracted with 70% (v/v) aqueous ethanol for 20 min at 1:10 solid-to-liquid ratio (V-103). The ethanol used for CPE extraction has been extracted from wine lees in Area 300 (Figure 9.4).

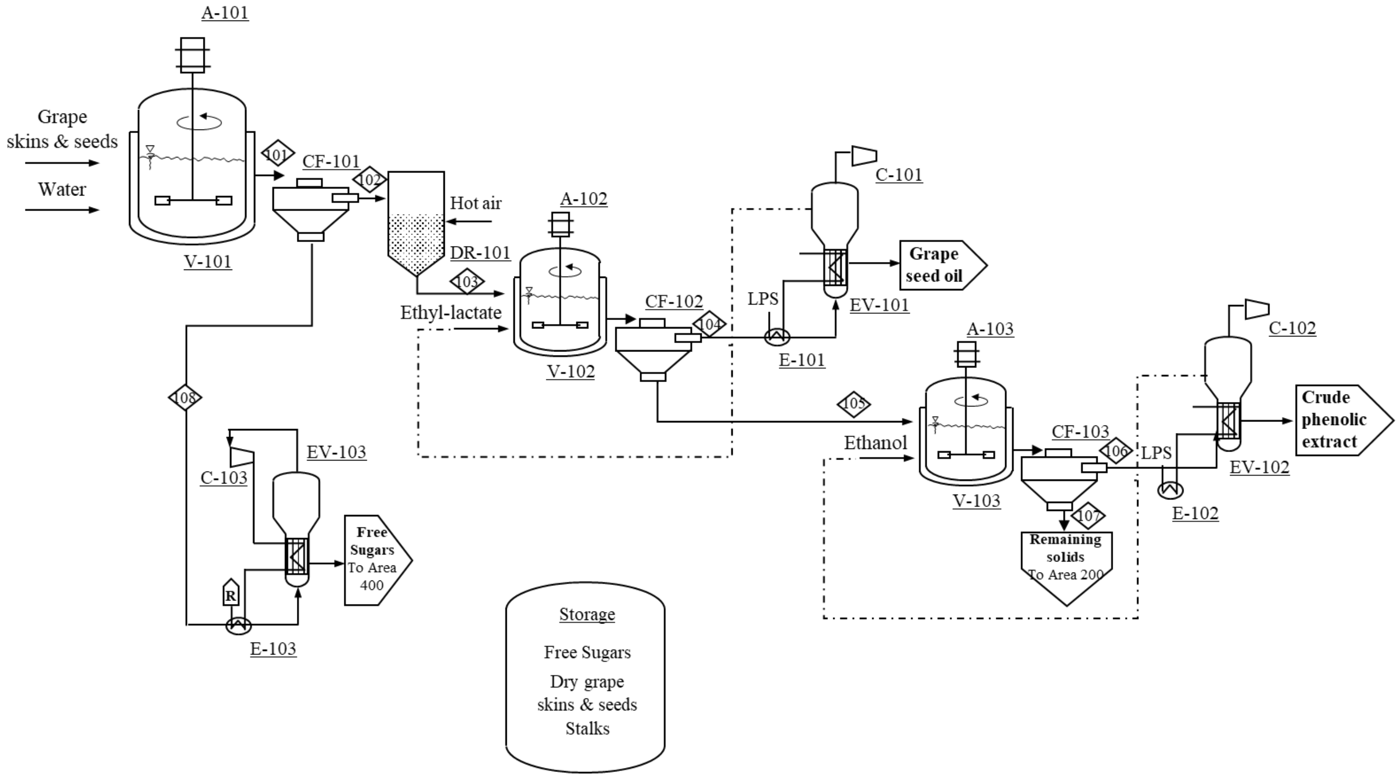


Figure 9.2 Process flow diagram of grape pomace processing (Area 100)

This is an important sustainability aspect in the proposed biorefinery as no commercial ethanol supply is required for CPE extraction. The centrifugal separator CF-103 is employed to separate the liquid stream, which is concentrated in the evaporator EV-102 under vacuum at 40°C for the recovery of the CPE. The ethanol solution is recycled in the extraction vessel V-103, while the remaining solids (stream 107) are directed to Area 200 for further treatment (Figure 9.3).

9.2.2 Grape stalks processing (Area 200)

Figure 9.3 presents the grape stalks treatment process. Stream 107 from grape pomace processing (Area 100) is mixed with grape stalks in V-201. The mixture is subjected to dilute aqueous (1.19%, w/v) sodium hydroxide pretreatment at 1:10 solid-to-liquid ratio and 30 min residence time. The mixed effluent is centrifuged (CF-201) and the liquid stream 202 is treated with 3 N HCl for 10 min in V-202 for CTE precipitation. The precipitated tannin-rich crude fraction is separated via centrifugation (CF-202) and dried (DR-201).

The solid residue (stream 205) obtained after centrifugation (CF-201) is fed into a mixing tank (V-203) and the pH is adjusted with dilute HCl. The slurry is fed into a vessel (V-204) together with water to achieve a solid concentration of 10% (w/v) and enzymes to hydrolyse the cellulose and hemicellulose fractions. The enzymatic hydrolysis is conducted for 48 h using the experimental results reported by Filippi et al. (2022). The sugar-rich hydrolysate is separated via centrifugation (CF-203) and subsequently used in the fermentation stage (Area 400).

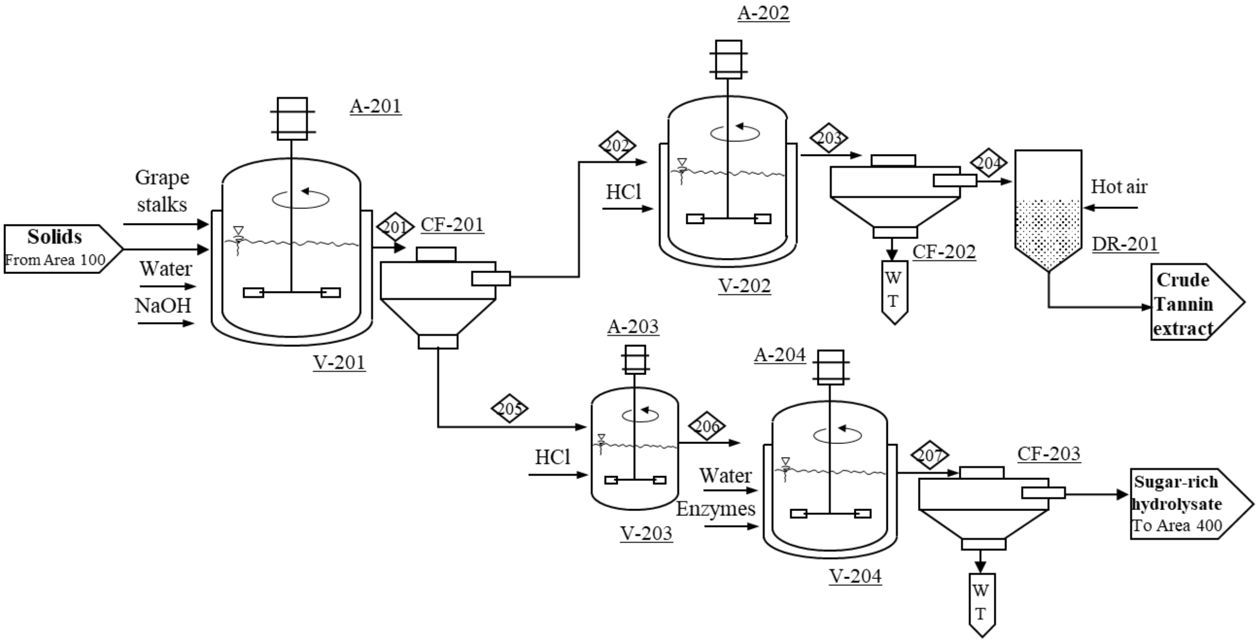


Figure 9.3 Process flow diagram of grape stalks processing (Area 200)

9.2.3 Wine lees processing (Area 300)

Area 300 presents the process flow diagram of wine lees fractionation (Figure 9.4). A centrifugal separator (CF-301) separates the solids from the liquid fraction. A distillation column (T-301) is then employed for ethanol recovery from stream 301. The recovered ethanol is used for CTE extraction in the biorefinery to eliminate the use of commercial ethanol. The phenolic compounds contained in solid lees are extracted with 50% (v/v) aqueous ethanol in a mixing tank (V-301) for 1 h. The slurry is directed towards a centrifugation step (CF-302). The liquid stream is fed into the evaporator EV-301 to separate the ethanol/water mixture from the CPE. After centrifugation, the solid stream 305 is transferred to a mixing tank (V-302) and suspended in water and HCl to precipitate the tartaric acid. After 10 min of continuous stirring, the tartaric acid-rich solution is separated from the solids by centrifugation (CF-303). Stream 311 is mixed with $CaCO_3$ and $CaCl_2$ to transform the soluble tartaric acid into the insoluble calcium tartrate according to the process presented by Dimou et al. (2016). Calcium tartrate is separated from the liquid in CF-306 and the solid stream (stream 313), containing 50% solids, is dried (DR-301) to obtain the final product.

Sunflower meal (SFM) is used as a solid substrate in the solid-state fermentation (TF-301) for the production of crude enzymes (mainly protease) using the fungal strain *Aspergillus oryzae*, as previously described by Kachrimanidou et al. (2021). The crude enzyme consortia are produced (TF-301) at a moisture content of 65% (w/w, on a wet basis). After 48 h, the whole solid state fermentation solids that contain the crude enzymes are mixed (V-304) with the aqueous liquid stream 308 obtained after ethanol distillation. The mixture is then centrifuged (CF-304) and the liquid stream 309, containing the crude enzymes, is fed in V-305 along with the wine lees solid stream 307. The enzymatic hydrolysis is carried out for 48 h at 40°C. The pH is adjusted with NaOH. After hydrolysis completion, the liquid stream, rich in free amino nitrogen (FAN), is separated via centrifugation (CF-305). The FAN-rich hydrolysate is used as fermentation nutrient supplement in Area 400.

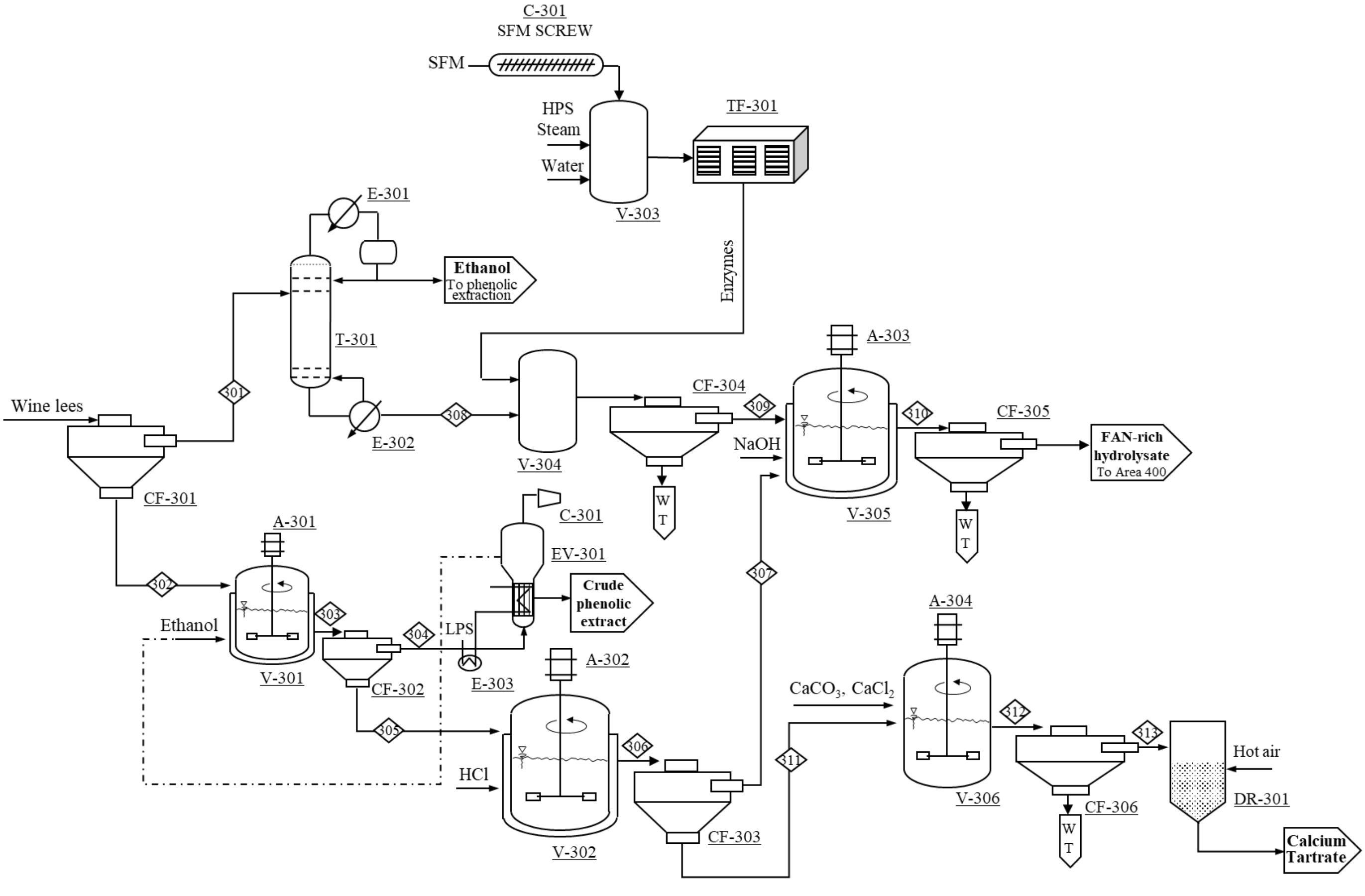


Figure 9.4 Process flow diagram of wine lees processing (Area 300)

9.2.4 Succinic acid production (Area 400)

Figure 9.5 presents the fermentative production of succinic acid as well as its downstream separation and purification (DSP) stages. The concentrated free sugars extracted from grape pomace (Area 100), the sugar-rich hydrolysate (Area 200) and the FAN-rich hydrolysate produced via enzymatic hydrolysis of wine lees (Area 300) are mixed (V-401) and sterilized in continuous operation mode using three heat exchangers (E-401, E-402, E-403). The sterilized stream is fed into the bioreactor F-403. Succinic acid production is carried out with the bacterial strain *A. succinogenes* at 37^{o}C under continuous sparging of CO_2. The inoculation bioreactor train (F-401, F-402) is used for inoculum preparation. After 47 h, 37.2 g/L succinic acid are produced with 0.64 g/g sugar to succinic acid conversion yield and 0.79 g/(L·h) productivity. Succinic acid crystals are subsequently purified using the DSP described by Alexandri et al. (2019).

The fermentation broth is centrifuged (CF-401) to remove the bacterial biomass. Stream 403 is fed to activated carbon columns (V-402) to achieve decolorisation and to remove impurities.

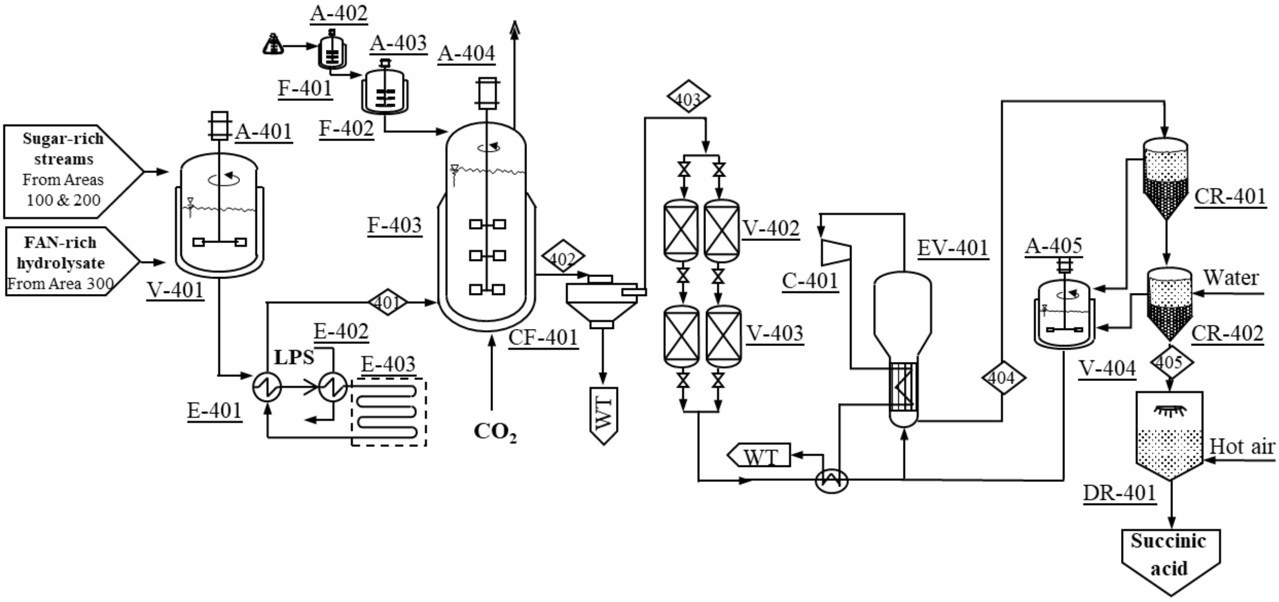


Figure 9.5 Process flow diagram of bio-based succinic acid production (Area 400)

The decolorized effluent is fed into cationic resin columns (V-403) to transform organic acid salts into their corresponding organic acids. The acidified liquid stream is then mixed with the liquid stream that is recycled from the crystallizers (CR-401, CR-402) and the resulting stream is concentrated using the MVR - forced circulation evaporator system (EV-401). Stream 404 is subsequently treated via crystallization in continuous crystallizers (CR-401, CR-402) at 4°C. The remaining liquid after crystallization is recycled to the evaporation stage. Dried succinic acid crystals are produced using a spray dryer (DR-401). The succinic acid crystal purity achieved is higher than 99.5%, while the overall succinic acid recovery yield in the DSP is ca. 95% (w/w).

9.3 Techno-economic assessment

Table 9.1 presents a summary of the Ceq.fob for all process equipment employed in grape pomace processing containing skins and seeds (Area 100), grape stalks processing (Area 200), wine lees processing (Area 300) and succinic acid production (Area 400). In Area 100, the main purchase equipment costs are attributed to the evaporator systems employed for sugar concentration, grape seed oil extraction and CPE extraction. In Area 200, the centrifugal separators CF-202 and CF-203 contribute the highest percentage of purchase equipment costs, reaching 42% and 33%, respectively. In Area 300, the evaporator system for CPE extraction from the solid fraction of wine lees contributes ca. 22% of the total purchase equipment costs in this section. In Area 400, where succinic acid crystals are produced, the bioreactors and agitators used contribute the highest percentage in the purchase equipment cost (ca. 56%), while the second highest purchase cost is attributed to the dryer DR-401 (20%). The overall FCI for the whole biorefinery is M$254.7. The FCI of the succinic acid production section (Area 400) contributes around 50% of the total FCI of the whole biorefinery.

The COM (M$145.59) of the whole biorefinery presented in Figures 9.2-9.5 has been estimated considering 30,250 t annual succinic acid production using 805,536 t/y winery waste containing 77% grape pomace, 12% grape stalks and 11% wine lees on wet basis. The COM has been estimated using the C_{UT} (M$27.2), the C_{OL} (M$6.36) and the FCI (M$254.7) presented in Table 9.1 for Areas 100-400 (Figures 2 and 3). Area 100 contributes the highest proportion of C_{UT} (50.3%) due to high electricity requirements in the evaporators (EV-101, EV-102, EV-103) used in this stage for the extraction of GO and CPE as well as for the concentration of the free sugars.

Table 9.2 presents the C_{RM} (M$39.75) employed in the proposed biorefinery. There is no nitrogen source supplementation in the fermentation medium used for succinic acid production because the hydrolysate produced from wine lees is rich in FAN that is sufficient for succinic acid production. The predominant cost of raw materials is attributed to the utilisation of HCl, which is employed in Areas 200, 300 and 400 for the extraction of CTE, pH correction after alkali treatment of lignocellulose-rich solids, extraction of CaT and succinic acid purification. It has been estimated that 32 workers per shift are required for plant operation corresponding to a C_{OL} of M$6.36.

The succinic acid production stage (Area 400) contributes the highest cost ($M62.89, 43%) in the overall COM (M$145.59) followed by Area 100 focusing on the extraction of free sugars, CPE and GO from grape pomace ($M43.99, 30%).

Table 9.1 Purchase equipment cost, FCI, cost of operating labor (C_{OL}) and cost of utilities (C_{UT}) for the proposed biorefinery

	Unit	**Description**	**Unit number**	**CEPCI$_{t0}$**	**Characteristic size (X_t)**	**FOB Cost (C_p@2018, M$)**	**Electricity (kWh/y)**	**Steam (t/y)**	**Process water (t/y)**
Area 100	V-101	Mixing tank[c]	1	521.9	V=2,133.7 m^3	0.550			
	A-101	Agitator[a]	1	521.9	P=254.34 hp	0.209	1,502,164.5		
	CF-101	Centrifugal separator[b]	3	444.2	Q= 71.12 m^3/h	2.123	736,560.0		
	EV-103	Evaporator[c]	6	521.9	A= 855.61 m^2	2.501	15,349,000.6		
	C-103	Compressor[a]	1	521.9	P=1,744.2 kW	0.448			
	E-103	Heat exchanger[a]	9	444.2	A=906.06 m^2	3.171			
	DR-101	Dryer[d]	1	525.4	A=7.85 m^2	0.367	7,189,418.8	2,761.1	
	V-102	Mixing tank[c]	1	52xc 1.9	V=371.27 m^3	0.313			
	A-102	Agitator[a]	1	521.9	P=442.56 hp	0.362	2,613,766.2		
	CF-102	Centrifugal separator[b]	1	444.2	Q=49.50 m^3/h	0.546	736,560.0		
	EV-101	Evaporator[c]	1	521.9	A= 57 m^2	0.397			
	C-101	Compressor[a]	1	521.9	P=1,191.8kW	0.373	10,488,178.7		
	E-101	Heat exchanger[a]	1	444.2	A= 47.65 m^2	0.039		70,602.5	
	V-103	Mixing tank[c]	1	521.9	V=88.44 m^3	0.205			
	A-103	Agitator[a]	1	521.9	P=105.42 hp	0.093	622,648.7		
	CF-103	Centrifugal separator[b]	3	444.2	Q=70.82 m^3/h	2.116	736,560.0		
	EV-102	Evaporator[c]	1	521.9	A= 544.93 m^2	0.426			
	C-102	Compressor[a]	6	521.9	P=2,600.0 kW	3.254	137,281,842.2		
	E-102	Heat exchanger[a]	1	444.2	A=33.63 m^2	0.034		58,712.7	
	Unitary utility cost						0.0674 $/kWh	9.45 $/t	0.0154 $/t
	Workers A100		7						
	Total Ceq.fob (M$)					**17.531**			
	FCI A100 (M$)				**5 × Total Ceq.fob A100 =**	**87.653**		**C_{UT} A100 (M$/y) =**	**13.680**
Area 200	V-201	Mixing tank[a]	1	521.9	V=18.93 m^3	0.026		175,300.6	
	A-201	Agitator[a]	1	521.9	P= 22.57 hp	0.026	133,293.5		
	CF-201	Centrifugal separator[b]	1	444.2	Q=30.29 m^3/h	0.403	237,600.0		
	V-202	Mixing tank[a]	1	521.9	V=49.73 m^3	0.026			
	A-202	Agitator[a]	1	521.9	P=59.27 hp	0.056	350,082.2		
	CF-202	Centrifugal separator[b]	3	444.2	Q=79.55 m^3/h	1.702	736,560.0		
	DR-201	Dryer[d]	1	525.4	A= 5.00 m^2	0.220	1,877,409.4	721.0	
	V-203	Mixing tank[a]	1	521.9	V=4.89 m^3	0.026			
	A-203	Agitator[a]	1	521.9	P=5.84 hp	0.013	34,477.5		

	V-204	Mixing tank[a]	1	521.9	V=163.18 m^3	0.042		51,514.2	
	A-204	Agitator[a]	1	521.9	P=194.51 hp	0.162	1,148,813.1		
	CF-203	Centrifugal separator[b]	2	444.2	Q= 65.27 m^3/h	1.328	736,560.0		
	Unitary utility cost						0.0674 $/kWh	9.45 $/t	0.0154 $/t
	Workers A200		3						
	Total Ceq.fob (M$)					**4.030**			
	FCI A200 (M$)				**5 × Total Ceq.fob A200 =**	**20.150**		**C_{UT} A200 (M$/y) =**	**2.866**
Area 300	CF-301	Centrifugal separator[b]	1	444.2	Q= 12.61 m^3/h	0.271	237,600.0		
	T-301	Distillation column[d]	1	240.0	N=22	0.167			
	E-301	Heat exchanger[a]	1	444.2	A=25.91m^2	0.027			1,098,950.9
	E-302	Heat exchanger[a]	1	444.2	A=38.42 m^2	0.031		31,800.2	
	V-301	Mixing tank[a]	1	521.9	V=34.33 m^3	0.026			
	A-301	Agitator[a]	1	521.9	P=40.93 hp	0.042	241,711.8		
	CF-302	Centrifugal separator[b]	1	444.2	Q=27.47 m^3/h	0.382	237,600.0		
	EV-301	Evaporator[c]	1	521.9	A=65.45 m^2	0.402			
	C-301	Compressor[a]	1	521.9	P=1,873.6 kW	0.464	16,488,554.4		
	E-303	Heat exchanger[a]	1	444.2	A=73.57 m^2	0.049		128,433.2	
	V-302	Mixing tank[a]	1	521.9	V=3.10 m^3	0.202			
	A-302	Agitator[a]	1	521.9	P=4.16 hp	0.013	5,697.7		
	CF-303	Centrifugal separator[b]	1	444.2	Q=4.05 m^3/h	0.207	118,800.0		
	V-303	Mixing tank[a]	1	521.9	V=14.07 m^3	0.202			
	TF-301	Tray SS bioreactors[b]	1	390.4	A=112.59 m^2	0.105			
	CF-304	Centrifugal separator[b]	1	444.2	Q=7.22 m^3/h	0.230	118,800.0		
	V-305	Mixing tank[c]	1	521.9	V=495.89 m^3	0.128		1,969.9	
	A-303	Agitator[a]	1	521.9	P=591.09 hp	0.488	3,491,056.9		
	CF-305	Centrifugal separatorb	1	444.2	Q=8.26 m^3/h	0.238	118,800.0		
	V-306	Mixing tank[a]	1	521.9	V=2.05 m^3	0.197			
	A-304	Agitator[a]	1	521.9	P=2.44 hp	0.013	14,390.0		
	CF-306	Centrifugal separator[b]	1	444.2	Q=0.82 m^3/h	0.183	118,800.0		
	DR-301	Dryer[d]	1	525.4	A=1.12 m^2	0.170	246,705.6	94.7	
	Unitary utility cost						0.0674 $/kWh	9.45 $/t	0.0154 $/t
	Workers A300		5						

	Total Ceq.fob (M$)					**4.199**			
	FCI A300 (M$)				**5 × Total Ceq.fob A300 =**	**20.997**		**C_{UT} A300 (M$/y) =**	**4.084**
Area 400	E-401	Heat exchanger[a]	2	444.2	A=823.77 m^2	0.639			
	E-402	Heat exchanger[a]	1	444.2	A=86.28 m^2	0.054			
	E-403	Holding tube[a]	1	500	l=0.12 m	0.146		16,341.8	
	F-403	Bioreactor[a]	11	521.9	V=645.79 m^3	6.899			
	A-404	Agitator[a]	11	521.9	P=769.78 hp	7.047			
	F-401/402	Seed bioreactor[a]	1	521.9	V=64.58 m^3	0.187			5,603,523.4
	A-401/402	Seed agitator[a]	1	521.9	P=76.98 hp	0.070	42,466,129.1		
	CF-401	Centrifugal separator[b]	2	444.2	Q=52.92 m^3/h	1.143	868,604.2		
	V-402/V-403	I.E. resins[b]	2	521.9	V=53.18 m^3	0.671			
	EV-401	Evaporator[c]	1	521.9	A=1,195.9 m^2	1.639	24,389,732.2	10,851.9	
	CR-401	Crystalizer[c]	1	525.4	M=24,519.90 kg/h	1.011	5,861,653.8		
	CR-402	Crystalizer[c]	1	525.4	M=9,090.38 kg/h	0.616	246,076.1		
	DR-401	Dryer[c]	1	525.4	M=424.39 kg/h	5.119	18,044,328.1		
	Unitary utility cost						0.0674 $/kWh	9.45 $/t	0.0154 $/t
	Workers A400		19						
	Total Ceq.fob (M$)					**25.163**			
	FCI A400 (M$)				**5 × Total Ceq.fob A400 =**	**125.814**		**C_{UT} A400(M$/y) =**	**6.591**
Total	**Total FCI A100-400 (M$)**					**254.66**			
	Total C_{OL} A100-400 (M$)					**6.36**			
							Total C_{UT} A100-400 (M$)		**27.221**

[a] Dheskali et al., 2017, [b] Peters, Timmerhaus and West, 2003, [c] Turton et al., 2018, [d] Kookos, 2007

Table 9.2 Raw materials cost (C_{RM}) for the proposed biorefinery using winery waste

Material	**Amount (t/y)**	**Total cost (M$/y)**
Ethyl-lactate	5,552.6	6.163
NaOH	22,188.7	8.875
HCl	203,702.3	12.426
$MgCO_3$	4,065.9	4.066
CO_2	16,919.5	2.538
Other nutrients	2,536.5	1.633
$CaCO_3$ (t)	1,059.0	0.159
$CaCl_2$ (t)	1,059.0	0.159
Enzymes	681.5	2.869
SFM	107.0	0.027
Process water	1,931,283.1	0.839
Total C_{RM} (M$)		39.75

9.3.1 Effect of biorefinery development on the cost-competitiveness of succinic acid production

The proposed biorefinery using 805,536 t/y winery waste (on wet basis) resulted in the annual production of 30,250 t SA, 8,819 t CPE, 3,763 t GO, 1,982 t CaT and 60,332 t CTE (Figure 1). Considering the annual succinic acid production (30,250 t/y) and the conversion yield achieved during fermentation (0.64 g/g), the annual sugar requirements is 47,266 t/y. Ioannidou et al. (2020) showed that the aforementioned sugar requirements are available in the winery wastes generated by the predominant wine producing countries in EU, namely Spain (184,000 t sugars/y), Italy (164,000 t sugars/y) and France (151,000 t sugars/y). Based on this estimation, the biorefinery concept presented in this study could be developed in Spain, Italy or France as a central processing facility using waste streams from many wineries. Further process improvement regarding succinic acid production efficiency could reduce further the winery waste requirements.

The main objective of this study was to present the potential of biorefinery development using winery waste on the reduction of the MSP of succinic acid. For this reason, the MSP of succinic acid has been estimated considering winery waste valorisation via either a single-product process or a multiple-product process where a range of market prices for the co-products has been considered. Figure 9.6 shows that the annual production of 30,250 t succinic acid using 805,536 t/y winery waste (on a wet basis) without any fractionation (single-product process scenario) leads to a MSP of \$4.42/kg$_{SA}$. The waste pretreatment and enzyme hydrolysis efficiency used in the estimation of MSP in the single-product process scenario were the same as the ones achieved in the biorefinery scenario regarding cellulose and hemicellulose to sugar conversion yields (Filippi et al., 2022). This MSP is significantly higher than the current market price of bio-based succinic acid (\$2.94/kg$_{SA}$) (E4tech et al., 2015) that is currently used in various applications, ranging from the traditional food and pharmaceutical markets to the production of bio-based polymers and polyester polyols (Ladakis et al., 2018).

The material balances presented in Figure 9.1 have been used to estimate the MSP of succinic acid at varying co-product market prices (Figure 9.6). The market prices of CPE, GO and CaT have been assumed based on their current market applications.

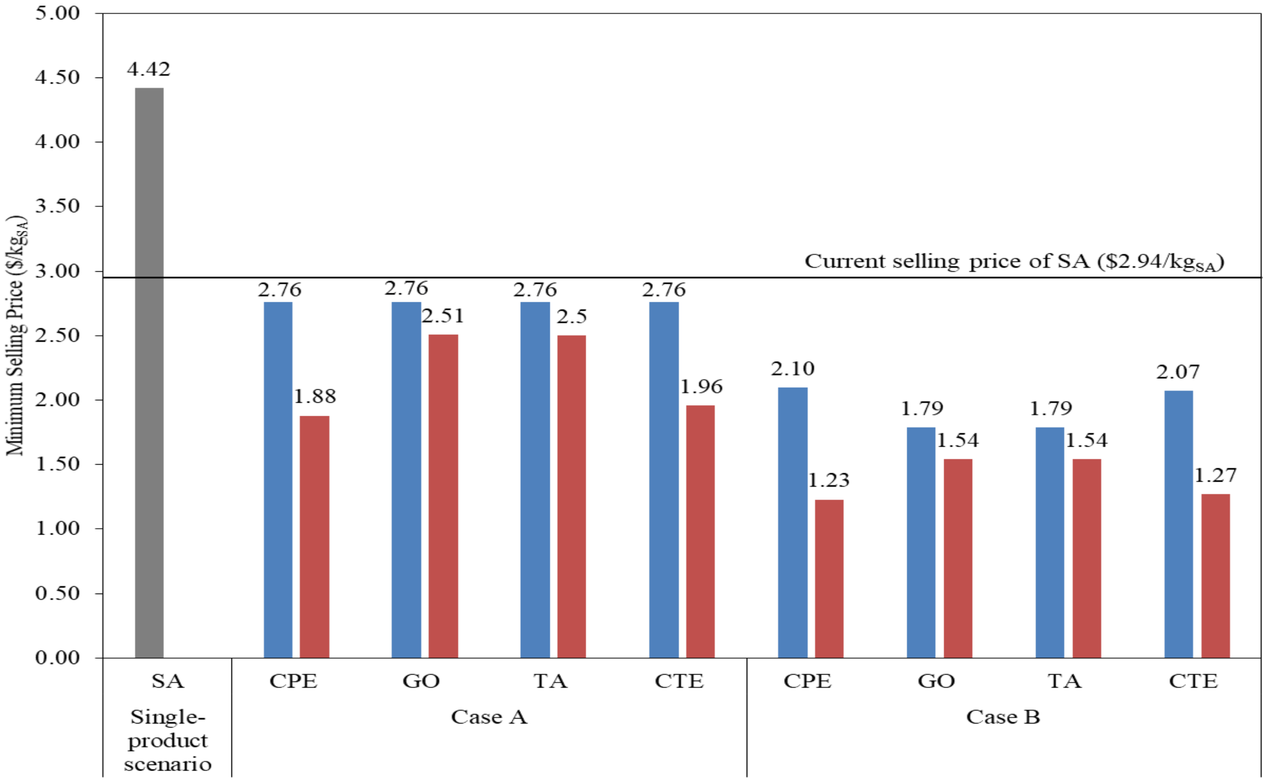


Figure 9.6 Estimation of MSP of succinic acid produced from winery wastes via either a single-product process (no biorefinery scenario) or a multiple-product process at varying co-product market prices using a minimum and maximum price range for each co-product. Case A: Blue bars correspond to minimum co-product market prices, while red bars correspond to maximum market price for the main co-product and minimum market prices for the other co-products. Case B: Blue bars correspond to minimum market price for the main co-product and average market prices for the remaining co-products, while red bars correspond to maximum market price for the main co-product and average market prices for the other co-products

Dimou et al (2016) reported that the market prices of antioxidant-rich extracts from grapes may vary within the range of \$10-100/kg depending on their purity and the active compounds contained in the extract. In this study, a low CPE market price range (\$4-7/kg) has been considered because no further purification has been considered in the performed process design. The GO extracted from grape pomace could be used in culinary, cosmetic and pharmaceutical applications (Jin et al., 2021). In this study, the GO market price range was assumed at \$3-5/kg considering that the GO market price may vary within the range of \$2-10/kg depending on its final application (Alibaba.com) and the market price (\$4/kg) considered by Jin et al. (2021). CaT is mainly used in the food industry (Dimou et al., 2016). The CaT market price range was assumed at \$2-6/kg depending on its final application (Alibaba.com) and literature-cited data (Dimou et al., 2016). The CTE extracted in this biorefinery concept as presented by Filippi et al. (2022) could be potentially used in the preparation of bio-based adhesives and resins that are suitable for the production of particleboards in order to substitute for phenol in the production of phenol–formaldehyde resins (Ping et al., 2011). The reagent used for condensed tannin extraction (e.g. NaOH, Na_2CO_3, $NaHCO_3$) and the process used to recover the condensed tannins (e.g. direct lyophilization or HCl treatment after NaOH treatment) affects the properties of the resins and the wood-based panels (Ping et al., 2012, 2011). For instance, the condensed tannins extracted with Na_2CO_3 led to the production of particleboards the properties of which passed relevant international standard specifications for interior grade panels (Ping et al., 2012). It should be pointed out that the adhesive properties of the crude tannin-rich extract extracted in this study has not been verified. Further research is needed to identify the adhesive properties of the tannin-rich extracts produced in this biorefinery concept. In this study, a conceptual approach has been employed to assess the biorefinery development potential if this tannin-rich extract is used for bio-based adhesive preparation. Adjustments in processing conditions and unit operations should be applied for the production of a suitable bio-based adhesive. The CTE market price range (\$0.8-1.2/kg) has been assumed considering the market price range of phenol used in the production of phenol-formaldehyde resins (Alibaba.com).

Figure 9.6 presents the MSP of succinic acid at varying co-product market prices using the market price ranges mentioned above. Case A in Figure 9.6 presents the MSP of succinic acid at two scenarios where each co-product market price varies between the minimum and maximum price, while the remaining co-products are set at their minimum prices. When the minimum prices of CPE (\$4/kg), GO (\$3/kg), CaT (\$2/kg) and CTE (\$0.8/kg) are used, then the MSP of succinic acid acquires the highest value (\$2.76/kg_{SA}). Even in this extreme case, the MSP of succinic acid is lower than the current market price of bio-based succinic acid (\$2.94/kg$_{SA}$). In the case that each co-product market price is set at the maximum price and the remaining co-products are set in their minimum market price, then the most influential co-product is the CPE where a MSP of succinic acid as low as \$1.88/kg$_{SA}$ is achieved. Case B in Figure 9.6 presents the MSP of succinic acid at two scenarios where each co-product market price varies between the minimum and maximum price, while the remaining co-products are set at their average prices. The CPE is the most influential co-product as the MSP of succinic acid varies from \$2.10/kg$_{SA}$ to \$1.23/kg$_{SA}$ when the market price of CPE varies from \$4/kg$_{CPE}$ to \$7/kg$_{CPE}$, while the average market prices of GO (\$4/kg), CaT (\$4/kg) and CTE (\$1/kg) have been used. Figure 9.6 shows that biorefinery development can lead to a significantly lower MSP of succinic acid than the current market price of bio-based succinic acid. It should be stressed that if the highest co-product market prices are considered then the MSP of succinic acid is \$0.58/kg$_{SA}$.

Figure 9.7 shows the variation of NPV as a function of the market price of each co-product considering that the succinic acid market price is equal to the current market price of bio-based succinic acid (\$2.94/kg$_{SA}$). The co-product market price range presented above has been used. In each case, the average market price of remaining co-products has been considered. It can be observed that the market prices of CPE and the CTE affect significantly the NPV of the whole biorefinery.

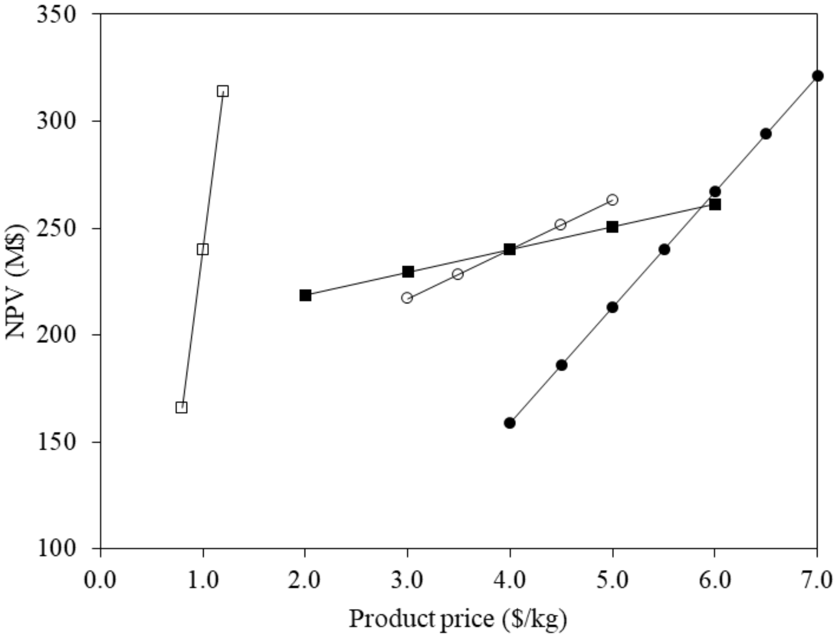


Figure 9.7 NPV variation as a function of the individual co-product market price considering CPE (●), GO (○), TA (■), CTE (□). In each case, the average market price of all remaining co-products has been considered, namely CPE (\$5.5/kg), GO (\$4/kg), CaT (\$4/kg) and CTE (\$1/kg)

In the case of CPE (Figure 9.7) this is attributed to their high market price, while in the case of CTE (Figure 9.7) this can be attributed to their high production capacity. The estimated DPP ranged from 7 years when the highest market prices of all co-products were considered to 20 years when the lowest co-product market prices were considered. The estimated NPV ranged from $M439.4 when the highest market prices of all co-products were considered to $M39.4 when the lowest co-product market prices were considered.

Most literature-cited studies focus on the techno-economic assessment of biorefinery development using individual winery waste streams. Jin et al. (2021) evaluated the profitability potential of three processing scenarios using 33,000 t/y grape pomace for the development of a single-product process producing only grape seed oil, a two-product process producing grape seed oil and polyphenols, and a three-product process producing grape seed oil, polyphenols and biochar. The latter biorefinery scenario was the most profitable one, leading to a NPV of $M111.7 and a payback period of 2.5 years, demonstrating that a multiple-product biorefinery approach ensures process profitability. Dimou et al. (2016) presented a sensitivity analysis based on techno-economic evaluation to assess the development of a profitable wine lees refining process depending on the MSP of the antioxidant-rich extract considering fixed market prices for calcium tartrate ($5/kg), ethanol ($0.6/kg) and yeast cells as animal feed ($1/kg). The COM was estimated at M$1.21 for 500 kg/h wine lees processing corresponding to a MSP of the antioxidants-rich extract of $122/kg. The MSP of the antioxidants-rich extract was reduced to $11.06/kg at 5,000 kg/h of wine lees utilisation. Vega et al. (2020) presented a techno-economic evaluation for polyphenol extraction from red wine pomace via two different extraction methods, solvent extraction and pressurized liquid extraction, in different solvent to dry weight ratios. The processing cost of polyphenol extraction (expressed in kg gallic acid equivalents, GAE) was in the range of €8-26/kg GAE.

9.4 Profitability risk assessment

The analysis is carried out by developing a techno-economic model (based on the results of process design and TEA) that evaluates the sensitivity to varying process and economic parameters. A single-point sensitivity was initially carried out using MATLAB by changing one variable at a time with case-specific limits. The most important variables (i.e. fermentation duration, unitary cost of steam, electricity cost, total C_{RM}) identified via single-point sensitivity are presented in Table 9.3, while their distribution curves are presented in Figure 9.8.

Table 9.3 Process variables and design parameters used in Monte-Carlo simulations for risk assessment of process profitability of wineries biorefinery development

Process variables	Range	Design parameters	Values
Fermentation duration of SA production (h)	39-59	SA annual production capacity (t/year)	30,000
Cost of steam ($/t)	8.0-12.0	Winery wastes annual quantity (t/year)	805,536
Electricity cost ($/kWh)	0.0674-0.2	SA concentration at the end of fermentation (kg/m^3)	37.2
Total C_{RM} (M$)	3.2×10^7-4.8×10^7	SA market price ($/kg)	2.94
Market price of co-products ($/kg)	CPE : 4.0, 5.5, 7.0 GO : 3.0, 4.0, 5.0 TA : 2.0, 4.0, 6.0 CTE : 0.8, 1.0, 1.2		

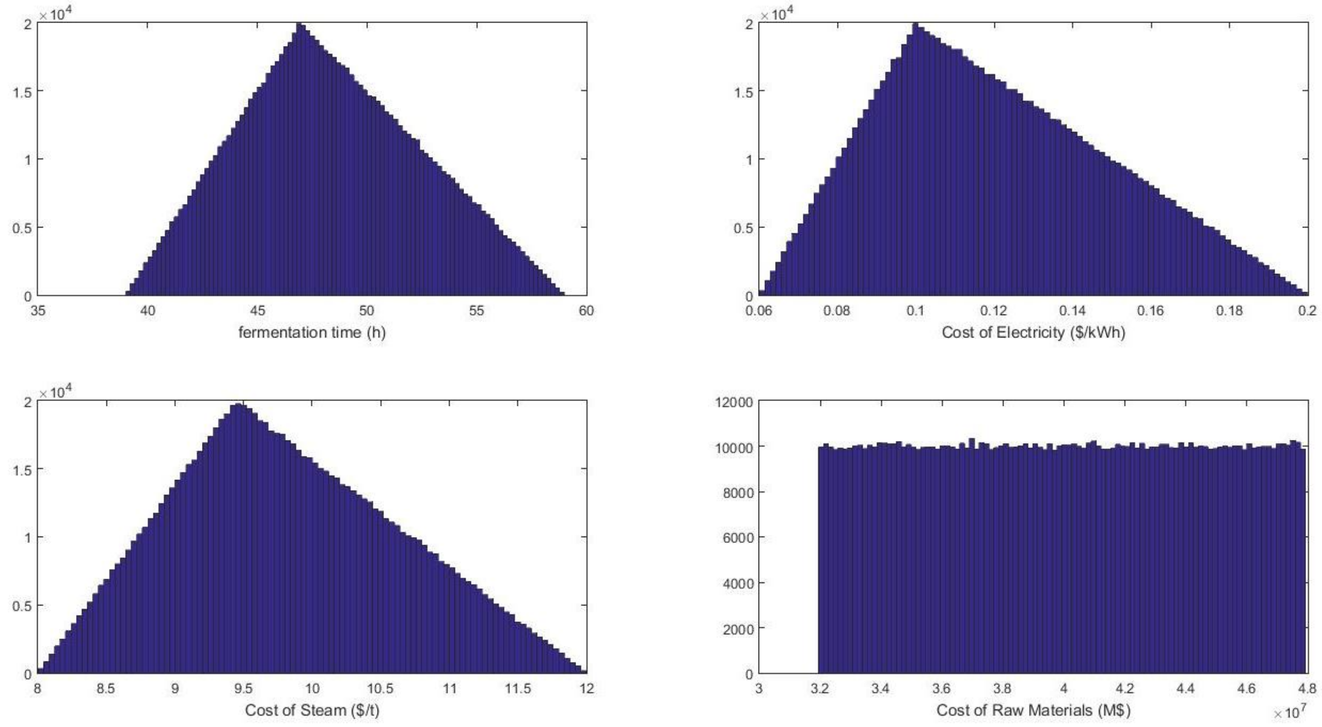


Figure 9.8 Input uncertainties. a) SA fermentation time (h), b) electricity cost ($/kWh), c) heating steam cost ($/t), d) total C_{RM} (M$).

Monte-Carlo simulations were subsequently carried out to identify the probability to develop a profitable biorefinery of winery wastes by estimating the NPV using the most important variables and their corresponding value ranges presented in Table 9.3. The design parameters used in the techno-economic model are the ones presented in the process design section, while case-specific design parameters are presented in Table 9.3. It should be pointed out that three different cases have been assessed considering the market price of co-products. CPE, GO, TA and CTE market prices have been varied at three distinct values, their minimum, average and maximum possible market price.

Figure 9.9 presents the probability of NPV to be positive and thus the proposed winery wastes biorefinery to be profitable. It can be observed that the probability for a profitable biorefinery development is 100% or close enough (98%) when the co-products are sold both at their maximum and their average market prices (green and blue line). The probability to achieve a positive NPV when the co-products of the biorefinery are sold at their minimum market prices (black line) is close to 25%. The main conclusion of the risk assessment study is that the proposed winery wastes biorefinery could be profitable in all different cases and even at the worst-case scenarios of the values of process variables.

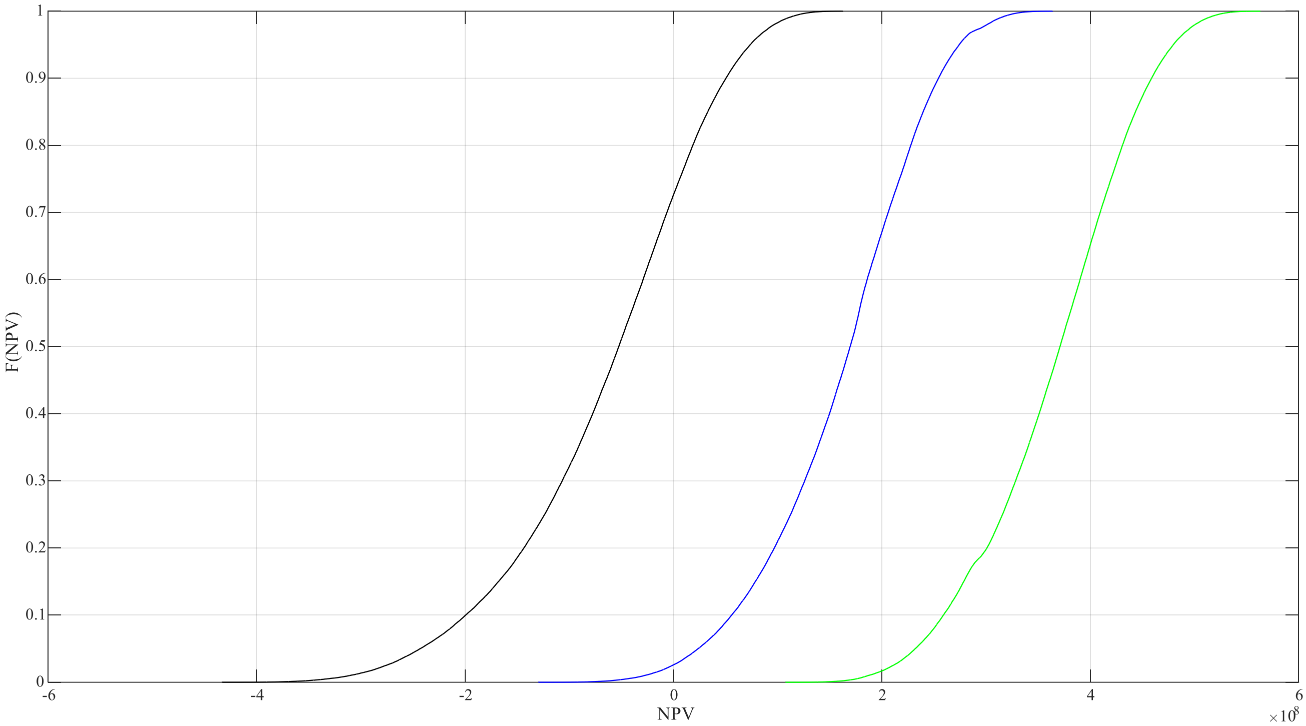


Figure 9.9 Probability to achieve positive NPV (million $) for winery wastes biorefinery development. Minimum market price of co-products (black line), average market price of co-products (blue line) and maximum market price of co-products (green line).

9.5 Life Cycle Assessment

9.5.1 Goal and scope

The aim of this study is to assess the environmental performance of a biorefinery using wineries wastes. A "cradle-to-gate" LCA approach has been employed for the analysis, considering as functional unit 1 kg of dry waste stream after the production of 2.15 kg wine. The composition of 1 kg wet waste is 77% grape skins and seeds (75% moisture content), 12% grape stalks (50% moisture content) and 11% wine lees (20.8% solid content). The system boundaries for the LCA includes the treatment of grape pomace (skins and seeds) for the production of GO and CPE as well as the extraction of the free sugars, the treatment of stalks for the extraction of CTE and the production of a sugar-rich hydrolysate, the wine lees treatment for the production of CPE, CaT and a FAN-rich hydrolysate, and finally succinic acid production and purification.

9.5.2 Life Cycle Inventory

The life cycle inventory that includes the mass and energy inputs and outputs of the whole biorefinery is presented in Table 9.4. The construction of the inventory was based on the developed process flow diagrams. The presented quantities are related to the treatment of 805,536 t of wet winery waste. After the analysis, the results have been expressed to the selected functional unit. Electricity generation from grid and steam generation using natural gas have been considered in this study. The environmental impact of the winery wastes was taken from Fusi et al. (2014) where a "cradle-to-grave" LCA was presented to estimate the environmental performance of 750 mL Sardinian white wine production. Fusi et al. (2014) implemented economic allocation to distribute the environmental impacts among the main product (wine) and the waste streams. The environmental impact has been estimated as 8.21×10^{-4} kg CO_2-eq per kg grape pomace and wine lees, while no impact was attributed to grape stalks. It should be mentioned that carbon sequestration via grape cultivation and the release of CO_2 during wine fermentation have not been taken into consideration in the LCA conducted in this study.

In this study, the LCA was carried out using the CML 2001 (Jan. 2016) methodology, as the most cited methodology for environmental assessment (Guinée et al., 2002). The final results are expressed using the quantitative indicators most frequently used in literature, namely Global Warming Potential (GWP) and Abiotic Depletion Potential (ADP fossil).

Table 9.4 Life cycle inventory for the proposed biorefinery using winery waste streams

Inputs		**Outputs**	
Raw material / Utility	**Value**	**Product**	**Value**
Pomace (t)	619,643	Succinic acid (t)	30,250
Stalks (t)	99,143	Grape-seed oil (t)	3,763
Lees (t)	86,750	Crude phenolic extract (t)	8,819
Ethyl-lactate (t)	5,553	Calcium tartrate (t)	1,982
NaOH (t)	22,189	Crude tannin extract (t)	60,332
HCl (t)	203,702		
$MgCO_3$ (t)	4,066		
CO_2 (t)	16,919		
Other nutrients (t)	2,536		
$CaCO_3$ (t)	1,059		
$CaCl_2$ (t)	1,059		
Enzymes (t)	681		
SFM (t)	107		
Electricity (kWh)	292,823,588		
Steam (t)	599,751		
Water (t)	1,931,283		

9.5.3 Life Cycle Impact Assessment

The estimated environmental performance of the selected impact categories (GWP and ADP fossil) of the winery wastes biorefinery is presented in Figure 9.10. The FU used is 1 kg total dry waste. Figure 9.10 presents the greenhouse gas emissions per FU for the total biorefinery (1.47 kg CO_2-eq/FU) as well as for the individual processing stages (Areas 100-400 in Figures 2 and 3). Grape pomace (0.51 kg CO_2-eq/FU) and grape stalks (0.44 kg CO_2-eq/FU) processing contribute the highest GWP including the individual environmental impact of the wastes, namely 2.61×10^{-3} kg CO_2-eq/FU for grape pomace and zero GWP for grape stalks. The ADP fossil for the whole biorefinery (25.20 MJ/FU) is presented in Figure 9.10. The grape pomace (7.85 MJ/FU) and the grape stalks (7.82 MJ/FU) processing stages contribute the highest requirements in non-renewable energy followed by succinic acid production (6.43 MJ/FU) and wine lees processing (3.10 MJ/FU). The environmental impacts of both impact categories are mainly attributed to the utilities consumed for the recovery of the solvents, drying requirements, bioreactor operation and the concentration of free sugars extracted from grape pomace.

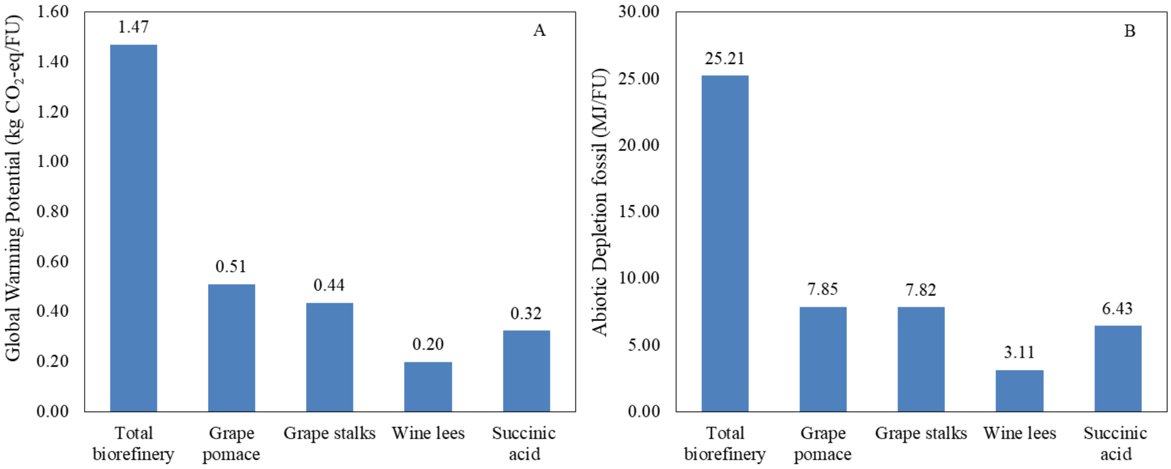


Figure 9.10 Global Warming Potential (A) and Abiotic Depletion Potential (B) per kg dry total winery waste expressed for the whole proposed biorefinery and the individual processing stages (Areas 100-400) focusing on grape pomace, grape stalks and wine lees treatment as well as succinic acid production.

Environmental impact assessments of individual winery waste valorisation have been reported in the literature. Cortés et al. (2019) reported the GWP (1.33 kg CO_2-eq/kg wine lees), the ADP (0.435 kg oil-eq/kg wine lees), the terrestrial acidification (4.85×10^{-3} kg SO_2-eq/kg wine lees), and freshwater eutrophication (0.22×10^{-3} kg P-eq/kg wine lees) of wine lees valorisation for the production of antioxidant-rich extract, calcium tartrate and yeast cells. Ncube et al. (2021) presented the environmental impact assessment of conventional wineries integrated with the production of either tartrate or grape seed oil in order to develop circular patterns. The estimated environmental impact categories for a winery integrated with grape seed oil extraction from pomace were presented considering 1 bottle of Asprinio wine as functional unit, namely 9.39×10^{-3} kg CO_2-eq for GWP and 2.76×10^{-3} kg oil-eq for fossil resources scarcity (equivalent to ADP fossil). Vega et al. (2020) reported 19 different midpoint indicators for all scenarios assessed for polyphenol extraction from red wine pomace (expressed as kg gallic acid equivalents, GAE). GWP ranged from 27.28 to 171.88 kg CO_2-eq/kg GAE depending on the solvent to dry weight ratio selected for the extraction process, while fossil resources scarcity (equivalent to ADP fossil) ranged from 8.96 to 57.04 kg oil-eq/kg GAE. Ferreira et al. (2018) presented the environmental impact of heat production from grape stalk pellets. Eleven indicators were estimated for the production of 1 MJ heat from grape stalks pellets with GWP and ADP values of 1.45×10^{-2} kg CO_2-eq/MJ and 0.16 MJ/MJ, respectively.

The environmental impact results presented in literature-cited publications cannot be easily compared to the results of this study due to the complexity of implementing the LCA methodology in different biorefineries and the selection of different functional units. The FU selected in this study aimed at evaluating the environmental impact per kg dry waste in order to allow the future comparison of different biorefinery concepts with the valorisation potential of the same waste resource.

Chapter 10 Concluding remarks and future perspectives

The smooth transition to the circular economy era will only be achieved if processing of renewable resources overcomes technological, economic, environmental and social challenges. The commercialization and competitiveness of biorefineries is dependent on technological breakthroughs that also comply with sustainability criteria for the production of bio-based products with improved sustainability performance than petrochemical products. The long-term growth of the bio-based and sustainable business models depends on various aspects including the selection of the appropriate feedstocks, adoption of a highly efficient biorefinery approach, where applicable, optimisation of fermentation efficiency and selection of the most effective DSP technology.

This PhD thesis focused on the assessment of sustainability potential of novel biorefineries for the production of bio-based products. State of the art on resource efficiency and biorefinery development, bio-based chemicals and polymers as well as sustainability issues was discussed in Chapter 2 through a critical literature review. Various feedstocks were evaluated considering their composition and potential for biorefinery development. The market performance of succinic acid and PBS was reported. The criteria and indicators for sustainability assessment reported in literature-cited publications were reviewed.

Based on the objectives of this PhD thesis, in the first section of the scientific work (Figure 3.1), sustainability and profitability assessment of a SBP-based biorefinery was performed for the production of PBS. The LCC methodology was implemented, by combining process costs with environmental externality costs, in order to compare the obtained results with base case and conventional scenarios. Cost-competitive PBS production was achieved in a SBP-based biorefinery leading to MSP reduction of 54.3% as compared to glucose-based and corn stover-based processes, respectively. The life cycle cost of PBS production is lower than GPPS only in the case that a SBP-based biorefinery is developed. These results do not include the EoL phase and thus could be further improved considering that the fossil-derived products have a higher environmental impact than bio-based products in the EoL stage. Chapter 5 illustrated that SBP-based biorefinery development ensures sustainable production of PBS as compared to fossil-derived counterparts and single product bioprocesses using glucose syrup and corn stover, even when the PBS is sold at a market price equal to those of its fossil counterpart.

In the second section, the sustainability assessment of OFMSW valorisation was carried out under different concepts and assumptions. Initially, Chapter 6 presented the sustainability assessment of SA production using an EMB-based sustem for simultaneous SA production and extraction.

Process design, TEA, profitability risk assessment and LCA were carried out demonstrating that the EMB-based technology improves the sustainability aspects of SA production when compared to the performance of conventional SA production processes. Furthermore, the GWP and ADP values estimated for the EMB-based SA bioprocess using renewable energy are lower than low pH yeast cultures and conventional bacterial cultures reported in the literature when no co-products are considered. The development of the EMB system at lower pH *Y. lipolytica* fermentation leading to further reduction in NaOH requirements, the integration of CHP and the production of co-products in an OFMSW-based biorefinery could further improve the sustainability of SA production.

The next step was to evaluate the SA production via an OFMSW-based biorefinery integrated with the extraction of oils and proteins (Chapter 7). The developed biorefinery resulted in 100% oils recovery, 68% protein recovery and sugar-rich hydrolysate production that was subsequently used for SA production. The sensitivity analysis related to the market price of the co-products proved that the achieved MSP_{SA} estimated through the proposed biorefinery could be significantly lower than the current market price of bio-based SA. Improved environmental impact could be achieved by reducing energy consumption and producing additional bio-based products and energy from the remaining solids.

OFMSW was subsequently valorised for the development of four biorefinery concepts targeting the production of different end-products (Chapter 8). The techno-economic and environmental impact of these biorefineries were evaluated. Lactic acid, succinic acid, HMAs and PUDs were produced with biosurfactants being the common end-product in each case. Furthermore, two scenarios were considered for comparison purposes to account for current OFMSW management practices and estimate possible GHG emissions savings. The competitive MSP of end-products and the GHG savings as compared to conventional end-products and OFMSW management practices demonstrate the high potential of OFMSW-based biorefinery development. Combining the developed processes with production of biofertilizer and biogas from remaining solids of alternative biorefineries would enhance overall process sustainability. The utilisation of renewable energy and the substitution of chemicals and solvents by electricity by novel electrification processes will improve further overall process sustainability. The production of LA and SA from waste streams at fermentation efficiencies currently achieved in the industry using corn-derived glucose will also enhance process profitability and sustainability.

In the final section (Chapter 9), a biorefinery using the three main waste streams generated by wineries for the production of bio-based succinic acid and value-added co-products, namely crude phenolic-rich extract, grape seed oil, calcium tartrate and crude tannin-rich extract, was developed.

Process design, TEA, LCA and profitability risk assessment were performed, while the potential reduction in succinic acid production cost through integrated biorefinery development was evaluated. The development of marketable co-products is critical in order to achieve process sustainability. Biorefining of winery waste could lead to the development of a sustainable and novel bioeconomy business model with new market opportunities and efficient waste management. The profitability potential and environmental impact of a biorefinery using winery waste for the production of succinic acid and various co-products has been presented. Future studies should focus on the development of specific end-products from each extracted fraction with specific market applications. In this way, biorefinery scenarios will be assessed in more detail providing more accurate estimation of process profitability and environmental impact. Furthermore, improving the fermentation efficiency of succinic acid production is also important in order to reduce raw material requirements and production costs.

The results presented in this PhD thesis demonstrate that sustainable biorefineries could be developed for the production of bio-based chemicals and polymers, utilizing various IFSS and OFMSW. The stated general objective was achieved after the extensive sustainability assessment of selected biorefineries and relevant comparisons with benchmarks and fossil counterparts. Nevertheless, after the completion of this PhD, several future work recommendations were identified.

Even though two important bio-based products (succinic acid and PBS) were evaluated in this study for their potential sustainable production using different technologies, there are still several biobased chemicals and polymers under development which need to be evaluated under the biorefinery development approach. Such way, clearer conclusion would be drawn about their sustainability and their prospects for future development.

The sustainability of proposed biorefineries were evaluated using either first (corn-derived glucose syrup) or second (SBP, corn stover, OFMSW, winery wastes) generation feedstocks. However, it would be useful to assess more second generation feedstocks (e.g. non-food industrial crops, forestry residues etc.) and include also types from third generation feedstock, such as microalgae. Such feedstocks could lead to sustainable production of bio-based products that could be competitiveness in the market.

An important aspect in biorefinery development was utilities requirements for plant operation. Electricity and steam, which are utilised in all cases as base case scenario, are mainly derived from fossil resources, as electricity was considered to be taken from the grid and steam was produced from natural gas. Biorefinery design should rely entirely on renewable resources (e.g. waste streams) for the production of bio-based products and onsite heat and energy co-generation. Energy utilisation and bio-based product synthesis should be evaluated simultaneously as this is the only way to develop sustainable processes.

This work was based on process design, TEA and LCA methodologies that were implemented for the sustainability assessment of all proposed biorefineries, while profitability risk assessment, LCC and social assessment methodologies were utilised in case-specific studies. An important suggestion for future work is the consideration of all above-mentioned methodologies under a common framework, for the holistic evaluation of sustainability. This framework will take into account at the same time the three main pillars, including also the environmental and social impacts of a biorefinery in the risk assessment. Therefore, the constructed framework will be a useful tool for multicriteria and decision-making scenarios when planning the development of industrial processes.

A limitation of this PhD thesis was the selection of system boundaries. All biorefineries were assessed as “cradle-to-gate”, trying to be concise for both TEA and LCA at the same time. However, important parts of a complete value chain were excluded as, for example, waste handling processes, logistics and the EoL phase. Assessing all stages of a value chain in a systematic way by eliminating at the same time possible uncertainties that affect the inventory data, can offer an improved and more realistic evaluation of its sustainability performance and can also reveal possible trade-offs among considered burdens. In particular, by taking into consideration alternative EoL recirculation schemes (e.g. mechanical, chemical, energy, nutrient recycling, etc.) in a proper manner, circular bioeconomy principles will be strengthened and implemented towards the development of circular and sustainable biorefineries.

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