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DESIGN AND ENERGY INTEGRATION OF A LIGNOCELLULOSIC BIOREFINERY

THESIS PROJECT OF THE STUDENT

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ABSTRACT

In this thesis project a lignocellulosic biorefinery which produces a big number of useful biochemicals was designed and integrated. Part of this thesis project took place in collaboration with EPFL (École polytechnique fédérale de Lausanne), in Lausanne.

The finite source of the fossil fuels, as well as their major contribution in the increase of GHG emissions, led the developed countries to seek out for alternative renewable energy sources. One of the most effective and abundant source of this kind, is the lignocellulosic feedstock. For this reason, wheat straw, which belongs to this category, was used as feedstock for the designed biorefinery. Its main components are cellulose, hemicellulose and lignin, to which wheat straw disintegrates through a complex organosolv pretreatment process.

Each process included in the biorefinery was designed and simulated in Aspen Plus V7.2, by taking into consideration their properties and the bioconversion technologies through which they are produced. After the full completion of the process design of the biorefinery, thermal, mass and economic data were extracted from the simulation results and were used for the energy integration of the biorefinery

The energy integration of each process in a biorefinery is extremely important in order to ensure big energy savings in the final plant. In this thesis project, the energy integration was estimated with two different approaches.

Firstly, Osmose, a linear programming program, was used, which was developed in EPFL. This program provided the ability to calculate the size of the defined additional utilities for each chemical path of the biorefinery. Additionally, the possible profitability of each final product was calculated. The energy savings for the integrated chemical paths were also calculated.

For the second approach, a program based on the transshipment model developed by Papoulias and Grossman was created in GAMS. This time, each process was integrated individually. However, the important difference is that during this process, the most cost-efficient utility combination, through a series of utility combinations, is pointed out. The Grand Composite Curves for each process were designed. Again, the energy savings for each integrated process were indicated. Through the comparison of the results of these two methods, useful conclusions can occur regarding the profitability the energy requirements of the final products.

ΕΚΤΕΤΑΜΕΝΗ ΠΕΡΙΛΗΨΗ (Abstract in Greek)

Στην παρούσα διπλωματική εργασία, θα σχεδιαστεί και θα ολοκληρωθεί ενεργειακά ένα βιοδιυλιστήριο το οποίο παράγει χρήσιμα βιοχημικά προϊόντα, κυρίως για τη σύνθεση βιοπλαστικών. Μέρος της εργασίας αυτής εκπονήθηκε σε συνεργασία με το πανεπιστήμιο EPFL στη Λωζάννη.

Η πεπερασμένη διαθεσιμότητα πετρελαϊκών πηγών καθώς και η σοβαρή επιβάρυνση του περιβάλλοντος από τις εκπομπές διοξειδίου του άνθρακα, οι οποίες οφείλονται κυρίως στην καύση των ορυκτών καυσίμων, οδήγησαν τις ανεπτυγμένες χώρες στην αναζήτηση νέων εναλλακτικών πηγών ενέργειας. Τα τελευταία χρόνια, ιδιαίτερη μνεία γίνεται στη χρήση βιομάζας για την παραγωγή βιοκαυσίμων και βιοχημικών. Τα κύρια οφέλη που μπορεί να προσδώσει η ευρεία διάδοση τέτοιου είδους τεχνολογιών στη βιομηχανία είναι πρωτίστως η ανανεώσιμη φύση της βιομάζας, καθώς και οι μειωμένες εκπομπές αερίων του θερμοκηπίου κατά την επεξεργασίας της, σε σχέση με τα ορυκτά κλάσματα. Τα κλάσματα βιομάζας που χρησιμοποιούντο αρχικά ως πρώτη ύλη συμπεριελάμβαναν άμυλο, ζάχαρη, λίπη και φυτικά έλαια, το οποίο όμως δημιούργησε μια ανταγωνιστική σχέση μεταξύ της βιομηχανίας των βιοδιυλιστηρίων και της βιομηχανίας τροφίμων. Για το λόγο αυτό ξεκίνησαν να χρησιμοποιούνται πήγες βιομάζας δεύτερης γενιάς, οι οποίες δεν αποτελούν επιλογή για τροφή. Η κύρια κατηγορία της δεύτερης γενιάς και η περισσότερο υποσχόμενη, είναι η βιομάζα λιγνοκυτταρικής βάσης, όπως οι μη βρώσιμες καλλιέργειες, το άχυρο, το καλαμπόκι και το ξύλο. Το κοινό χαρακτηριστικό όλων αυτών των πηγών ενέργειας είναι ότι αποτελούνται από τρία βασικά δομικά χαρακτηριστικά: την κυτταρίνη, την ήμικυτταρίνη και τη λιγνίνη. Η αφθονία τέτοιων πηγών βιομάζας είναι ένας από τους λόγους που προτιμάται η χρησιμοποίηση λιγνοκυτταρίνης ως πρώτη ύλη ενός βιοδιυλιστηρίου Ως βιοδιυληστήριο, ορίζεται μια εργοστασιακή μονάδα παραγωγής η οποία ολοκληρώνει διάφορες διεργασίες μετατροπής της βιομάζας σε βιοκαύσιμα, βιοχημικά προϊόντα και ισχύ.

Το πρώτο πράγμα που πρέπει να καθοριστεί κατά το σχεδιασμό ενός βιοδιυλιστηρίου είναι το είδος και ο τρόπος προεπεξεργασίας της βιομάζας, κάτι που αποτελεί μια ιδιαίτερα κοστοβόρα διαδικασία. Αυτό είναι και ένα από τα βασικά μειονεκτήματα της βιομάζας. Η σύνθεση και η αποθήκευση πρώτων υλών από βιομάζα είναι πιο περίπλοκη από το πετρέλαιο. Επίσης, η πρώτες ύλες της βιομάζας είναι πιο διάσπαρτες από τις πετρελαϊκές. Το γεγονός όμως ότι η αξιοποίηση τέτοιων πηγών ενέργειας μπορεί να βελτιώσει αισθητά την ποιότητα ζωής, απλά μετατρέπει αυτά τα προβλήματα σε προκλήσεις για την επιστημονική κοινότητα.

Στο συγκεκριμένο βιοδιυλιστήριο που σχεδιάστηκε, ως πρώτη ύλη εισάγεται το στάχυ, το οποίο υπόκειται σε μια βιοχημική προεπεξεργασία με τη βοήθεια οξέων, η οποία σχεδιάστηκε από την εταιρεία CIMV στη Γαλλία. Έπειτα, προσδιορίστηκε η κατάλληλη τεχνολογία μετατροπής της βιομάζας ανάλογα με το επιθυμητό προϊόν. Οι τεχνολογίες αυτές χωρίζονται σε δυο μεγάλες κατηγορίες, τις θερμοχημικές (πυρόλυση, αεριοποίηση, κ.ά.) και τις βιοχημικές (ζύμωση, αναερόβια χώνεψη, υδρόλυση, υδρογόνωση). Στο συγκεκριμένο βιοδιυληστήριο θα εφαρμοστεί ένας συνδυασμός των παραπάνω τεχνολογιών.

Στο σχεδιαζόμενο βιοδιυλιστήριο παράγονται διάφορα προϊόντα, κάθε ένα από τα οποία έχει ως πρώτη ύλη ένα από τα τρία βασικά κλάσματα της λιγνοκυτταρικής βιομάζας: τη λιγνίνη, τη γλυκόζη (υδρολυόμενη κυτταρίνη) ή τη ξυλόζη (υδρολυόμενη ημικυτταρίνη). Εφαρμόζοντας στη λιγνίνη ταχεία πυρόλυση, παράγονται φαινολικά ολιγομερή και βιοκάρβουνο, το οποίο μετά από έντονη πυρόλυση με παρουσία οξυγόνου, μετατρέπεται σε ενεργό άνθρακα. Ο ενεργός άνθρακας είναι ιδανικός για το φιλτράρισμα των αποβλήτων και των τοξικών χημικών από επιθυμητά προϊόντα, είτε υγρά είτε αέρια.

Τα προϊόντα που παράγονται χρησιμοποιώντας ως πρώτη ύλη τη γλυκόζη είναι και τα περισσότερα. Το νάιλον-66, ένα χημικό το οποίο διακρίνεται για τη χημική του σταθερότητα, είναι ένα από αυτά. Η γλυκόζη υπόκειται σε ζύμωση και μετατρέπεται σε σακχαρικό οξύ, το οποίο με τη σειρά του υδρογονώνεται σε αδιπικό οξύ, το οποίο τελικά μετά από πολυμερισμό μεταμορφώνεται σε νάιλον-66. Επίσης, παράγονται πολυαμίδια των οποίων η δομή βασίζεται στην αντίδραση συμπύκνωσης μεταξύ μιας αμινομάδας και του φορανδοξυλικού οξέος (2,5-FDCA). Το χημικό αυτό παράγεται μέσω της ζύμωσης της 5-υδρομεξυμεθυλοφουρφουράλης (5-HMF) η οποία δημιουργείται μέσω της αφυδάτωσης της γλυκόζης. Τέτοιου είδους πολυμερή συναντούν πολλές εφαρμογές στη βιομηχανία των πλαστικών. Ένα άλλο βιολογικό πολυαμίδιο που παράγεται σε αυτό το βιοδιυλιστήριο είναι το φουρονικό πολυαιθυλένιο (PEF) μέσω του πολυμερισμού 2,5-FDCA σε συνδυασμό με αιθυλενογλυκόλη, η οποία προκύπτει από υδρογόνωση της γλυκόζης. Το πολυμερές PEF είναι ικανό να αντικαταστήσει επάξια το ευρέως διαδεδομένο πλαστικό PET. Τέλος, ποσότητα ισοσορβίτη παράγεται μέσω καταλυτικής αφυδρογόνωσης της σορβιτόλης, που με τη σειρά της δημιουργήθηκε μέσω υδρογόνωσης της γλυκόζης. Ο ισοσορβίτης που παράχθηκε, εισάγεται ως πρόσθετο στο PEF, κι έτσι δημιουργείται το ενισχυμένο πολυμερές, PEIF.

Τα προϊόντα που παράγονται από τη ξυλόζη είναι σαφώς λιγότερα, αλλά εξίσου χρήσιμα στη βιομηχανία. Για παράδειγμα, το δισοκυανικό διφαινυλομεθάνιο (diisocyanate) παράγεται μέσω μιας καταλυτικής αντίδρασης από το 3,5-διμεθυλισοξαζόλιο (furamine) και μπορεί να χρησιμοποιηθεί για την παραγωγή πολυουρεθανών ελαστομερών. Το διμεθυλισοξαζόλιο δημιουργείται από την αντίδραση αμμονίας με φουρφουράλη, η οποία προκύπτει μέσω της αφυδάτωσης της ξυλόζης. Τέλος, η ξυλιτόλη υπόκειται σε ζύμωση για την παραγωγή 1,2,4-βουτανετριόλης, η οποία νιτροποιείται για την παραγωγή τρινιτρικής 1,2,4-βουτανετριόλης.

Όλες οι παραπάνω διεργασίες μοντελοποιήθηκαν στο Aspen Plus V7.2 λαμβάνοντας υπόψη της ιδιότητες και της θερμικές τους αντοχές, καθώς και τα όρια λειτουργίας των μονάδων που χρησιμοποιήθηκαν για τις αντιδράσεις μεταξύ διαφορετικών χημικών και για τους διαχωρισμούς μιγμάτων. Επίσης, σε όλες τις διεργασίες, η ποσότητα των πρώτων υλών που απέρριπτε το σύστημα, ανακυκλωνόταν στην τροφοδοσία με σκοπό την όσο το δυνατή μεγαλύτερη εξοικονόμηση. Μοντελοποιώντας διεργασίες στο πρόγραμμα αυτό, υπήρξε η δυνατότητα εξαγωγής των ενεργειακών και μαζικών ισοζυγίων για κάθε διεργασία, καθώς και οικονομικών δεδομένων που αφορούν το πάγιο κόστος της κάθε μιας.

Εξίσου σημαντική όμως είναι και η ενεργειακή ολοκλήρωση της κάθε διεργασίας που ακολουθεί μετά τον αρχικό σχεδιασμό της, καθώς με τον τρόπο αυτό εξοικονομούνται τεράστια ποσά ενέργειας. Στη διπλωματική αυτή, έγινε ενεργειακή ολοκλήρωση των διεργασιών του βιοδιυληστηρίου με δύο διαφορετικές προσεγγίσεις.

Αρχικά, χρησιμοποιήθηκε ένα πρόγραμμα γραμμικού προγραμματισμού, το Osmose, το οποίο κατασκευάστηκε στο EPFL σε μια πλατφόρμα του Matblab, και το οποίο τελεί ακόμα υπό βελτίωση. Μέσα από το συγκεκριμένο πρόγραμμα, το κάθε χημικό μονοπάτι της διεργασίας ολοκληρώθηκε ενεργειακά θεωρώντας ότι το σύνολο της ποσότητας των ενδιάμεσων προϊόντων που παράγονται, καταναλώνεται για την παραγωγή των τελικών προϊόντων. Έτσι, διαπιστώθηκαν το μέγεθος των ενεργειακών αναγκών για την παραγωγή του καθενός τελικού προϊόντος ξεχωριστά, σύμφωνα με τις θερμές και ψυχρές παροχές που ορίστηκαν. Εκτός από αυτό, υπολογίστηκε το πιθανό κέρδος που μπορεί να αποφέρει η παραγωγή του κάθε προϊόντος (τελικού πάντα), λαμβάνοντας υπόψη το κόστος των πρώτων υλών και την τιμή των προϊόντων και των παραπροϊόντων που είναι διαθέσιμα προς πώληση στην αγορά. Θεωρήθηκε ότι η εκάστοτε αγορά μπορεί να απορροφήσει όλη την ποσότητα χημικών που παράγεται από το βιοδιυλιστήριο. Διαπιστώθηκε ότι το μόνο επικερδές προϊόν ήταν το νάιλον-66. Τέλος, καταγράφηκε η ενεργειακή εξοικονόμηση για το κάθε ολοκληρωμένο χημικό μονοπάτι.

Η δεύτερη προσέγγιση της ενεργειακής ολοκλήρωσης των διεργασιών του βιοδιυλιστηρίου έγινε κατασκευάζοντας ένα πρόγραμμα στο GAMS με βάση το μοντέλο μεταφόρτωσης (transshipment model) που έχει αναπτυχθεί από τους Papoulias και Grossman και βασίζεται ουσιαστικά στη μέθοδο Linnhoff. Αυτή τη φορά, κάθε διεργασία που περιλαμβάνεται στο βιοδιυλιστήριο ολοκληρώθηκε ενεργειακά ξεχωριστά. Η βασική διαφορά όμως είναι ότι το πρόγραμμα που κατασκευάστηκε επέτρεψε την ενεργειακή ολοκλήρωση της κάθε διεργασίας για πολλούς διαφορετικούς συνδυασμούς θερμών παροχών και τον υπολογισμό του βέλτιστου οικονομικά συνδυασμού. Συγκεκριμένα, τα 3 επίπεδα ατμών υψηλής πίεσης και τα 4 επίπεδα ψυχρών παροχών που επιλέχθηκαν έμειναν σταθερά για όλους τους συνδυασμούς. Τα επίπεδα ατμών που εναλλάσσονταν ανά τριάδες ήταν 6, μέσης και χαμηλής πίεσης. Από όλους αυτούς τους συνδυασμούς, τελικά στη βέλτιστη λύση προέκυψαν τα επίπεδα ατμών στις θερμοκρασίες 160 ℃, 120℃ και 100℃. Η λύση δίνει επίσης το μέγεθος της κάθε παροχής που απαιτείται για κάθε διεργασία. Επιπροσθέτως, το πρόγραμμα στο GAMS έτρεξε και μια φορά μόνο με τη θερμότερη και τη ψυχρότερη θερμή παροχή, έτσι ώστε να κατασκευαστεί το Μεγάλο Σύνθετο Γράφημα για κάθε διεργασία. Πάνω σε κάθε γράφημα φαίνονται τα επίπεδα και το μέγεθος των βέλτιστων παροχών, έτσι όπως ορίστηκαν από το πρόγραμμα. Και σε αυτή την προσέγγιση, υπολογίζεται η ενεργειακή εξοικονόμηση της κάθε διεργασίας, καθώς και το συνολικό ενεργειακό κόστος για την παραγωγή καθενός από τα τελικά προϊόντα.

Τέλος, συμπεραίνεται ότι ενώ το Osmose είναι ένα εύχρηστο και αξιόπιστο εργαλείο, δε δίνει τη δυνατότητα της αυτόματης εύρεσης του πιο οικονομικού συνδυασμού ενεργειακών παροχών. Επίσης, δε λαμβάνει υπόψη του ότι η ενεργειακή ολοκλήρωση του συνόλου ενός χημικού μονοπατιού δεν είναι πάντα εφικτή στην πραγματικότητα. Δηλαδή, το γεγονός ότι ένα προϊόν χρησιμοποιείται για την παραγωγή κάποιου άλλου στο ίδιο βιοδιυλιστήριο, δε σημαίνει ότι βρίσκονται απαραίτητα σε κοντινή τοποθεσία. Η μεταφορά ενέργειας λοιπόν μεταξύ τους θα ήταν τεχνικά και οικονομικά ανέφικτη.

Εν κατακλείδι, προτείνεται η συνέχιση της ενεργειακής ολοκλήρωσης αυτού του βιοδιυλιστηρίου στο πλαίσιο μιας Συνολικής Μονάδας, όπου θα λαμβάνει χώρα εναλλαγή θερμότητας μεταξύ διαφορετικών χημικών μονοπατιών. Κάτι τέτοιο θα επιφέρει ακόμα μεγαλύτερη εξοικονόμηση ενέργειας και συνεπώς χρημάτων.

TABLE OF CONTESTS

ΞΕΝΗ ΟΡΟΛΟΓΙΑ (English terminology translated in Greek)

1,2,4-butanetriol trinitrate	1,2,4 – τρινιτρική βοθτανετριόλη
1,3-diazole	1,3 - διαζόλη
2,5-FDCA	φορανδοξυλικό οξύ
3,5-dimethylisoxazole	3,5 - διμεθυλισοξαζόλιο
5-HMF	5 - υδροξυμεθυλοφοθρφοθράλη
acetic acid	ασετικό οξύ
adipic acid	αδιπικό οξύ
ammonium hydroxide	υδροξείδιο του αμμωνίου
biochar	βιοκάρβουνο
cellulose	κυτταρίνη
dehydration	αφυδάτωση
diphenylmethane diisocyanate	διισοκυανικό διφαινυλομεθάνιο
energy integration	ενεργειακή ολοκλήρωση
fermentation	ζύμωση
glucaric acid	σακχαρικό οξύ
Grand Composite Curve	Μεγάλο Σύνθετο Γράφημα
hemicellulose	ημικυτταρίνη
hexamethylene diamine	εξαμεθυλενοδιαμίνη
hydrogenation	υδρογόνωση
isosorbide	ισοσορβίτης
lignin	λιγνίνη
lignocellulosic biorefinery	βιοδιυλιστήριο λιγνοκυτταρικής βάσης
linear programming	γραμμικός προγραμματισμός
multiplication factor	πολλαπλασιαστής
PEF	φουρονικό πολυαιθυλένιο
PEIF	ενισχυμένο φουρονικό πολυαιθυλένιο
phenolic oligomers	φαινολικά ολιγομερή
pinch analysis	μεθοδολογία του κόμβου ανάσχεσης
pyrolysis	πυρόλυση
refrigeration cycle	κύκλος ψύξης
temperature intervals	θερμοκρασιακά διαστήματα
transshipment model	μοντέλο μεταφόρτωσης

TABLE OF FIGURES

TABLE OF TABLES

1. INTRODUCTION

1.1 General purpose - Incentives for the production of renewables

At the beginning of the century, scientific studies had shown that if the greenhouse gases emissions continue to increase in the same pace, at the end of the century the concentration of carbon dioxide in the atmosphere will be doubled. The European Union has expressed its intention to reduce GHG emissions by 80% in 2050. Global warming has been associated with carbon dioxide emissions (GHG emissions), largely originating from the combustion of fossil fuels. Thus, the negative effect fossil fuels have on the climate and the finite nature of their availability indicated the need of exploiting alternate clean energy sources. As a result, during the last years, an effort is being made in the global industry for today's crude oil-refineries to be gradually replaced by equivalent bio-refineries, which will of course produce equivalent products. Biomass is considered to be the most promising energy source to mitigate the greenhouse emissions. The use of biomass as feedstock offers unique advantages, since it is the only natural source that can provide feedstock both for biofuel production and for the manufacture of chemicals and materials. Conclusively, in the 21st century, the development of the bio-refineries technology has been extremely rapid. In fact, the Ministry of Economic Affairs has defined some very ambitious policy targets for biomass in the long term (2040), namely 30% fossil fuel substitution in the power and transport section and 20-45% fossil-based raw material substitution in the industrial sector. [3,4,7,8,11]

In this thesis project a biorefinery aiming for the production of chemicals will be designed and integrated. During the designing of the biorefinery, the technologies which have to be applied for the manufacturing of the products will be taken into account, as well as the properties of the required chemicals. Subsequently, each process which is included in the biorefinery will be integrated individually, by using two different tools, one developed in EPFL and one developed in NTUA. The energy savings in each case are going to be recorded and the results which are given from each tool are going to be compared. In addition, the most cost-efficient process for a certain final product will be indicated.

The use of biomass as a replacement for petroleum of liquid fuels and industrial organic chemicals would have immediate and far-reaching environmental benefits.

- Firstly, biomass resources are renewable. Most are annually renewable. This means that the carbon exhausted into the atmosphere as carbon dioxide when liquid fuels are burned would be recycled into new plant growth in the following years' crops. This factor alone will greatly improve air quality worldwide, and directly address the issue of global warming as a result of greenhouse gas emissions.
- Secondly, entire biomass resource needs are available domestically for many countries. No imports are needed. In the United States for example, 360 million tons per year of non-fossil carbon raw materials are available to

replace some, if not all, of the demand for petroleum for liquid fuels and industrial organic chemicals.

- Thirdly, the assembly and refining of these resources will create a large number of jobs, primarily in rural areas.
- Fourthly, the production and/or conversion of biomass resources to liquid fuels and organic chemicals involves processing steps that usually reduce the toxic burden associated with the petrochemical production of these products.
- Lastly, the required tonnage of carbon-rich biomass can be derived largely through the recycling of biomass for example. This provides a very economical input for the biorefinery. [11]

1.2 From 1st to 2nd generation biomass feedstock

Initially, the biomass feedstock which was used for the production of biofuels included starch, sugar, fats and vegetable oil. The products deriving from these raw materials were named first generation biofuels, the most popular types of which being biodiesel, vegetable oil, syngas, biogas and bioalcohols. This generation of biofuels has proven to offer some CO2 benefits and help to improve domestic energy security. However, there is one fundamental disadvantage in the production of this kind of biofuels. The feedstock needed for the production of first generation biofuels is also used for the production of food. In June 2011, the World Bank in cooperation with nine other international agencies published a report which advised to cease biofuel subsidies, as the use of food stock for fuel production contributed to the increase of food prices. In addition to that, the most popular type of first generation biofuels, biodiesel, is claimed not to be particularly effective when it comes to the reduction of GHG emissions. [6,8]

Therefore, emerging from the “food or fuel” debate, an alternative way of production of biofuels had to be developed. This led to the development of second generation biofuels, which are produced from cellulose which is a basic component of woody biomass, agricultural residues and wastes. These materials are often associated with lignin, and this is the reason why they are called lignocellulosic biomass, which derives from the non-food available materials from plants. At the moment, the main biofuels included in this category are bioethanol, Fischer-Tropsch diesel (FT-diesel) or BTL (Biomass-to-Liquids), Bio-SNG (Synthetic Natural Gas) and Bio-DME (Dimethyl Ether). Bioethanol is a substitute of gasoline and it is produced through the fermentation of sugars extracted from the lignocellulosic feedstock. BTL, Bio-SNG and Bio-DME can be used instead of diesel, in gasoline vehicles and in diesel vehicles with some moderations respectively. They are produced from syngas which is formulated through the gasification of the lignocellulosic feedstock. For the production of BTL, syngas is transformed into liquid hydrocarbons, for the production of Bio-SNG, syngas is transformed into methane and for the production of Bio-DME, syngas is transformed into DME. [6,7,8]

However, biofuels is not the only category of bio-products which appeals to the world industry. The economy of the industry is depended on a big part on a number of chemicals and products which derive from the oil and natural gas industry. This is indicated by the fact that although only 4% of the crude oil inputs are used for the production of chemicals, it accounts for almost 40% of its profit margins. Again, the finite nature of fossil fuels, the availability of large amounts of biomass and the low cost of the production of bioethanol, suggest that the use of biomass for the production of chemicals holds a lot of potential. In some reports, it was estimated that the world's renewable chemical market is going to reach a level of 76.8 billion US dollars by the year 2017 (Global Industry Analysts 2010). [7]

Another reason for the wide interest invested in the production of renewable chemicals is the mild conditions under which their production is carried out and the much lower impact on human health and environment in comparison to the conventional chemicals. Similar to a petroleum refinery, a biorefinery has to integrate conversion processes with the required equipment to biomass, with the aim of producing high-value low-volume and low-value high-volume products.

According to an NREL (National Renewable Energy Laboratory) and PNNL (Pasific Northwest National Laboratory) study, among the chemicals with the most potential for success are 1,4-succinic, -fumaric and –malic acids, 2,5-furan dicarboxylic acid, levulinic acid, 2-hydroxy proprionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol. [7]

During the last years, third and fourth generation biorefineries have been developed by using as feedstock algae and vegetable oil/biodiesel respectively. However, these kinds of biorefineries are still in the early stage of development. Table-1 sums up the feedstocks which are used for each biorefinery generation accompanied with some examples of products.

Table 1: Classfication of biorefineries based on their generation technologies

Generation	Feedstocks	Examples
First-generation biorefineries	Sugar, starch, vegetable oils, animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second-generation biorefineries	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioalcohols, bio-oil, bio-DMF, Biohydrogen, bio-Fischer-Tropsch diesel
Third-generation biorefineries	Algae	Vegetable oil, biodiesel
Fourth-generation biorefineries	Vegetable oil, biodiesel	Biogasoline

2. 2ND GENERATION BIOREFINERIES

2.1 The Biorefinery Concept

A bio-refinery is described as a facility which integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass. By isolating all the added value from the biomass feedstock in a bio-refinery, the production of waste is reduced significantly, which results in the reduction of the overall environmental impact. By the production of a variety of products, these facilities can exploit the differences in biomass components and intermediates, and maximize the value derived from the biomass feedstock.

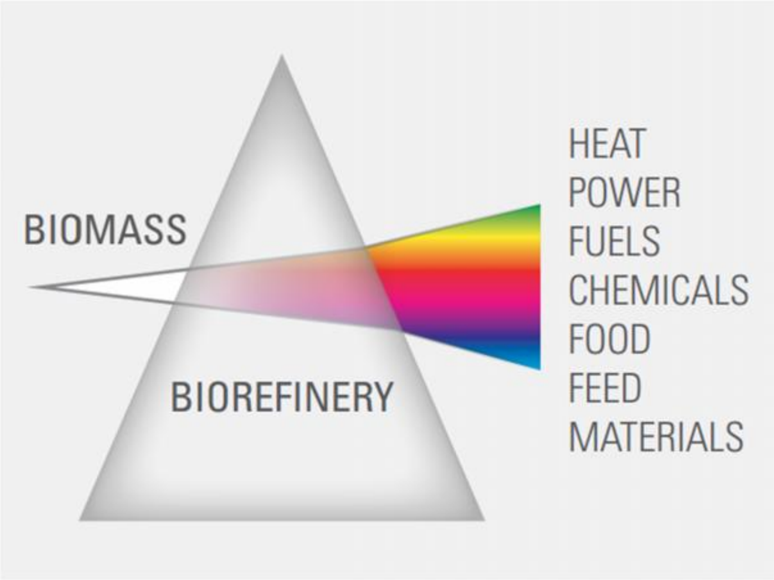


Figure 1: Endless possibilities of the biorefinery concept

Although the transition to a bio-refinery economy would require a huge investment in new infrastructure to produce, store and deliver bio-refinery products to end users, an approach like this is imposed by the current energy policies around the world addressing environmental issues. Such policies include environmentally friendly technologies that increase energy supplies and encourage cleaner, more efficient energy use, as well as air pollution, the greenhouse effect, global warming and climate change. [3]

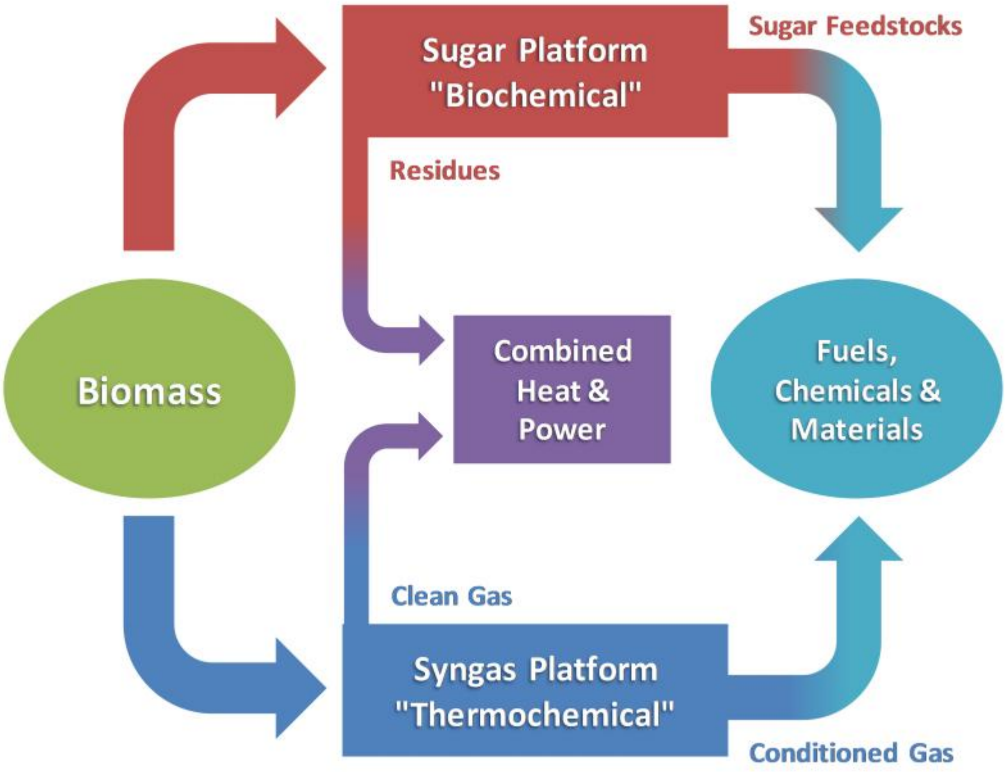


Figure 2: A schematic diagram of the biorefinery concept

As it is shown in figure-1, in a biorefinery, biomass can be processed into plastics, chemicals, fuels, heat and power. Processing technologies are more advanced for chemicals and fuels. The concept of a biorefinery is considered to be a very innovative approach, since it can integrate different technologies to obtain maximum value from biomass feedstocks by producing multiple value-added products. The variety of feedstocks and possible conversion technologies is extremely large. [3]

Table 2: Classification of biorefineries based on their feedstocks

	Feedstocks	Products
Green biorefinery	Grasses and green plants	Ethanol
Cereal biorefinery	Starch crops, sugar crops and grains	Biothanol
Oilseed biorefinery	Oilseed crops and oil plants	Vegetable oil and biodiesels
Forest biorefinery	Forest harvesting residues, barks, sawdust, pulping liquors and fibers	Fuels, energy, chemicals and materials
Lignocellulosic biorefinery	Agricultural wastes, crop residues, urban wood wastes, industrial organic wastes	Lignocellulosic ethanol, bio-oil and gaseous products

Table 3: Classification of biorefineries based on their conversion routes

Biorefinery	Products
Biosyngas-based	Syngas, hydrogen, methanol, dimethyl ether, FT diesel
Pyrolysis-based	Bio-oil, diesel fuel, chemicals, oxygenates, hydrogen
Hydrothermal upgrading-based	C_xH_x, diesel fuel, chemicals
Fermentation-based	Bioethanol
Oil plant-based	Biodiesel, diesel fuel, gasoline

Biorefineries can be classified based on their feedstocks or their conversion routes. Tables 2 and 3 show the different categories of biorefineries according to these two criteria. [3] The different kinds of biomass feedstocks, as well as the various bioconversion technologies which are applied in a biorefinery will be discussed in the following paragraphs.

2.2 Biomass utilization

2.2.1 Types of Biomass

The biomass feedstock of a bio-refinery can include non-fossilized and biodegradable organic material originating from plants, animals and microorganisms. Generally, it includes products, by-products, residues and waste from agriculture, forestry and related industries, but also the non-fossilized and biodegradable organic fractions of industrial and municipal solid waste. Gases and liquids recovered by the decomposition of non-fossilized and biodegradable organic material are also included in this category. Biomass is an energy source which is highly productive, renewable, carbon neutral and easy to store and transport, and thus it has drawn worldwide attention. [3]

There are several types of biomass which can be used for the synthesis of biochemicals. However, the most promising source is the lignocellulosic feedstock. The main reason is that lignocellulosic crops generally have very high GHG efficiency, since they have lower input requirements and the energy yield per hectar is much higher.

The three structural components of biomass are cellulose, hemicellulose and lignin. Their formulas are $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$ and $C_{10}H_{11}O_{0.5}$ respectively. Cellulose is a linear polymer composed of repeating anhydroglucose units, which are bound together with β-(1,4)-glycosidic linkages. Cellulose is hydrolyzed to produce glucose. Hemicelluloses are amorphous polysaccharides, like for example xylans, glucans and galactans. Hemicellulose differentiates with cellulose in the way that it does not contain only glucose units, but also a number of different pentose and hexose monosaccharides. It also tends to be much shorter in length than cellulose. The pentose sugars from hemicellulose are a source of furfural and its derivatives and numerous xylose products. [3,11]

Finally, lignin is a network polymer made up of multi-substituted, methogy, arylpropane and hydroxyphenol units. The resulting thermosetting polymer serves as the glue that holds the strands of cellulose and hemicellulose together in plant fibers to provide structure and strength.

Together, the three polymers make up the largest biologically derived resource on earth, the lignocellulosics. The lignocellulose structure is the basis of the semi-rigid fibers found in all multi-celular plants. The structural difference between a corn stalk, a tree, a flower stem and a piece of waste paper is the difference between the relative amounts of cellulose, hemicellulose and lignin present and the shape and length of the fibers formed by the interwined lignocellulosic chains. The abudance of lignocellulosics is the basis for regarding them as the key input resources for the biorefinery strategy. [3,11]

A lignocellulosic feedstock should grow on marginal land, a land which cannot be used effectively to grow food. The more common lignocellulosic feedstock is the miscanthus, the giant reedgrass, Jatropha and other seed crops, switchgrass, short rotation coppice of willow and poplar, halophytes, rusby or Virginia mallow, and more. But the most beneficial are the crop residues from energy crops like sugar beet, sugar cane, energy cane and sweet sorghum.

Crop residues

Following the harvest of many traditional agricultural crops, like corn and wheat, residues such as stalks, leaves and cobs, referred to as corn stover and wheat straw, are left in the field. Part of these residues can be collected and used as feedstock in a lignocellulosic biorefinery. Corn stover and wheat straw are the main crop residues which are used for energy production. Corn stover has a greater potential than wheat straw, since the later has lower energy content and also fewer tons of wheat straw can be collected per acre than corn stover. [15]

The production of liquid fuels and industrial chemicals from biomass relies mainly on the utilization of lignocellulosic feedstocks. These materials are available, easily assembled and storable in large quantities. In addition, they have the potential to be converted into products which are identical, or functionally equivalent, to current petroleum base liquid fuels and industrial chemicals.

2.2.2 Biochemical pretreatment

Before anything else, the lignocellulosic biomass has to undertake a biochemical pretreatment in order to be decayed into its three structural components: cellulose, hemicellulose and lignin. If this stage is omitted, only the 20% of the theoretical sugar yield of the lignocellulose can be exploited. Biomass materials are solids that include a sizable aqueous component. They also have a richly varied chemical structure. This means that the goal of biomass utilization is, in part, preservation of the intrinsic functional structures while depolymerizing the original material. In general, initial treatment of biomass materials includes steps of drying and physical size reduction. [8,11,12]

There are several different pretreatment techniques (physical or chemical) to separate cellulose from its protective sheath of lignin and increase the surface area of the cellulose crystallite by size reduction and swelling. Many of them have been tested with the aim of settling in the more cost-efficient and harmless for the environment.

1) Physical Pretreatment
    a) Milling and grinding
    b) High-pressure steaming and steam explosion
    c) Extrusion and expansion
    d) High-energy radiation
    e) Pyrolysis
2) Chemical Methods
    a) Alkali treatment (e.g. NH_3, NH_4SO_3, NaOH)
    b) Acid treatment (e.g. H_2SO_4, HCl, H_3PO_4)
    c) Gas treatment (e.g. ClO_2, NO_2, SO_2)
    d) Oxidizing agents (e.g. H_2O_2, O_3)
    e) Cellulose solvents (e.g. Cadoxen, CMCS)
    f) Solvent extraction of lignin (e.g. ethanol-water, benzene-ethanol, ethylene glycol, butanol-water)
    g) Swelling agents
3) Biological methods
    a) Lignin-consuming microorganisms (fungi, e.g. *Phanerochaete chrysosporium*; bacteria, e.g. *Nocardica* sp.)
    b) Cellulose-attacking microorganisms (fungi, e.g. brown rot)
    c) Lignin and cellulose-attacking microorganisms (fyngi, e.g. ehite and red rot)
    d) Lingin and/or cellulose attacking insects (e.g. termites)

Chemical puling methods

Chemical and chemical-thermal pulping processes of lignocelluloses can be divided into two main groups:

1) Processes with lignin and cellolignin as residues
    a) Steam/pressure processes (autohydrolysis)
    b) Hydrolysis with weak acids

    c) Hydrolysis with concentrated acids or water-free acids
2) Processes with cellulose and cellulose/hemicellulose as residues
    a) Alkaline pulping
    b) Sulfate pulping
    c) Sulfite pulping
    d) Organosolv process
    e) Phenol process (Batelle)
    f) Extraction with H_2O (pressure, high temperature)

Thermal and mechanical methods were ruled out as carbon and energy costly (indirect production of CO_2). Chemical techniques on the other hand, raise different obstacles, as the biomass is contaminated by producing biochemical inhibitors as by-products and thus neutralization processes have to be added in the facility, which raise significantly the cost of the biorefinery. Till now, the more advantageous pretreatment method was achieved by the use of microorganisms. One of the main benefits of microorganisms is that they can be activated under mild conditions, and as a result there is no need in spending money in maintaining extreme pressure and temperature conditions. This kind of pretreatment is called biochemical pretreatment and in the contrary to chemical pretreatment, chemical by-products are not produced. [8,11]

2.2.3 Chemistries

A biomass conversion technology for the production of a certain product is considered suitable if it meets the following criteria:

- If the product is a fuel, it has to have a high and positive net energy value. This term expresses the positive balance between the energy in the resulting fuel and the energy used during the process.
- The mass ratio between the amount of the product and the amount of biomass which is used for the production should be above 1.
- The net environmental effect of the overall process should also be positive, or else there would be no point replacing a conventional petroleum product with a product which does not reduce carbon dioxide emissions. [14]

The process chemistries used in the depolymerization of biomass materials and their products are depicted in Fig. 5. These processes include:

2.2.3.1 Thermochemical conversion technologies

The energy that is contained in biomass can be exploited in various ways, such as pyrolysis, gasification or liquefaction. Those methods belong to the category of thermochemical processes.

Pyrolysis

Pyrolysis is the first stage of any thermochemical conversion process and it is applied to convert organic materials into usable synthetic fuels. This process includes the treatment of biomass at moderate temperatures (300 to 600℃) in the absence of oxygen to cause partial depolymerization of the material. The products resulting from this process are a volatile hydrocarbon-rich gas mixture, bio-oil, char and ash. [3,11,14]

$x\ C_6H_{10}O_5 + y\ C_4H_{5.9}O_{3.3} + z\ C_9H_{10}O_2(OCH_3)_r + ASH \rightarrow a\ CH_4 + b\ CH_{1.9}O + c\ C_{(s)} + ASH$ (1)

In the above chemical reaction, the number of moles of each component which are reacted is represented by the variables x, y and z. The number of moles of each component which are produced is represented by the variables a, b and c. The prices in which these variables will correspond each time depend on the composition of the feedstock.

A differentiation in the temperature, the pressure, or the rate of heating in the process can result in a quite different set of products. Slow heating rates tend to favor production of volatile gases (CO, CO_2, hydrogen, methane, ethylene), organic acids and aldehydes, mixed phenols and char. High heating rates tend to minimize liquid production and maximize gas production. [3,11,14]

Pyrolysis is considered to be the most efficient regarding the conversion of biomass and thus the most promising method to compete with non-renewable fossil fuel resources. This estimation is based on the fact that the liquid products which are produced through biomass pyrolysis, such as crude bio-oil or slurry of charcoal of water, outweigh other similar products in a variety of fields like transport, storage, combustion, retrofitting and flexibility in production and marketing. [3]

Gasification

Gasification is a high temperature (>700℃) treatment of biomass in the absence of oxygen but with addition of steam, and possibly CO_2, to maximize the production of synthesis gas (syngas), a mixture of H_2, CO, CO_2 and CH_4. Syngas is the main output of this process. Along with syngas, volatiles and carbon dioxide are produced. The chemical production of the gasification process is shown in equation 2. [3,11,14]

$a\ CH_4 + b\ CH_{1.9}O + c\ C_{(s)} + d\ H_2O_{(g)} \rightarrow [e\ H_2 + f\ CO]_{syngas} + g\ CH_4 + h\ CO_2$ (2)

Syngas has more versatility than the conventional solid biomass. It can be used directly as a fuel for the production of process heat and stream, or as a chemical intermediate in the production of ammonia, methanol, and higher alcohols, organic acids and aldehydes, synthetic gasoline (using Fischer-Tropsch processing) and isobutene. It can also be used in gas turbine to produce electricity. Subsequently, this kind of technology gives the opportunity to the industries to have at their disposal clean fuel gases or synthesis gases. The main and very important use of this technology is the reduction of the investment costs of biomass electricity generation through the use of gas turbine technology. [3,11]

Thermochemical Liquefaction

The biomass feedstock for a liquefaction process is more likely to be in liquid form. Thermochemical liquefaction, or else direct liquefaction, involves pyrolytic processing with addition of H_2, CO, CO_2 and selected catalysts to convert the biomass into hydrocarbons, mixed phenols (from the lignin fraction) and light gases. The key to commercial utilization of liquefaction processing is the separation and recovery of the multiple products created during the liquefaction process. [3,11]

Hydrolytic Liquefaction

On the other hand, during the hydrolytic, or else indirect liquefaction, a variety of catalysts is being used, in order to depolymerize polysaccharides into their component sugars. These aqueous-phase reactions are used to provide basic polymers, for example cellulose and fermentable sugars for further processing, or hexose and/or pentose sugars for chemical conversion into other organic compounds. Some catalysts which are appropriate for the hydrolysis of biomass into smaller fragments, are alkali salts, like sodium carbonate and potassium carbonate, acids, or enzymes. The residue of this process is affected greatly by the amount of lignin that is contained in the feedstock. An increased content in lignin results in the production of increased residue during liquefaction. [3,11]

2.2.3.2 Biochemical conversion processes

Biochemical conversion of biomass involves the use of bacteria, microorganisms and enzymes to breakdown biomass into gaseous or liquid fuels, such as biogas or bioethanol. The most popular biochemical technologies are anaerobic digestion and fermentation. Anaerobic digestion is a series of chemical reactions during which organic material is decomposed through the metabolic pathways of naturally occurring microorganisms in an oxygen depleted environment. Biomass wastes can also yield liquid fuels, such as cellulosic ethanol, which can be used to replace petroleum-based fuels. [35]

Anaerobic Digestion

Anaerobic digestion is the natural biological process which stabilizes organic waste in the absence of air and transforms it into biofertilizer and biogas. Anaerobic digestion is a reliable technology for the treatment of wet, organic waste. Organic waste from various sources is biochemically degraded in highly controlled, oxygen-free conditions circumstances resulting in the production of biogas which can be used to produce both electricity and heat. Almost any organic material can be processed with anaerobic digestion. This includes biodegradable waste materials such as municipal solid waste, animal manure, poultry litter, food wastes, sewage and industrial wastes.

An anaerobic digestion plant produces two outputs, biogas and digestate, both can be further processed or utilized to produce secondary outputs. Biogas can be used for producing electricity and heat, as a natural gas substitute and also a transportation fuel. A combined heat and power plant system (CHP) not only generates power but also produces heat for in-house requirements to maintain desired temperature level in the digester during cold season. In Sweden, the compressed biogas is used as a transportation fuel for cars and buses. Biogas can also be upgraded and used in gas supply networks. [35]

Fermentation

Through the biochemical processing, microorganisms or/and enzymatic reactions are used to convert a fermentable substrate into recoverable products. Hexoses, particularly glucose, are the most frequently used fermentation substrates, but pentoses, glycerol and other hydroxycarbons are also used. Fermentations are the most commonly performed in aqueous solution, with the final products present in modest concentration. [11] Fermentation is also being used extensively in the biorefinery developed in this project. The basic fermentation process involves the conversion of a plant's glucose (or carbohydrate) into an alcohol or acid. Yeast or bacteria are added to the biomass material, which feed on the sugars to produce ethanol (an alcohol) and carbon dioxide. The ethanol is distilled and dehydrated to obtain a higher concentration of alcohol to achieve the required purity for the use as automotive fuel. The solid residue from the fermentation process can be used as cattle-feed and in the case of sugar cane; the bagasse can be used as a fuel for boilers or for subsequent gasification.

Hydrolysis

During the hydrolysis of lignocellulosic biomass enzymes (or other catalysts) enable the sugars within cellulose and hemicellulose in the pretreated material to be separated and released in order to be converted to several chemicals. The process converting the biomass biopolymers to fermentable sugars is called hydrolysis. There are two major categories of methods employed. The first and older method uses acids as catalysts, while the second uses enzymes called cellulases. Feedstock pretreatment has been recognized as a necessary upstream process to remove lignin and enhance the porosity of the lignocellulosic materials prior to the enzymatic process. A new generation of enzymes and enzyme production technologies are needed to cost-effectively hydrolyze the cellulose and hemicellulose in biomass to free the sugars for conversion. An effort is being made to identify the most productive, naturally occurring enzymes and then use a variety of techniques to increase their efficiency. Research objectives also include lowering the cost of the enzyme unit operation in the sugar extraction process (saccharification). [37]

Hydrogenation

The catalytic hydrogenation of the dehydration sugars products (C5 and C6) is mainly interesting because reaction products as 2-methylfuran, furfuryl alcohol (C5), 2,5-bis(hydroxymethyl)tetrahydrofuran and 2,5 dimethylfuran are very useful for industrial applications such as polymer synthesis, solvents and production of petroleum. Most of the catalytic systems reported in the literature for these conversions are heterogeneous catalysts, only one nanoheterogeneous system in liquid phase has been reported for the hydrogenation of biomass-derived compounds. Indeed, colloids can give very interesting results in terms of activity and selectivity under mild reaction conditions in organic and aqueous solvents [38].

3. PROBLEM DESCRIPTION

3.1 Chemical Synthesis by Lignocellulosic Feedstock

Cellulose recovered from a lignocellulosic matrix using hydrolytic liquefaction can be treated with several reagents to make materials such as cellulose acetate, nitrocellulose and rayon. Xylose from hydrolytic depolymerization of hemicellulose can be further reacted in the same process to make furfural. Furfural is the starting point for a large family of derivative chemical and polymer products. For example, the adipic acid and the hexamethylene diamine used in the original synthesis of Nylon-6,6 were made by acid hydrolytic depolymerization of hemicellulose from oat hulls, followed by chemical synthesis of the monomers and condensation polymerization to form Nylon-6,6. [11]

There are several possible ways of using lignocellulosic biomass for production of fuels and chemicals. Because the initial production steps involve solid materials, preparation and handling of the raw materials is more complicated and costly than using petroleum liquids. Also, biomass materials are more disperse and less dense than petroleum. This means that assembly and storage of the raw materials is more complicated than for petroleum.

Finally, some of the biomass resources, notably crops and crop residues, are cyclical in production. This means that storage and integration with other resources are necessary in the design and management of a biorefinery complex.

However, these disadvantages are outweighed by the environmental benefits of the lignocellulosic biorefineries and the abundance of their feedstock.

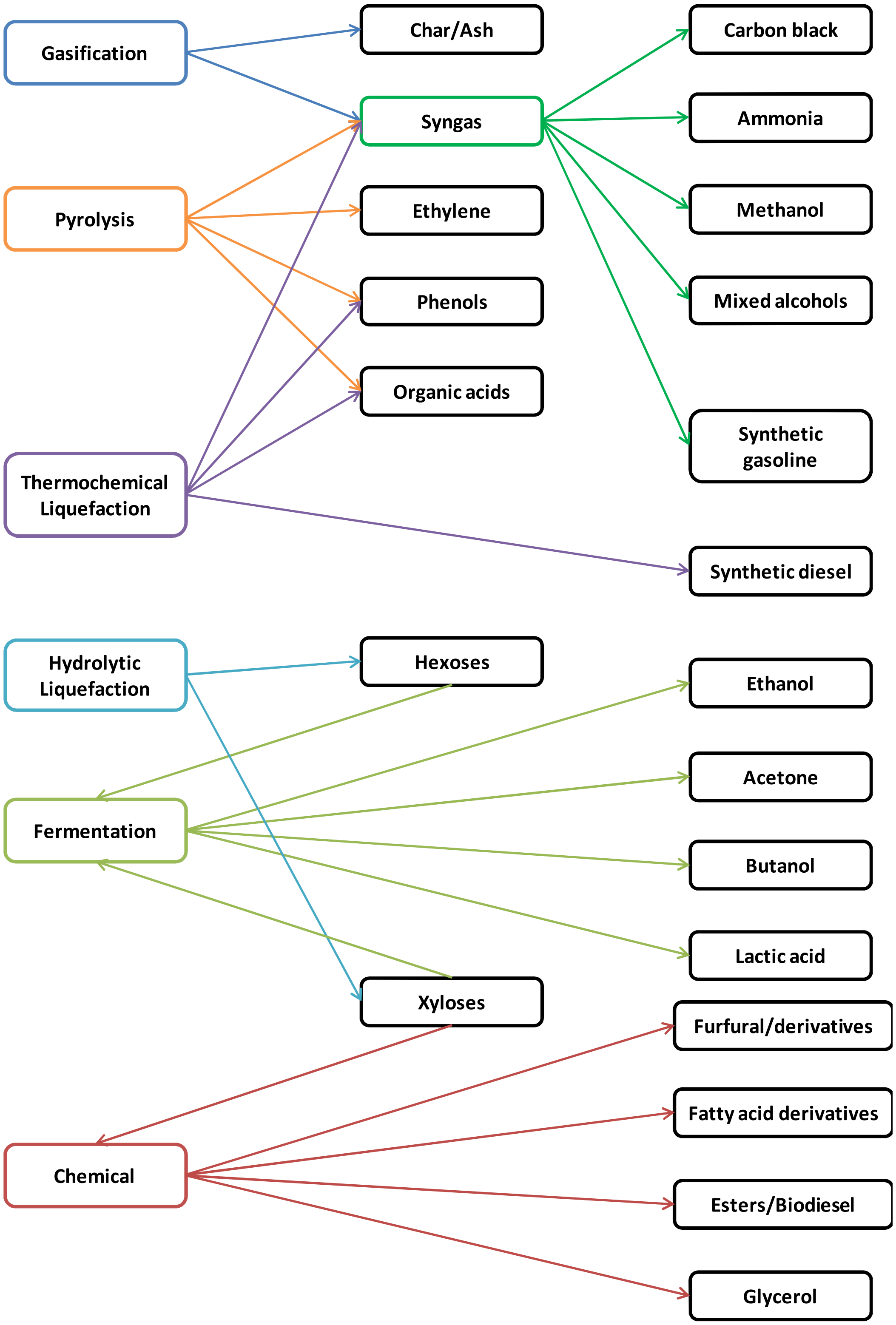


Figure 3: Biomass-derived industrial organic chemicalsMultiplicity and complexity

The lignocellulosic biorefinery which is going to be designed and integrated in this thesis includes a lot of different chemical paths for the production of many different biochemicals. Thus, the problem concerning the integration of this industrial plant is characterized by high multiplicity and complexity.

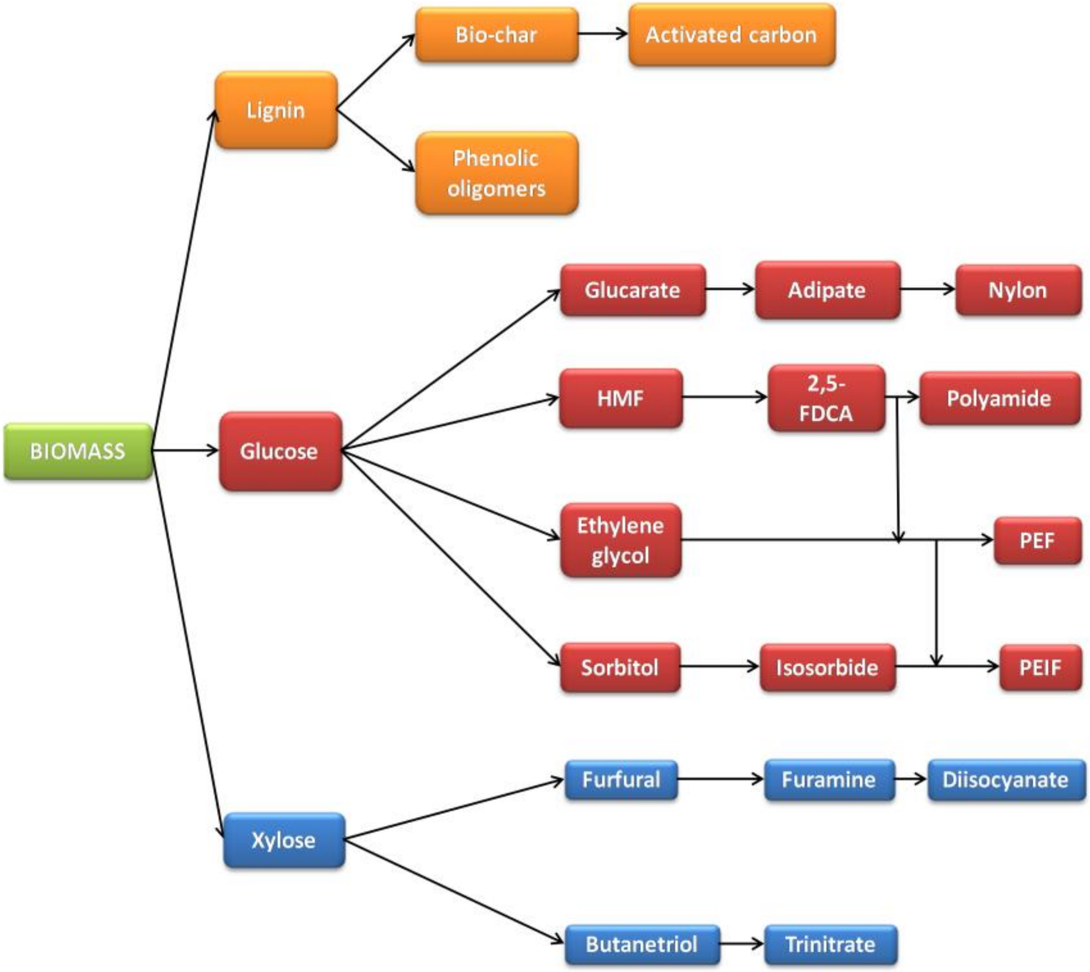


Figure 4: A schematic graph of the chemical paths of the biorefinery

The competitive paths of the biorefinery are shown in Figure 3. (Biocore,2014)

During the design and integration of the above biorefinery, a lot of different aspects have to be taken into consideration, and a huge number of decisions have to be made, the most basic of which are:

- The kind of biomass feedstock which is going to be used.

- The biochemical pretreatment method for the disintegration of the biomass feedstock.
- Decide which bioconversion processes are going to be applied in the plant, according to the desired products.
- Gather the essential information on in order to simulate the overall process in an industrial scale with the aid of a suitable software.
- Use the energy and economic data extracted from the process design models for advanced process integration of the biorefinery to minimize process energy demand.
- Study the cost-efficiency of each product, according to energy consumption.

It is easily conducted that different chemistries will have to be integrated in this biorefinery, thus it is very important to have gathered reliable information regarding the bioconversion processes that concern the production of each product. The main chemistries which are being applied in this certain biorefinery are pyrolysis, fermentation, hydrolysis, dehydration, hydrogenation, amination and of course polymerization.

The synthesis of a biorefinery is a big challenge and thus reliable data of integrated and optimally designed flowsheets are needed. Having defined the chemical paths of the biorefinery, it is important to make sure that the chemical reactions which take place in each step are feasible. Then, by developing each conversion in a continuous process, the economic feasibility of these chemical paths is verified.

It is obvious that the analysis of a biorefinery cannot be focused only in one analysis stage. A deep analysis and examination of the biorefinery paths proposes a multi-stage analysis which offers significant results for the evaluation of the biorefinery chemical paths. The main analysis stages are three: flowsheeting, energy integration and economic evaluation.

Given a big set of bio- and thermo- chemical paths, there is the need to develop and re-engineer the reaction-separation systems targeting to high purity high value added products. For a sustainable solution, low operating and energy costs have to be secured. In this scope, integration should be applied in any case to build energy efficiencies and detect potentials for energy synergies. Economic analysis data are also needed to evaluate profitability margins and secure economic feasibility paths.

3.2 Process Systems Engineering (PSE) Tools

As it has already been mentioned, it is not only about finding the most appropriate and efficient technology that will be applied for the production of a certain product, it is also about making the biorefinery cost-effective. This can mainly be achieved by minimizing the capital operating and energy cost of the facility. The concept of an integrated biorefinery, which consists of many different biomass conversion technologies, serves exactly this purpose: the improvement of the overall efficiency of the system. The significance of Process Systems Engineering (PSE) tools for the optimal design of processes is extremely important. Some of the most basic tools included in this package are market analysis, techno-economic study, cost accounting, pinch analysis, life cycle assessment (LCA) and supply chain (SC) analysis. [9,10] All these stages of analysis can be combined to make a multi-stage analysis and evaluate the best paths among competitive paths. In this assignment, this is going to be achieved by integrating the biorefinery, using the pinch analysis method, and by minimizing its operational and energy cost.

4. METHODOLOGY

The main goal of this project is to optimize the operation of the "candidate" processes and create a very good and thermodynamically based database of optimum biorefinery processes. When a synthesis like this, which includes completed flowsheets, mass and energy balances and economic data, has been built according to reliable data and careful calculations, it is safe to continue synthesizing a sustainable, integrated and even high profitable biorefinery. The multi-stage analysis which is being applied in this project to synthesize a sustainable, integrated and even high profitable biorefinery, incorporates flowsheeting, energy integration and economic analysis and is presented in this chapter.

4.1 Process Flowsheeting

The process modeling of each chemical path of a biorefinery in an industrial scale is a fundamental step in the design of an integrated biorefinery. Thus, the use of a simulation tool which gives accurate and reliable results is extremely important. Process simulation enables many different operating situations to be observed with minimal outlay, allowing the equipment and plant to be designed to be safe and efficient from the start.

In addition, simulation programs can also be used to optimize operating parameters for existing plants. In this way industries are very often able to lower their operating costs without the need for time-consuming and costly experiments on their production facility. [19]

The software which covers the needs of the designer in a satisfactory way is "Aspen Plus". In this thesis the version "Aspen Plus V7.2" is going to be used for the process modeling of this lignocellulosic biorefinery.

Aspen Plus solves the critical engineering and operating problems which arise throughout the lifecycle of a chemical process, such as designing a new process, troubleshooting a process unit or optimizing operations of a full process. The process simulation capabilities of Aspen Plus enables engineers to predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, they can simulate actual plant behavior. [19]

In order for a certain process to be developed, reactions and knowledge from practitioners and experimental groups have to be taken into consideration. The major European research project named Biocore, provided all the information needed to simulate in an industrial scale the biorefinery shown in figure 4. This information included the following:

- The chemical paths of the lignocellulosic biorefinery.
- The biomass feedstock which is being used.
- The biochemical pretreatment of the biomass.
- The biochemical conversion technologies that were applied in the biorefinery.
- The reactions and the auxiliaries needed for the production of the intermediates final products.

When simulating a process in a flowsheet, the route which will be followed to separate the products, by-products and waste from each other is equally important with the one which will be followed for the creation of the product in the first place. This means, that special attention has to be paid in the downstream process to secure high quality of high value added end products. There are numerous ways to separate the desired product from the rest chemicals, like evaporators, flash units or distillation columns.

During the flowsheeting of a process, it is important to define realistic and plausible circumstances under which a separation or a distillation of certain components takes place. Of course, extreme temperatures of pressures should be avoided as much as possible, as these results not only in high energy cost but also in much higher equipment cost. Another important factor which should be taken into consideration when a distillation column is designed is the temperatures of the streams exiting the column. The temperature of each stream should not allow any of its components to be disintegrated or transformed.

When the goal of separating the desirable product from the by-products, the waste and the remained resources has been achieved, there is one more important step before it can safely be said that the simulation procedure has been completed. This includes the recovery of the resources which have not reacted or the auxiliaries which were used to help the reaction, like the catalysts. If those streams are recycled back to the feed, the amount of money which will be saved is quite important, as the industry will have to buy a significantly lower amount of resources in order to satisfy its needs.

4.2 Energy Integration

The theory of the energy integration of a process started to develop in the late 70s and is now a well-established methodology in the field of the world industry. Linhhoff is the one who developed the Pinch Analysis method, by which the energy used in process industries is minimized. In other words, energy is being recovered and minimum energy cost is being secured. Through the integration of a designed process, a sustainable use of the resources and the energy can be indicated by redefining the industrial unit. During this procedure, more energy efficiency opportunities come to surface, which can be applied in a way that a chemical industry can be sustainable and productive.

The main purpose is to calculate the energy savings and figure out the most cost-effective process in the biorefinery designed above. Our main concern in this thesis is the cost of the energy used in the plant and the potential reduction of it through the energy integration of the processes.

Additionally, an effort was made to model this problem in a computer code. In this way the selection of the best and most economic combination of utilities is possible.

4.2.1 Defining the problem

In order to integrate each chemical path resulting in a final product, the osmose tool by EPFL is being used, which is based on the basic methodology of pinch analysis. In addition, a transshipment model of linear programming is being used for the calculation of the minimum utility needs of each process. This model was first formulated from Papoulias and Grossman (1983) and it is actually the basic heat cascade idea of Linnhoff translated in a linear mathematical formulation, as an optimization problem, in order to minimize the energy cost. [31] The results extracted from this model are being compared with the energy results extracted from osmose. The data regarding the energy cost of the utilities are used along with the rest economic data of the processes (investment, operating costs) to define which the most cost-effective process is.

Both methods constitute a linear programming problem, which in the first case is going to be solved on a Matlab platform called Lua, and in the second case by building the model in the GAMS program (General Algebraic Modeling System), in order for the problem to be automated.

During the initial designing of a biorefinery a lot of crucial decisions have to be taken, but the most important one is the choice of which products are going to be produced, but also the processes through which this will happen. In the case of the biorefinery which has been designed in this thesis the intermediate products have the potential to be modified into a lot of different final products. Thus it is important to define which intermediate products and in which amounts are going to be used for the production of the final products.

4.2.2 Modeling of a linear programming problem

Every problem which can be adjusted in a linear programming formula has the following elements:

- the variables of the problem,
- the objective function that needs to be optimized,
- the constraints which have to be met in for a reliable solution of the problem,
- the parameters of the problem.

The variables of a problem are the elements which can be affected by the user. The aim is actually to define the best possible prices for these variables. This is way they are also called decision or control variables. In linear programming variables are always continuous and non-negative.

The objective function is the criteria according to which the best prices of the variables are defined. Each one takes a price in order for the objective function to be maximized or minimized.

The constraints are linear relationships between the variables. They define the range of the possible solutions.

The parameters are the data which are used as input in the problem. They are real number which have the role of a factor of a variable in the objective faction or in the constraints.

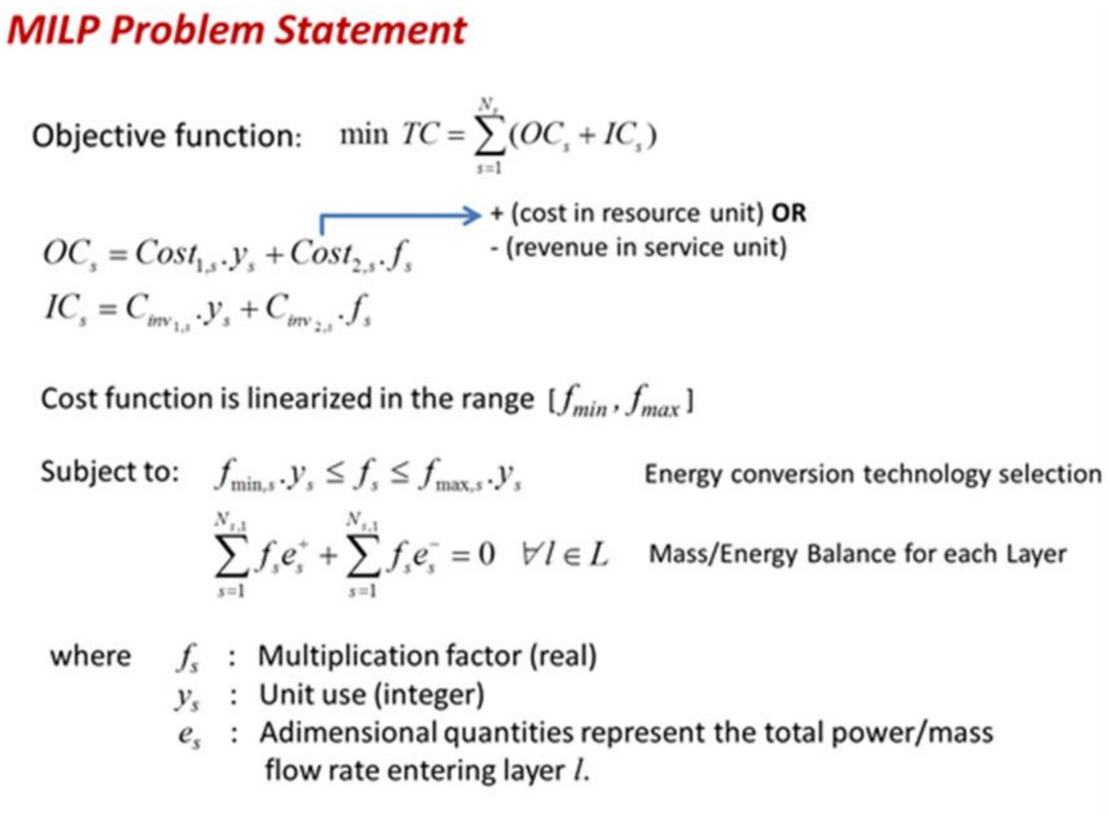
4.2.3 OSMOSE Tool

Before making any computation regarding for example the optimization or the sensitivity analysis on an energy system, it is necessary to model it. However, in many cases, several softwares (some professional and some not) have to be used, what induces a lot of data transfer. An efficient and useful tool for the energy integration and the estimation of the cost of each process in a biorefinery was created in the “Industrial Energy Systems Laboratory”, in the Mechanical Engineering Department, in EPFL and was used for the purpose of this thesis. It is called OSMOSE and was developed in a Matlab platform called Lua.

The main purpose of OSMOSE tool is to manage in only one tool two basic steps for the design of a process:

1. The modelization (Representation of an existing system)
2. The Computation (Calculations performed on the model)

OSMOSE was first developed in the context of Bolliger's work [32] and is now the result of the ongoing research carried out by the Industrial Process & Energy Systems Engineering (IPESE) group. Inside OSMOSE, energy integration is performed. The techniques inside, allow to qualify an energy system with regard to the minimal energy requirement. It also computes the units that are needed to satisfy the heating and cooling demands of the process (e.g. boiler or cooling unit). Once the energy integration has been performed, the system can be considered as being defined. However, it may be interesting to define some values reflecting the performances of the system. It is possible to program any function that computes the energy efficiency, the costs or the environmental impacts [32].



MILP Problem Statement

Objective function: $\min \ TC = \sum_{s=1}^{N_s} (OC_s + IC_s)$

$OC_s = Cost_{1,s} \cdot y_s + Cost_{2,s} \cdot f_s$

+ (cost in resource unit) **OR**
- (revenue in service unit)

$IC_s = C_{inv_{1,s}} \cdot y_s + C_{inv_{2,s}} \cdot f_s$

Cost function is linearized in the range $[f_{min}, f_{max}]$

Subject to: $f_{\min,s} \cdot y_s \le f_s \le f_{\max,s} \cdot y_s$ Energy conversion technology selection

$\sum_{s=1}^{N_{s,l}} f_s e_s^+ + \sum_{s=1}^{N_{s,l}} f_s e_s^- = 0 \quad \forall l \in L$ Mass/Energy Balance for each Layer

where f_s : Multiplication factor (real)
y_s : Unit use (integer)
e_s : Adimensional quantities represent the total power/mass flow rate entering layer l.

However, the same energy demands can be covered through different combinations of steam pressures. The osmose tool does not yet allow the optimization of the combination of utilities which can be applied in each process according to their cost. The user can only define as input the number of the hot and cold utilities which he prefers to use along with their prices. When the model runs, it presents the minimum size of these utilities which is needed for the process along with the final energy cost. This means it is extremely time consuming to try a big number of different combinations and to compare the cost of each combination utility. A more efficient way to define the cheapest combination of utilities is developed in the Transshipment model, the methodology of which is analyzed in the following paragraphs.

4.2.4 Transshipment Model

In this chapter, the model which has been proposed by Papoulias and Grossman will be analyzed. [39] According to this model, the heat capacity is transferred from the sources (hot streams) to the sinks (cold streams). In order to be thermodynamically sure that there can be a heat exchange between streams, this exchange takes place through intermediate stations.

Temperature Intervals

The intermediate stations of the transshipment model represent the temperature intervals in which the heat transfer between streams is applicable. In order for these streams to be defined, firstly the hot and the cold streams of the process have to be moved $–DT_{min}/2$ and $+DT_{min}/2$ respectively. As DT_{min}, we define the minimum temperature difference in which it is assumed that heat transfer is feasible. DT_{min} depends on the equipment which is used. With this shift of the streams it is ensured that the minimum temperature difference will be respected even if heat transfer between streams of the same shifted inlet and outlet temperature respectively occurs. After the temperatures are shifted, the temperature intervals can be defined based on the inlet temperatures of the process streams, the maximum and the minimum inlet or outlet temperature streams, and the inlet temperatures of the additional utilities, if they are between the range of the maximum and minimum temperature of the process streams.

Analysis of the transshipment model

The transshipment model for predicting the minimum utility cost given an arbitrary number of hot and cold utilities can be formulated as follows. First, it is considered that there are *k* temperature intervals which are based on the inlet temperatures of the process steams, highest and lowest steam temperatures, and of the intermediate utilities whose inlet temperatures fall within the range of the temperatures of the process steams. It is assumed that the intervals are numbered from the top to the bottom. The schematic approach of the model is presented in figure 5.

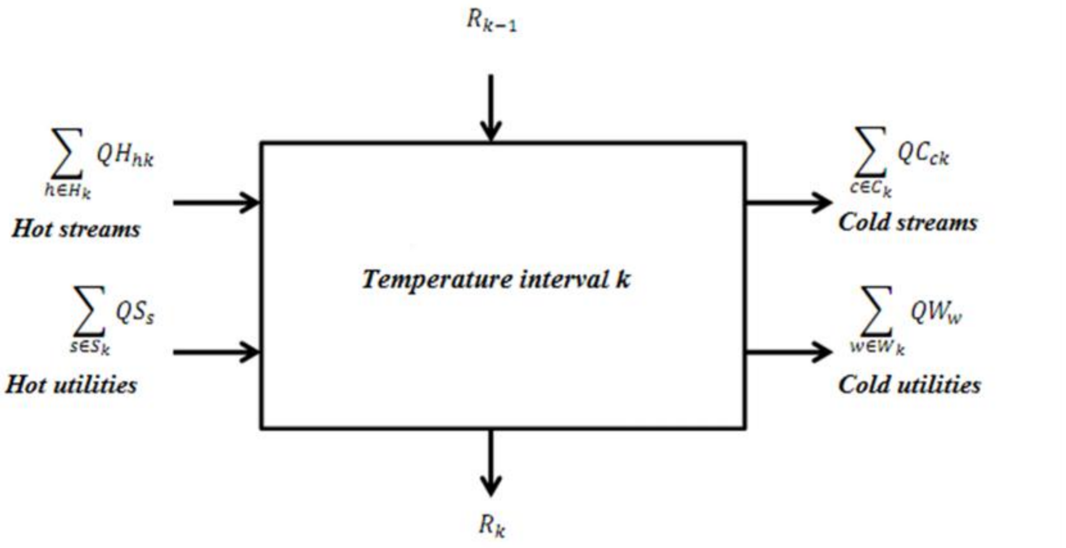


Figure 5: Heat flows in interval k

A process is assumed with H hot streams and C cold streams in which S hot utilities (i.e. steams) and W cold utilities (i.e. fresh water) can be used. Then, the following groups can be defined:

H_k = {h | *hot stream h which provides heat in temperature interval k*}
C_k = {c | *cold stream c which provides heat in temperature interval k*}
S_k = {s | *hot utility s which provides heat in temperature interval k*}
W_k = {w | *cold utility w which removes heat in temperature interval k*}

Afterwards, the heat supply of the hot streams and the heat demand of the cold streams in every temperature interval are calculated. This calculation is depended on the shifted inlet and outlet temperatures of the streams, as well as the heat capacities in combination with the temperatures which define the limits of the temperature interval.

After these calculations, the known parameters of the problem are:

QH_{hk} : heat supply of hot stream h in temperature interval *k*
QC_{ck} : heat demand of cold stream c in temperature interval *k*
CS_s : unit cost of hot utility *s*
CW_w : unit cost of cold utility *w*

and the variables of the problem are:

QS_s : heat supplied by hot utility *s*
QW_w : heat removed by cold utility *s*
R_k : heat residual exiting temperature interval k

The model is described by the following equations:

$$\min Z = \sum_{s} CS_s QS_s + \sum_{w} CW_w QW_w$$

s.t.

$$R_k - R_{k-1} - \sum_{s \in S_k} QS_s + \sum_{w \in W_k} QW_w = \sum_{h \in H_k} QH_{hk} - \sum_{c \in C_k} QC_{ck}$$

where k =1,2, … , K

$QS_s \geq 0, QW_v \geq 0, R_k \geq 0$ where k = 1, … , K -1

$R_0 = 0, R_k = 0$

The above objective function represents the total utility cost and aims in the minimizing of this cost, while the equation below represents the heat balance around each temperature interval k. This goal is achieved by maximizing the heat exchange between the streams of the process, always in the boundaries imposed by the restrictions and by using the utilities with the smallest cost where possible.

The full model written in GAMS can be found in Appendix B.

4.3 Economic evaluation

The calculation of the investment and operating cost of each process is a fundamental step in order to proceed to the analysis which is going to be made in this thesis. The investment cost is calculated with the help of the Economic Evaluation add-in of Aspen Plus V7.2. Aspen Plus V7.2 can also estimate the investment and operating cost of the designed facility depended on default and simulator data. This tool contains built-in engineering and cost content to produce comprehensive and accurate conceptual estimates. It enables the designer to rapidly and confidently evaluate capital investment projects early in the design process, understand the economic implications of engineering decisions and effectively manage the project. [20] The Aspen Economic Evaluation will be used for the estimation of the investment and operating cost of each process of the lignocellulosic biorefinery. The investment cost which is calculated is mainly depended on the type and the capacity of the unit. The calculation of the operating cost is not interely accurate, but it can give us a sense of the magnitude of its value.

5 THE REAL LIFE BIOREFINERY

5.1 Introduction

Biocore provided the technology regarding the production of each of these chemicals. In this information were included the chemical reactions and the conditions in which they needed to take place (temperature and pressure), as well as the solvents and the catalysts that were essential for the activation of the reactions. The patented CIMV organosolv process which was simulated in Aspen Plus V7.2 was also provided, according to which the biomass feed (wheat straw) was fractioned in lignin, glucose and xylose. The production of each one of the products and intermediates that derive from those three fractions of biomass will be simulated in Aspen V7.2 in separate flowsheets. In the following section, the technology and the logic behind the design of each chemical path will be developed.

5.2 Value Chain Paths

As it was mentioned before, bio-based materials require pretreatment by chemical, physical or biological means to open up the structure of biomass. A very effective technology regarding the biomass fractionation has been developed by the French company CIMV (Compagnie Industrielle de Materiére Végétale). This patented organosolv technology is owned and has been used by the Biocore project, in order to extract biomass in the three main components, that being cellulose, hemicellulose and lignin. This biochemical pretreatment technology is being used in this biorefinery, too. In that way, biomass can be used most efficiently. In addition, the CIMV process can use as feedstock not only cereal by-products, but as well as forestry residues or short rotation woody crops. [4]

The content of cellulose in any type of biomass, rarely exceeds 50%. In order for the process to be much more effective, the other main components of biomass (hemicellulose and lignin) have to be extracted too. The CIMV organosolv technology solves this problem. It is basically a pulping technique that uses an organic solvent to solubilize lignin and hemicellulose. The main advantages of this technology are two:

- The first one, is the ability that is given to the designer to obtain relatively high quality lignin adds value to process stream, otherwise considered as waste.
- Secondly, organosolv solvents can be easily recovered by distillation, leading to less water pollution and elimination of the odor that is usually produced by other respective methods.

CIMV in France has developed a process in which wheat straw is treated with acetic acid (30%), formic acid (55%) and water (15%) for 3,5 hours at 105 °C under atmospheric pressure. The fibres that are obtained are screened and bleached. In these conditions, the lignin is dissolved and the hemicelluloses are hydrolysed to mono and oligo saccharides. Organic acids are collected by concentration of the cooking liquor and then lignin is precipated by adding water and high pressure flitration. [4]

Biocore optimized the extraction of cellulose, hemicellulose and lignin by improving the CIMV organosolv process through process design and integration. This resulted in a 90% exploitation of the biomass. The biomass feed that was used initially in CIMV is wheat straw, but there were also used other types of feeds, such as rice straw, hardwood and short rotation coppice poplar. However, to use a different feed effectively, certain modifications were required to be made in the organosolv process. [4]

In this lignocellulosic biorefinery, wheat straw will be used as feedstock. The basic inputs and the outputs of the CIMV process are indicated in the following figure.

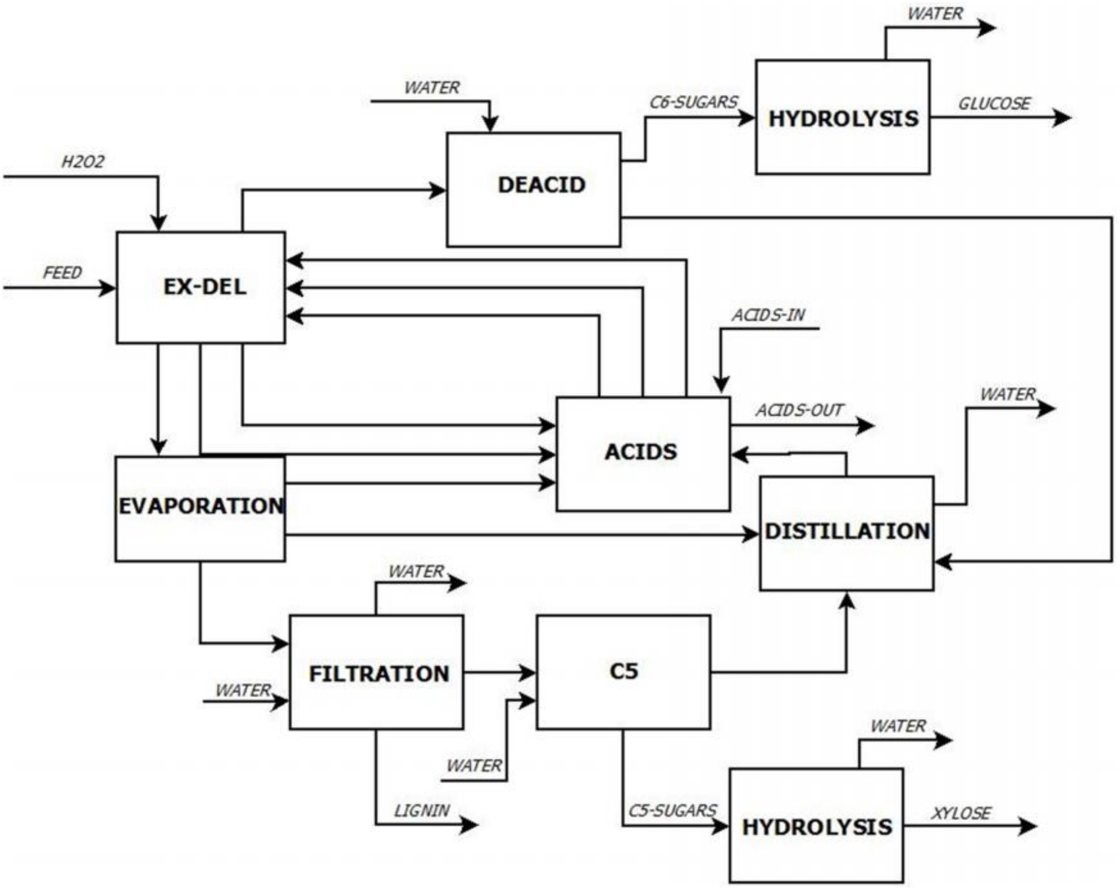


Figure 6: Graphic figure of the CIMV process along with the C5- and C6-Hydrolysis

The energy and the mass balances in this process where extracted from Aspen Plus V7.2, along with an estimation of the investment and operating cost of the process. These data are shown in Appendix A, in the tables 53 and 54. The respective data of the C5 and C6 hydrolysis are presented in tables 55 and 56.

In the biorefinery which has been designed for the purpose of this thesis a big number of different bio-chemicals is being produced. In figure 6 the capacities of each intermediate and final product of the biorefinery are being presented. All intermediate and final products have above 99% purity, so it is safe to make the assumption that the intermediate product which is used as input in the next process is pure.

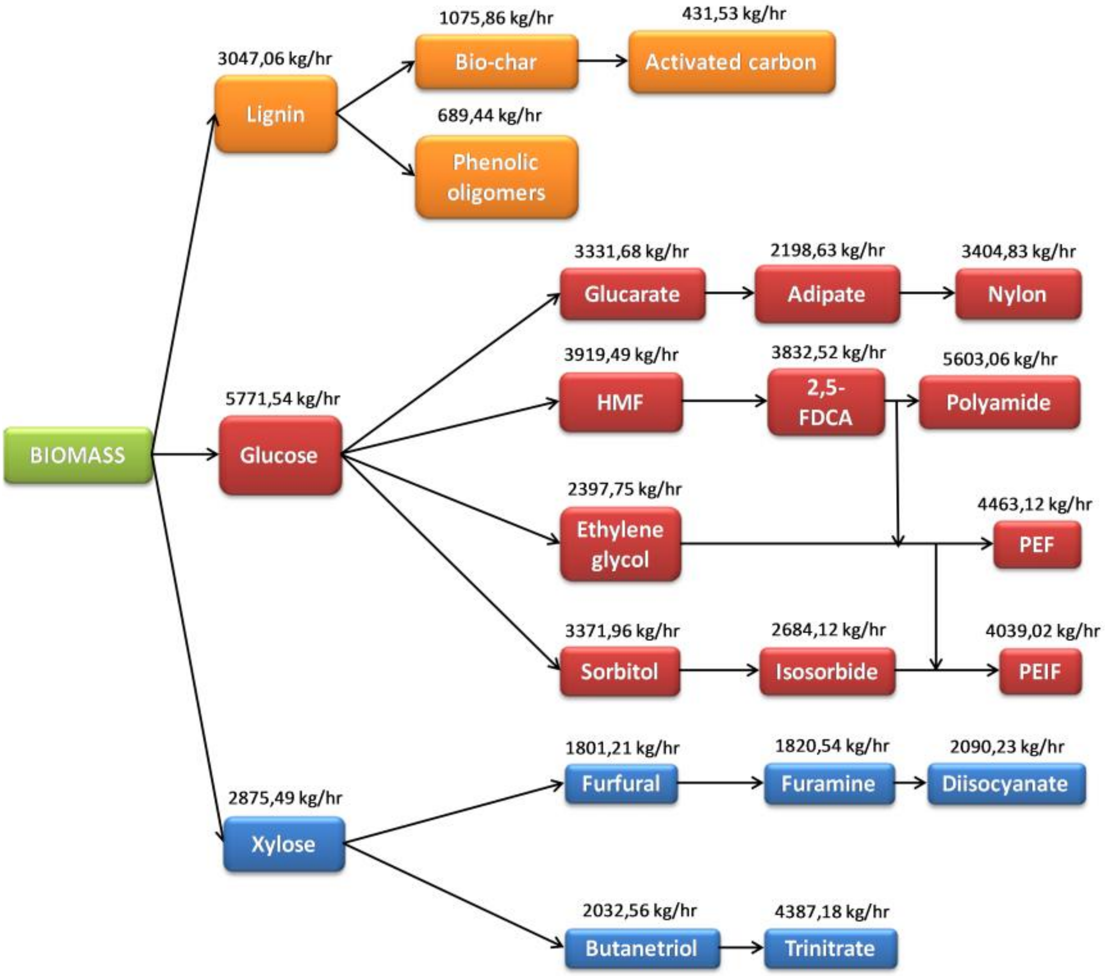


Figure 7: Chemical paths of the biorefinery along with the capacities of intermediates and final products

Lignin Products

In this industrial plant lignin is converted in activated carbon and phenolic oligomers. Despite the fact that along with them, phenolic monomers are also produced, the product which is of more interest at the time are phenolic oligomers. Although phenolic monomers are valued chemicals for commodity products and precursors of biofuels, phenolic oligomers found in bio-oil are non-volatile, viscous and highly reactive, thus it is more difficult for them to be converted into useful products. In addition, the yield of phenolic monomers is usually close to 10wt%, whereas phenolic oligomers constitute the majority of lignin derivatives (~30 wt%). [21] For this reason, an effort is being made to find more effective ways to exploit phenolic oligomers.

Activated carbon from bio-char is also been produced. Bio-char is a fine-grained charcoal high in organic carbon and largely resistant to decomposition. It has the ability to reverse soil degradation and create sustainable food and fuel production in areas with severely depleted soils, scarce organic resources, and inadequate water and chemical fertilizer supplies. [22] When carbon is oxidized (activated), it becomes susceptible to absorption, the process of surface bonding for chemicals. This characteristic is the main reason for the popularity of activated carbon, as it is ideal for filtering waste and toxic chemicals out of liquids or gases. [23]

Cellulose Products

Glucose is being used as a resource for the production of the most products in this biorefinery. It is obvious from figure 4, that during the production of the final products deriving from glucose, there are also certain intermediates that are being produced.

The production of glucaric (saccharic) acid and adipic acid are the intermediate steps for the production of the final product, nylon-66. Nylon-66 is a very desirable product, as it is chemically extremely stable. It is resistant to weak acid and is only decomposed by strong mineral acid. Nylon-66 also has a good biological resistance. Apart from its use in carpeting, clothing and tire cord, it is widely used in bearings and gears due to its good abrasion resistance and self-lubricating properties.

Another significant path of glucose modification is the production of FDCA-based polyamides. 2,5-FDCA which is produced by 5-hydroxymethylfurfural (5,-HMF) is considered to be a very promising chemical, as it is the source of useful FDCA-based polyamides through a condensation reaction between an amino group and a carboxylic acid group, like occurring in FDCA. FDCA-based polyamides have a lot of applications in today’s industry. Carpets, textiles, engineering plastics for automotive production and electronic applications, are only some indications of the huge potential of this kind of polyamides. [25]

There is also another way to produce bio-based polyamide and specifically polyethylene furanoate (PEF) by polymerizing ethylene glycol and 2,5-FDCA. PEF is ia a very promising replacement of PET which is used for manufacturing plastic bottles and containers. It is evident, that the greater the share of the market covered by this product, instead of the respective oil-based, the better for the environment. Till now, major international companies, like Coca-Cola, have implemented PEF as a resource in their production line.

The final route of conversion of glucose in this biorefinery includes the production of isosorbide through sorbitol, in order for isosorbide to be added in PEF. The new resulting and enhanced polymer is called PEIF [Poly(ethylene isosorbide 2,5-furandicarboxylate)]. The use of bio-based isosorbide as a polymer additive has the potential to reduce the amount of petroleum feedstocks used in the polymer industry, lower emissions like carbon dioxide and offer a higher value-added alternative for corn growers and other agribusiness. [27]

Hemicellulose Products

The third major component of biomass, xylose, is converted through two different paths in this process. The first, results in the production of diisocyanate (diphenylmethane diisocyanate) and the second in the production of trinitrate (1,2,4-butanetriol trinitrate).

The first step in order to produce diisocyanate from xylose is the production of furfural. Due to its unsaturated bonds and aldehyde group, furfural is a highly versatile and key derivative used in the manufacture of a wide range of important chemicals and its demand is rapidly increasing in different fields, such as oil refining, plastics, pharmaceutical and agrochemical industries. [28] Afterwards, 3,5-dimethylisoxazole (furamine) is produced from furfural in order for it finally to be converted in diisocyanate. After diisocyanate is isolated, it can be used for polyurethane elastomers (rollers, packing, rubber vibration insulators, synthetic leather, etc.), spandex fibres and rubber shoe soles. [29] It is obvious that its applications cover a wide range of the market industry, and thus it is essential to develop a sustainable production process.

The second path of xylose conversion includes the production of the intermediate product 1,2,4-butanetriol. This chemical is extremely useful in energetic compounds. It can be nitrated to form the energetic material 1,2,4-butanetriol trinitrate, which is less shock sensitive, more thermally stable and less volatile than nitroglycerin. [30] The nitration takes place under the environmental conditions.

6. PROCESS FLOWSHEETING OF BIOREFINERY PATHS

During the design and simulation of the production processes in Aspen Plus V7.2, special attention was given in the following topics:

- The mass ratio of the resources in the feed was always aligned with the stoichiometry of each reaction.
- The streams did not reach a temperature where any of the desireable products would be decomposed irreversibly.
- The conditions under which the separation units functioned were feasible to be achieved in the industry.
- The recycling of the resources was made sure to keep the mass balance of the process steady.

6.1 Lignin based paths

As it was already mentioned, in this biorefinery, phenolic oligomers, biochar and activated carbon are produced from lignin. The process which is being followed along with the inputs and outputs of this process are indicated in the following figure.

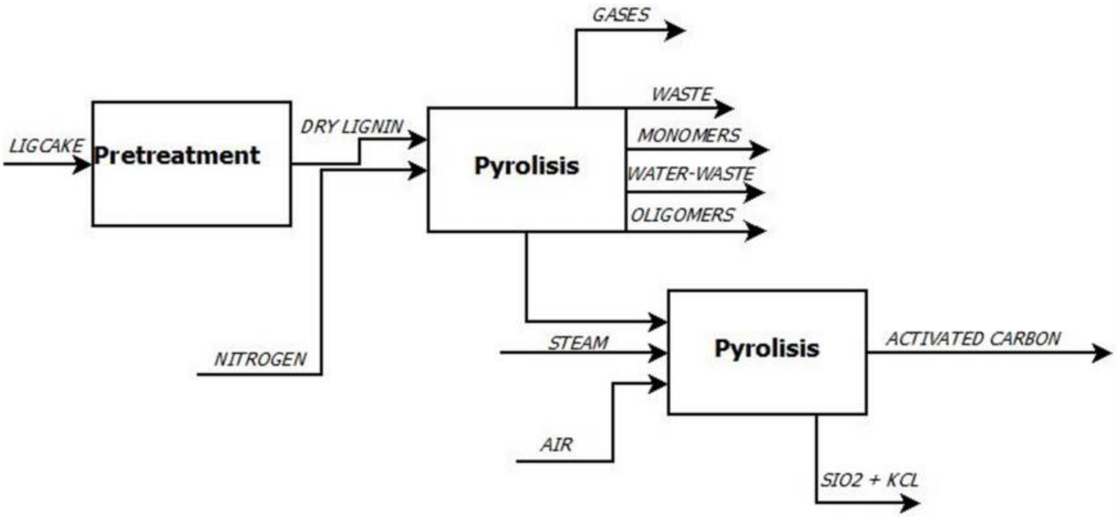


Figure 8: Process of the conversion of lignin to bio-char, activated carbon and oligomers

The lignin feed is pretreated with water and it is undertaking fast pyrolysis in the absence of oxygen under atmospheric pressure and a temperature of 500℃. A rapid quenching of the stream exiting the reactor can convert up to 75wt% of feedstock into bio-oil. The water soluble fraction of bio-oil mainly consists of lignin derived phenolic oligomers as well as phenolic monomers. [21] The phenolic oligomers are isolated via a series of distillation columns.

On the other branch of the process, the bio-char which is produced along with the rest of the solid components is divided from the liquids with the help of a cyclone.

Then, the pyrolysis of bio-char, while gas is pumped in the reactor in the temperature of 1000℃ and in atmospheric pressure, results in the production of activated carbon. The oxygenated gas inserts the reactor in such high temperature, in order for the oxygen to bond in the carbon's surface.

In tables 4 and 5 the thermal data and the input and output mass flows are respectively presented.

Table 4: Thermal data of lignin process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	500.00	400.00	-0.385	Hot
2	400.00	150.00	-0.993	Hot
3	98.90	25.00	-0.035	Hot
4	152.85	25.00	-0.085	Hot
5	192.00	25.00	-0.013	Hot
6	364.93	25.00	-0.147	Hot
7	-18.60	-19.60	-1.266	Hot
8	99.90	98.90	-3.739	Hot
9	153.85	152.85	-2.945	Hot
10	58.82	59.82	1.059	Cold
11	363.92	364.92	3.829	Cold
12	191.01	192.01	2.931	Cold
13	25.00	350.00	0.280	Cold
14	80.01	500	1.930	Cold
15	59.81	90.04	0.025	Cold
16	-19.60	166.67	0.136	Cold

Table 5: Mass balances of lignin process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
LIGCAKE	lignin	in	9.00
	silicon-dioxide	in	276.53
	potassium chloride	in	4.90
	water	in	2421.79
	acetic-acid	in	154.13
	formic-acid	in	19.94
	xylose	in	148.48
	citric-acid	in	1474.58
	solid lignin	in	1.76
NITROGEN	N2	in	8531.74
AIR	N2	in	2301.248
	O2	in	698.7516

STEAM	water	out	4000.00
SIO2+KCL	SIO2	out	276.53
	KCl	out	4.90
ACTIVATED CARBON	act-carbon	out	431.53
	water	out	2465.91
	CO2	out	2897.45
	CO	out	2280.97
GAS	N2	out	8531.74
	CO2	out	208.84
	CO	out	157.31
	CH4	out	43.40
WATER-WASTE	water	out	350.79
	guaiacol	out	17.04
	oligomer	out	1.060
WASTE	water	out	412.24
	methanol	out	34.40
	acetone	out	9.74
	acetic-acid	out	13.96
	guaiacol	out	41.52
	syringol	out	13.24
	p-ethylphenol	out	45.59
MONOMERS	water	out	13.02
	guaiacol	out	56.90
	syringol	out	54.97
	p-ethylphenol	out	4.89
	oligomer	out	5.06
OLIGOMERS	oligomer	out	689.44

6.2 Cellulose based paths

Glucose is the source of the most final products in this biorefinery. The process which is being followed as well as the bioconversion technologies applied in each chain, beginning from glucose and terminating in a final product, is described below.

Glucaric acid production

Glucose is filtered through a series of filters in order to be purified and afterwards, it is being dissolved in ammonium hydroxide and fermented to D-glucaric acid (saccharic acid). The fermentation of glucose takes place in the pressure of 1 bar and in the temperature of 30℃. The main reaction taking place is the following:

Glucose + $1.5O_2$ → Glucaric acid + H_2O

The amount of glucose which is not fermented into glucaric acid is recycled in the feed of the process. The process of the glucaric acid production is shown in figure 8. In tables 6 and 6 the thermal data and the input and output mass flows are respectively presented.

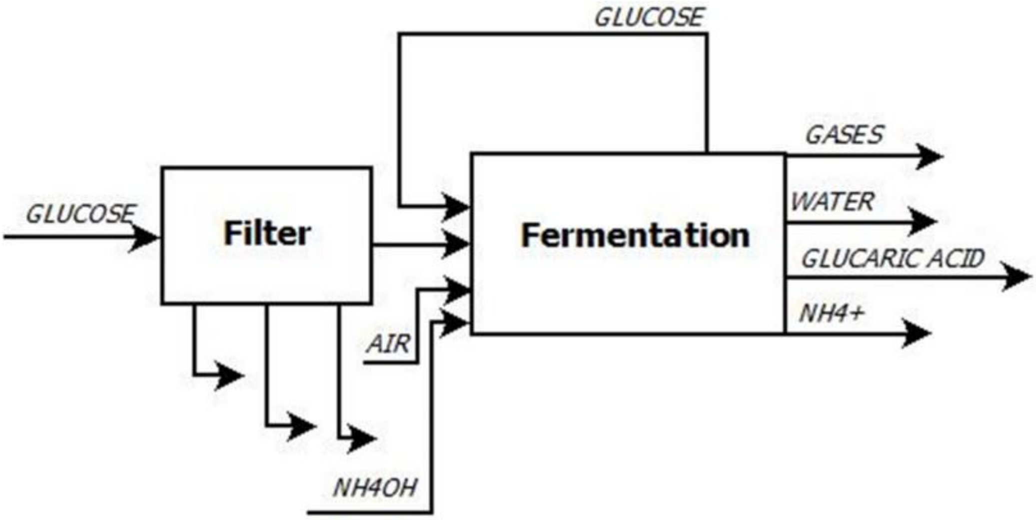


Figure 9: Process of the conversion of glucose to glucaric acid

Table 6: Thermal data of glucose to glucaric acid

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	200.00	30.00	-0.027	Hot
2	62.00	30.00	-0.195	Hot
3	29.99	25.00	-0.122	Hot
4	200.00	25.00	-0.284	Hot
5	198.00	25.00	-1.946	Hot
6	62.00	25.00	-0.065	Hot
7	62.00	25.00	-1.052	Hot
8	62.00	25.00	0.285	Cold

9	24.60	20.00	0.001	Cold
10	15.00	30.00	0.009	Cold
11	25.00	30.00	0.024	Cold

Table 7: Mass balances of glucose to glucaric acid

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
GLUCOSE	glucose	in	5771.54
	water	in	36045.08
	solid lignin	in	591.81
	dilactic-acid	in	1518.70
	Na+	in	158.27
	OH-	in	117.09
NH4OH	NH4+	in	83.49
	OH-	in	78.72
AIR	N2	in	3964.66
	O2	in	13096.57
1	water	out	720.90
	glucose	out	116.35
	solid lignin	out	591.81
	dilactic acid	out	1518.70
2	water	out	25786.62
	glucose	out	55.99
	Na+	out	126.61
	OH-	out	93.67
3	water	out	6962.41
	glucose	out	55.44
	Na+	out	25.32
	OH-	Out	18.73
GASES	water	Out	350.62
	O2	Out	3181.08
	N2	Out	13092.62
	CO2	out	50.83
WATER	water	out	2533.18
	glucose	out	6.54
NH4+	glucose	out	2533.09
	Na+	out	6.33
	OH-	out	83.40
	NH4+	out	83.49
GLUCARIC ACID	glucaric acid	out	3331.68

Adipic acid production

After the d-glucaric acid is isolated, it is hydrogenated along with hydrogen bromide and acetic acid, in adipic acid. This hydrogenation occurs under a 30 bar pressure and a temperature of 150℃. The reaction which takes place follows:

$$\text{Glucaric acid} + 4H_2 \rightarrow \text{Adipic acid} + 4H_2O$$

Adipic acid is separated from water and auxiliaries in a series of distillation columns. The auxiliaries and the glucaric acid which is not consumed by the reaction are being recycled to the feed stream.

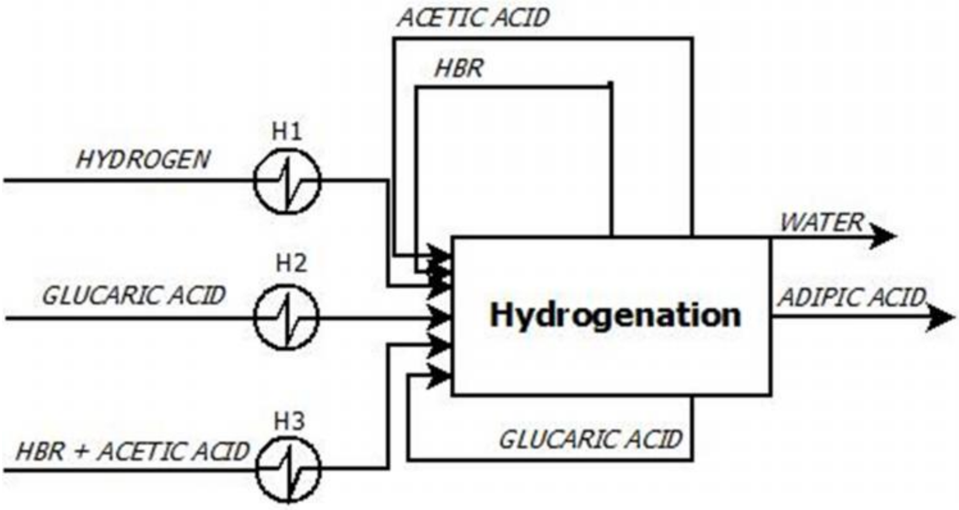


Figure 10: Process of the conversion of glucaric acid to adipic acid

In tables 8 and 9 the thermal data and the input and output mass flows are respectively presented.

Table 8: Thermal data of glucaric acid to adipic acid process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	503.98	150.00	0.001	Hot
2	503.98	25.00	0.0004	Hot
3	99.65	25.00	-0.093	Hot
4	117.58	20.00	-0.103	Hot
5	-3.07	-4.07	-1.632	Hot
6	100.65	99.65	-6.857	Hot
7	118.58	117.58	-0.933	Hot
8	118.58	117.58	-0.388	Hot
9	240.01	241.01	2.766	Cold
10	121.64	122.64	5.979	Cold
11	351.95	352.95	1.244	Cold
12	502.98	503.98	0.056	Cold
13	20.00	150.00	0.010	Cold

14	20.00	150.00	0.063	Cold
15	20.00	150.00	0.000	Cold
16	-4.07	150.00	0.036	Cold
17	117.58	150.00	0.098	Cold

Table 9: Mass balances of glucaric acid to adipic acid process

Stream Name	**Layer**	**Input/Output**	**Mass Flow (kg/hr)**
GLUCARIC	glucaric acid	In	3331.68
HBR+ACETIC ACID	HBR	In	9.60
	acetic acid	In	0.13
HYDROGEN	H2	In	121.31
WATER	water	out	1084.12
	acetic acid	out	0.84
	HBR	out	0.01
ADIPIC ACID	adipic acid	out	2198.63
	acetic acid	out	0.84

Nylon-66 production

Finally, nylon-66 is produced through the reaction and polymerization of adipic acid and hexamethylene diamine in a 1:1 feed ratio. The conditions under which nylon-66 is manufactured are 30 bars and 240˚C. The main reaction taking place is presented below:

Adipic acid + Hexamethylene → Nylon-66 + H_2O

It is then isolated through a series of steam stripping columns. During the reaction the whole amount of acipic acid and hecamethylene diamine is consumed, so there is no need for recycling.

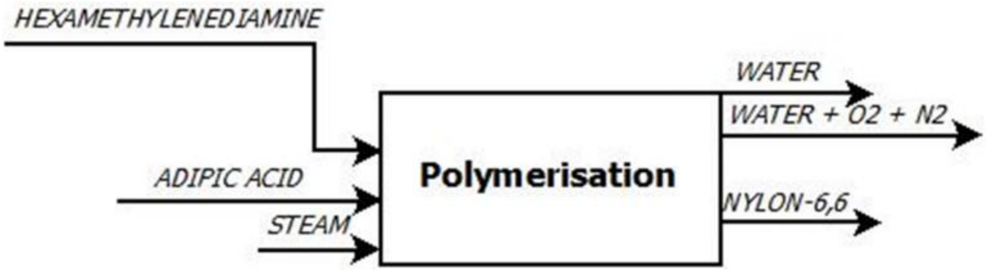


Figure 11: Process of the conversion of adipic acid to nylon-66

The thermal data and the input and output mass flows of this process are respectively presented in the tables 10 and 11.

Table 10: Thermal data of adipic acid to nylon-66 process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	150.00	25.00	-0.35	Hot
2	73.70	25.00	-0.03	Hot
3	78.89	25.00	-0.01	Hot
4	83.26	25.00	-0.002	Hot
5	20.00	240.00	0.27	Cold
6	20.00	240.00	0.26	Cold
7	15.00	150.00	0.03	Cold
8	15.00	150.00	0.01	Cold

Table 11: Mass balances of adipic acid to nylon-66 process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
ADIPIC	glucaric acid	in	2198.63
HEXAMETHYLENEDIAMINE	hexameth	in	1748.26
WATER	water	out	469.80
STEAM	O2	in	210.21
	N2	in	692.30
STEAM	O2	in	54.25
	N2	in	178.66
WATER+O2+N2	water	out	41.52
	O2	out	210.12
	N2	out	692.05
WATER+O2+N2	water	out	7.03
	O2	out	54.25
	N2	out	178.67
NYLON-66	water	out	23.71
	nylon-6,6	out	3404.83

5-HMF production

Firstly, in order to produce FDCA based polyamides, glucose has to undergo a catalytic dehydration with the aim to be converted in 5-hydroxymethylfurfural. [24] The auxiliaries which are used for this process are acetonitrile, 1,3-diazole and the solid catalyst molybdenum-trioxide. 5-HMF is synthesized through the reaction:

$$\text{Glucose} \rightarrow \text{5-HMF} + 3H_2O$$

5-HMF is isolated through a series of distillation columns and the auxiliaries along with the amount of glucose that is not consumed are being recycled back to the feed stream.

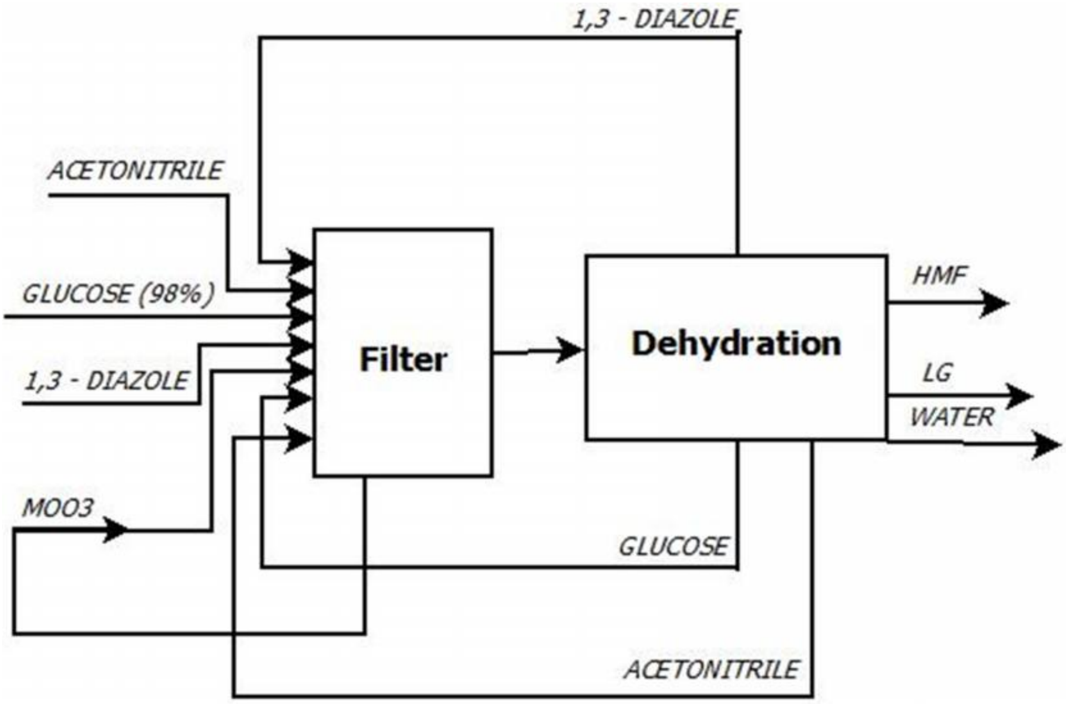


Figure 12: Process of the conversion of glucose to 5-HMF

In tables 12 and 13 the thermal data and the input and output mass flows are respectively presented.

Table 12: Thermal data of glucose to 5-HMF process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	154.08	120.00	-0.04	Hot
2	343.30	120.00	-0.01	Hot
3	120.00	78.37	-8.33	Hot
4	76.15	66.14	-1.80	Hot
5	343.30	120.00	-0.01	Hot
6	259.10	20.00	-0.57	Hot
7	205.91	25.00	-0.01	Hot
8	89.96	25.00	-0.32	Hot
9	78.25	77.25	-7.91	Hot
10	260.10	259.10	-0.63	Hot
11	77.16	76.16	-8.63	Hot
12	77.15	76.15	-364.74	Hot
13	67.13	66.13	-353.63	Hot
14	155.08	154.08	-0.42	Hot
15	258.44	259.44	8.35	Cold
16	342.30	343.30	0.63	Cold
17	153.74	154.74	8.69	Cold
18	80.06	81.06	364.79	Cold

19	88.81	89.81	353.66	Cold
20	204.91	205.91	0.42	Cold
21	60.00	120.00	1.68	Cold
22	15.00	120.00	0.00	Cold
23	15.00	120.00	0.00	Cold
24	66.13	76.16	1.75	Cold
25	81.06	120.00	5.20	Cold

Table 13: Mass balances of glucose to 5-HMF process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
GLUCOSE	glucose	in	5771.54
	water	in	147.32
ACETONITRILE	acetonitrile	in	4.45
1,3-DIAZOLE	1,3-diazole	in	0.022
WATER	water	out	4371.11
LG	LG	out	80.05
5-HMF	5-HMF	out	3919.48

2,5-FDCA production

Afterwards, 5-HMF is undergoing a catalytic fermentation with the help of sodium chloride and the solid catalyst platinum-monosulfide under a pressure of 6.9 bar and a temperature of 22℃. Furandicarboxylic acid (2,5-FDCA) is produced. 2,5-FDCA is produced according to the reaction:

$$5\text{-HMF} + 1.5O_2 \rightarrow 2,5\text{-FDCA} + H_2O$$

Sodium chloride is neutralized and 2,5-FDCA is distillated from the by-products.

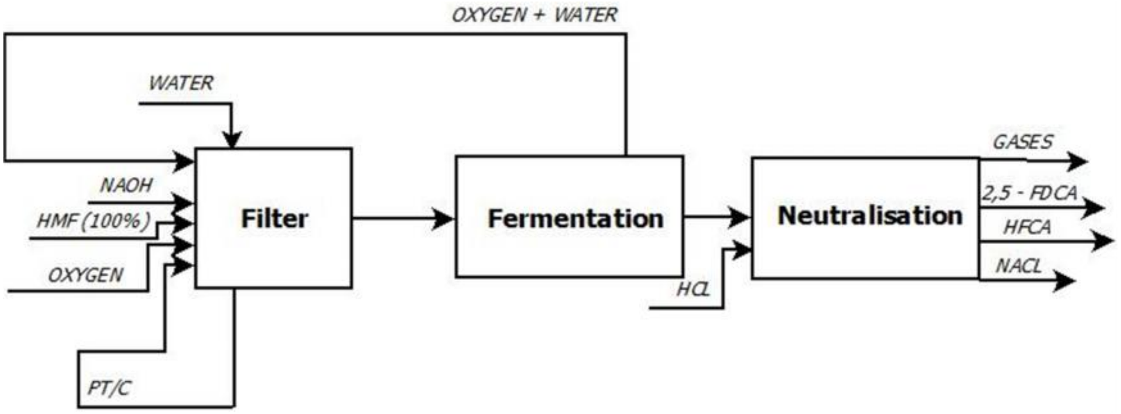


Figure 13: Process of the conversion of 5-HMF to 2,5-FDCA

The thermal data and the input and output mass flows of this process are respectively presented in the tables 14 and 15.

Table 14: Thermal data of 5-HMF to 2,5-FDCA process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	117.48	22.00	-149.21	Hot
2	100.52	50.00	-5.38	Hot
3	50.00	25.00	-0.02	Hot
4	81.46	25.00	-63.50	Hot
5	143.29	25.00	-0.42	Hot
6	221.88	25.00	-0.07	Hot
7	229.65	228.65	-1.52	Hot
8	99.52	100.52	93.65	Hot
9	299.74	300.74	61.64	Hot
10	279.91	280.91	1.35	Hot
11	99.71	99.91	0.01	Hot
12	15.00	99.91	64.17	Hot
13	15.00	99.91	-0.01	Hot
14	15.00	99.91	0.17	Hot
15	-20	99.91	0.04	Cold
16	15	50	0.02	Cold

Table 15: Mass balances of 5-HMF to 2,5-FDCA process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
5-HMF	5,HMF	in	3919.49
WATER	water	in	88405.97
NAOH	Na+	in	1428.98
	OH-	in	1057.19
OXYGEN	O2	in	1282.90
HCL	HCl	in	2449.72
NACL	NaCl	out	3632.71
GASES	water	out	89967.04
	HCl	out	183.37
HFCA	HFCA	out	927.51
2,5-FDCA	2,5-FDCA	out	3832.52

FDCA-based polyamide production

In the end, 2,5-FDCA is polymerized to an FDCA based polyamide. This polymerization is catalyzed by an amine which is isolated and recycled in order to minimize the cost of its purchase. The pressure in the reactor is 0.01 bar and the temperature 220°C. The basic reaction happening is the following:

2,5-FDCA + Amine → Polyamide + $2H_2O$

The FDCA–based polyamide is distilled from the water and cooled down to environmental temperature.

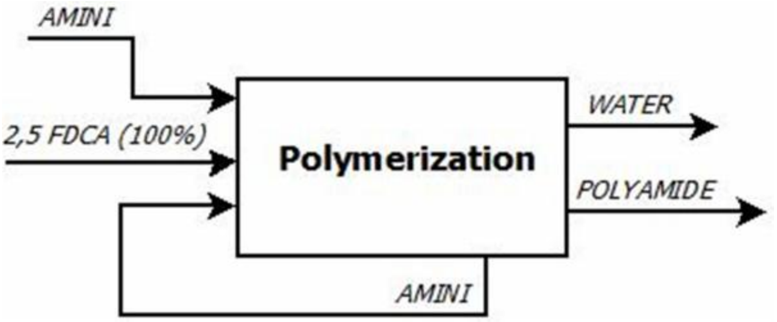


Figure 14: Process of the conversion of 2,5-FDCA to FDCA based polyamide

The thermal data and the input and output mass flows of this process are respectively presented in the tables 16 and 17.

Table 16: Thermal data of 2,5-FDCA to FDCA-based polyamide process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	478.54	220.00	0.004	Hot
2	99.65	25.00	-0.08	Hot
3	478.53	25.00	-1.03	Hot
4	100.65	99.65	-0.58	Hot
5	477.54	478.54	0.67	Cold
6	15.00	220.00	0.96	Cold
7	15.00	220.00	0.67	Cold

Table 17: Mass balances of 2,5-FDCA to FDCA-based polyamide process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
2,5-FDCA	2,5-FDCA	in	3832.52
	water	in	1.07
AMINI	amini	in	2655.19
WATER	water	out	885.72
POLYAMIDE	polyamide	out	5603.06

Ethylene glycol production

There is also another way to produce bio-based polyamide and specifically polyethylene furanoate (PEF), by the reaction and polymerization of glucose-derived ethylene-glycol and 2,5-FDCA.

At first, glucose is hydrogenated under a pressure of 60 bars and a temperature of 245℃ into ethylene glycol, which is then distilled and separated from the by-products. The reaction according to which ethylene glycol is synthesized is following:

$$\text{Glucose} + 3H_2 \rightarrow 3\text{Ethylene glycol}$$

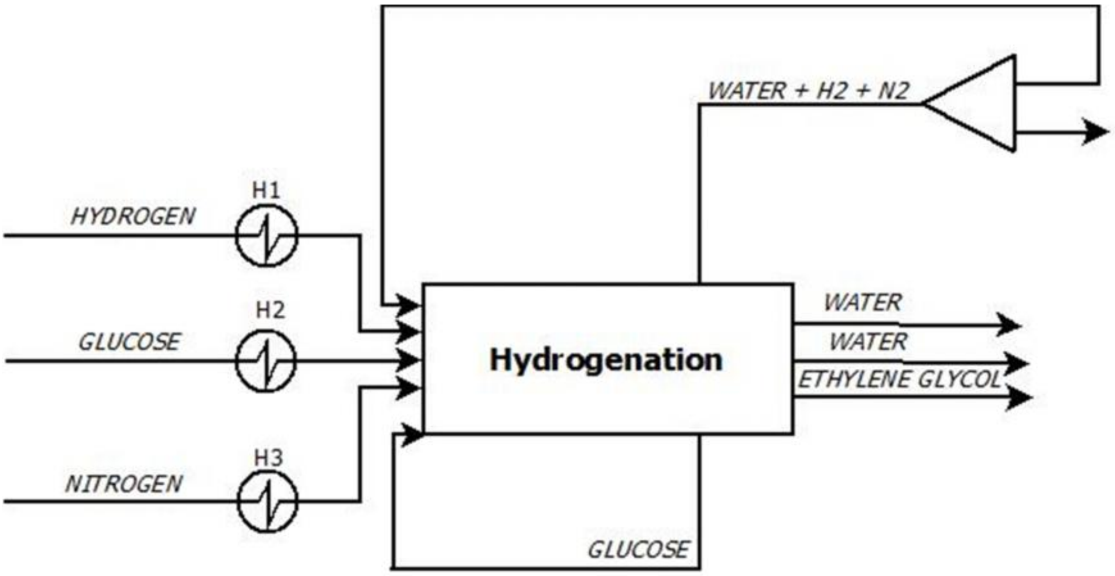


Figure 15: Process of the conversion of Glucose to Ethylene Glycol

After the reactor, a part of the water along with the gases (N_2,H_2) are separated with a flash and are being recycled in the feed. There are some cases when Aspen Plus V7.2 cannot close the mass balance if the whole stream is recycled back in the feed. This is the case in this process, and this is why before recycling it, a small amount of the stream (usually 10%) is split from the main current in order for the mass balance to be acceptable for the software. In tables 18 and 19 the thermal data and the input and output mass flows are respectively presented.

Table 18: Thermal data of Glucose to Ethylene Glycol process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	155.01	25.00	-0.20	Hot
2	409.56	25.00	-0.18	Hot
3	506.72	25.00	-1.23	Hot
4	101.54	20.00	-0.43	Hot
5	190.38	20.00	-0.43	Hot
6	156.01	155.01	-0.84	Hot
7	117.89	116.89	-1.47	Hot
8	102.54	101.54	-0.74	Hot
9	410.56	409.56	-0.82	Hot
10	223.14	224.14	2.10	Cold
11	463.59	464.59	1.81	Cold
12	189.38	190.38	1.28	Cold
13	506.46	507.46	0.92	Cold
14	105.00	190	0.32	Cold
15	20.00	190.00	1.09	Cold
16	20.00	190.00	0.06	Cold
17	25.00	50.00	0.20	Cold

Table 19: Mass balances of Glucose to Ethylene Glycol process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
GLUCOSE	glucose	in	5771.54
	water	in	1961.81
HYDROGEN	H2	in	1582.07
NITROGEN	N2	in	1246.67
WATER(WASTE)	water	out	1141.40
	ethylene glycol	out	11.84
WATER	water	out	571.22
ETHYLENE GLYCOL	ethylene glycol	out	2397.75

PEF production

Next, the whole amount of ethylene glycol that was produced, reacts with the whole amount of 2,5-FDCA that was produced in the previous chemical path. The monomer which derives from this reaction (int-PEF) is polymerized through a series of reactors under the pressure of 0.01 bars and the temperature of 220℃. [26] The reactions that took place is indicated below:

$$\text{2,5-FDCA} + 2\text{Ethylene glycol} \rightarrow (\text{int-PEF}) + 2H_2O$$

$$(\text{int-PEF}) \rightarrow \text{PEF} + \text{Ethylene glycol}$$

PEF is distilled from ethylene glycol, which is recycled in the feed.

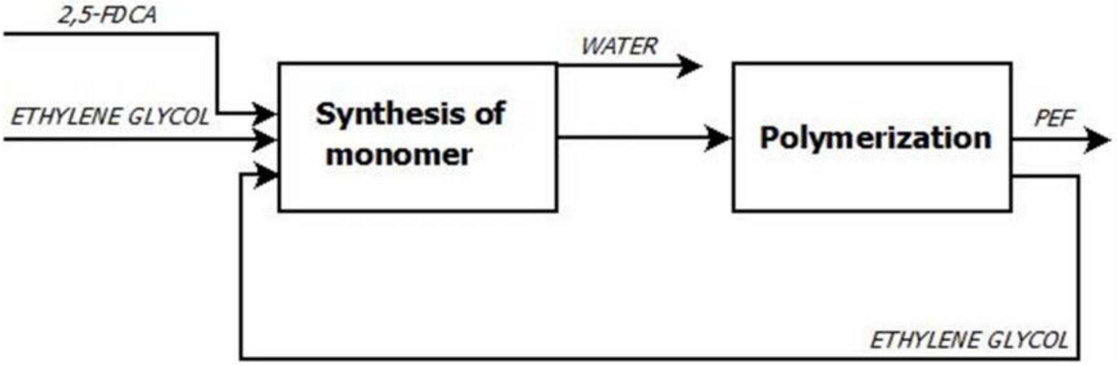


Figure 16: Process of the conversion of 2,5-FDCA and Ethylene Glycol to PEF

In tables 20 and 21 the thermal data and the input and output mass flows are respectively presented.

Table 20: Thermal data of Ethylene Glycol and 2,5-FDCA to PEF process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	99.11	20.00	-0.19	Hot
2	220.00	208.86	-0.90	Hot
3	55.65	25.00	-0.91	Hot
4	192.02	25.00	-0.17	Hot
5	100.11	99.11	-0.97	Hot
6	145.05	146.05	0.88	Cold
7	191.02	192.02	0.63	Cold
8	20.00	110.00	0.54	Cold

Table 21: Mass balances of Ethylene Glycol and 2,5-FDCA to PEF process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
2,5-FDCA	2,5-FDCA	in	3832.52
ETHYLENE GLYCOL	ethylene glycol	in	2397.75
WATER	water	out	884.64
	ethylene glycol	out	834.94
PEF	PEF	out	4463.12
	int-PEF	out	11.66
	ethylene glycol	out	35.87

Sorbitol production

The final route of the conversion of glucose in this biorefinery begins with the hydrogenation of glucose into sorbitol (P=50 bar, T=190℃). The gases and the water are separated from the main stream with a two-stage flash, whereas sorbitol is distilled to be isolated from glucose. The reaction which took place is:

$$\text{Glucose} + H_2 \rightarrow \text{Sorbitol}$$

Glucose is recycled in the feed. Part of the stream of glucose is removed for the same reason which was mentioned in the ethylene glycol flowsheet.

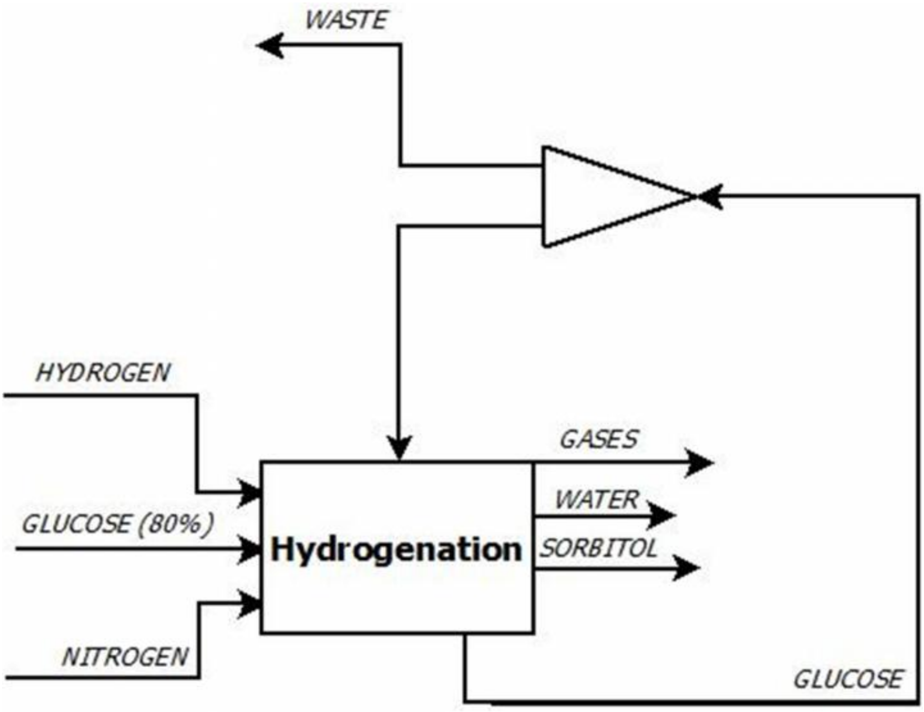


Figure 17: Process of the conversion of Glucose to Sorbitol

The thermal data and the input and output mass flows of this process are respectively presented in the tables 22 and 23.

Table 22: Thermal data of Glucose to Sorbitol process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	154.83	25.00	-0.12	Hot
2	158.54	25.00	-1.02	Hot
3	451.73	25.00	-0.79	Hot
4	169.10	168.10	-0.76	Hot
5	404.03	403.03	-0.76	Hot
6	524.40	525.40	2.93	Cold
7	506.37	507.37	0.35	Cold
8	20.00	190.00	1.21	Cold
9	105.00	190.00	0.33	Cold
10	20.00	190.00	0.07	Cold
11	25.00	50.00	0.12	Cold

Table 23: Mass balances of Glucose to Sorbitol process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
GLUCOSE	glucose	in	5771.54
	water	in	1442.89
HYDROGEN	H2	in	1753.74
NITROGEN	N2	in	1385.23
GASES	water	out	326.66
	H2	out	1716.28
	N2	out	1385.23
WATER	water	out	1116.15
	sorbitol	out	12.66
SORBITOL	sorbitol	out	3371.96

Isosorbide production

Sorbitol is undergoing a catalytic dehydration under the pressure of 1 bar and the temperature of 170℃ for the production of isosorbide. Isosorbide was produced through the following reaction:

$$\text{Sorbitol} + 2H_2O \rightarrow \text{Isosorbide}$$

The amount of sorbitol which is not converted into isosorbide, is recycled in the feed.

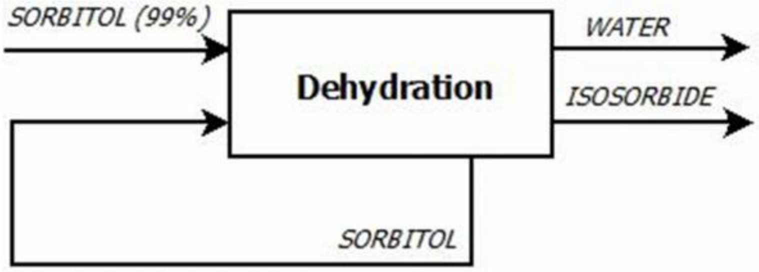


Figure 18: Process of the conversion of Sorbitol to Isosorbide

The thermal data and the input and output mass flows of this process are respectively presented in the tables 24 and 25.

Table 24: Thermal data of Sorbitol to Isosorbide process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	401.82	170.00	-0.07	Hot
2	158.77	25.00	-0.49	Hot
3	158.77	25.00	-0.08	Hot
4	159.77	158.77	-2.82	Hot
5	400.82	401.82	2.87	Cold
6	25.00	170.00	0.29	Cold

Table 25: Mass balances of Sorbitol to Isosorbide process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
SORBITOL	sorbitol	in	3371.96
WATER	water	out	644.29
	isosorbide	out	25.13
ISOSORBIDE	sorbitol	out	7.42
	water	out	23.66
	isosorbide	out	2684.12

PEIF production

Now, an amount of isosorbide is going to be added to the same amount of feed which was used for the production of polymer PEF, which was produced in the previous chemical path from ethylene glycol and 2,5-FDCA. Let's name this enhanced polymer PEF by the name of PEIF [Poly(ethylene isosorbide 2,5-furandicarboxylate)]. Whereas the feed of the process contains the whole amount of the produced ethylene glycol and 2,5 FDCA, the amount of isosorbide which is contained is the 93.12% of the amount which is produced, due to the stoichiometry of the reaction. PEIF is synthesized according to the reaction presented below:

2 2,5-FDCA + Isosorbide + Ethylene glycol → $3H_2O$ + PEIF

The monomer is polymerized and PEIF is isolated from water in a steam-stripping column. The amounts of the resources which do not react are being returned back in the feed.

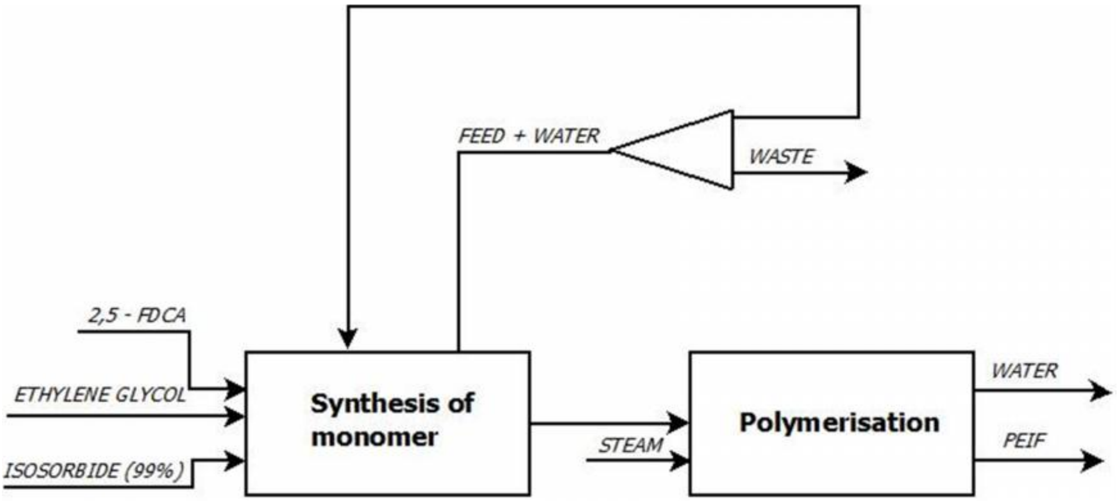


Figure 19: Process of the conversion of 2,5-FDCA, Ethylene Glycol and Isosorbide to PEIF

In tables 26 and 27 the thermal data and the input and output mass flows are respectively presented.

Table 26: Thermal data of Ethylene Glycol, 2,5-FDCA and Isosorbide to PEIF process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	260.00	25.00	-1.53	Hot
2	280.00	180.00	-0.12	Hot
3	213.49	25.00	-0.71	Hot
4	230.73	25.00	-0.23	Hot
5	25.00	260.00	0.52	Cold
6	25.00	260.00	1.26	Cold
7	25.00	260.00	0.40	Cold
8	260.00	280.00	0.07	Cold
9	25.00	300.00	0.78	Cold

Table 27: Mass balances of Ethylene Glycol, 2,5-FDCA and Isosorbide to PEIF process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
2,5-FDCA	2,5-FDCA	in	3832.52
ETHYLENE GLYCOL	ethylene glycol	in	2397.75
ISOSORBIDE	isosorbide	in	2499.47
	sorbitol	in	6.91
	water	in	22.03
STEAM	water	in	911.64
WASTE	isosorbide	out	418.44
	water	out	665.94
	ethylene glycol	out	1718.77
WATER	isosorbide	out	332.15
	ethylene glycol	out	47.78
	water	out	914.50
	PEIF	out	567.74
	sorbitol	out	6.71
PEIF	PEIF	out	4039.02

6.3 Hemicellulose based paths

The process followed in each chain for the production of the intermediates and final products by using xylose as a resource is described below.

Furfural production

In the first chemical path, xylose is undertaking an acid-catalyzed dehydration by using sulfuric acid in 8 atmospheres and 180°C. The product of this dehydration is furfural:

$$\text{Xylose} \rightarrow \text{Furfural} + 3H_2O$$

It is then separated from the by-products to be used as feed for the production of furamine. The larger amount of the sulfuric acid is being separated in the first evaporator and is recycled in the feed. The amount of sulfuric acid which exits the second evaporator is very small, so it is not considered necessary to be recycled.

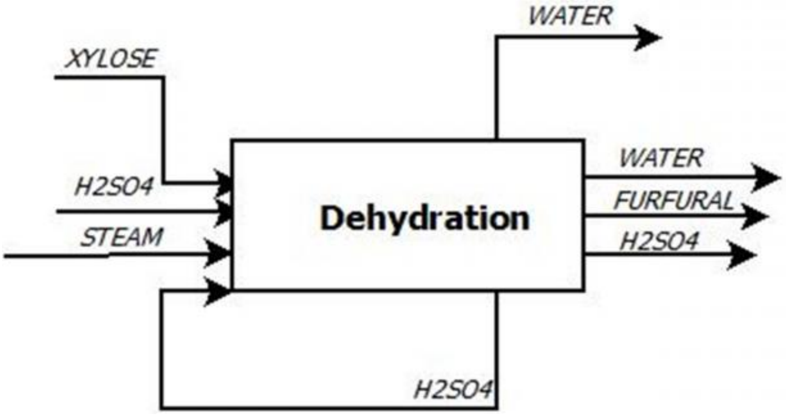


Figure 20: Process of the conversion of Xylose to Furfural

The thermal data and the input and output mass flows of this process are respectively presented in the tables 28 and 29.

Table 28: Thermal data of Xylose to Furfural process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	180.00	25.00	-51.28	Hot
2	310.85	25.00	-0.02	Hot
3	92.98	25.00	-0.01	Hot
4	156.14	20.00	-0.12	Hot
5	120.38	119.38	-2.57	Hot
6	94.00	93.00	-0.07	Hot
7	25.00	180.00	0.32	Cold
8	25.00	180.00	37.92	Cold
9	25.00	171.62	12.36	Cold
10	309,85	310,85	0,82	Cold
11	155,18	156,18	0,10	Cold

Table 29: Mass balances of Xylose to Furfural process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
XYLOSE	Xylose	in	2875.49
H2SO4	H2SO4	in	153.66
	water	in	48425.44
STEAM	water	in	15886.25
H2SO4	H2SO4	out	126.58
	furfural	out	2.28
WATER	water	out	53.65
	furfural	out	20.96
FURFURAL	water	out	3.89
	furfural	out	1801.21

Furamine production

Afterwards, furfural reacts with hydrogen and ammonia (amination) to produce furamine. This reaction occurs under the pressure of 90 atmospheres and the temperature of 75℃ and is shown below:

$$\text{Furfural} + H_3N + H_2 \rightarrow \text{Furamine} + H_2O$$

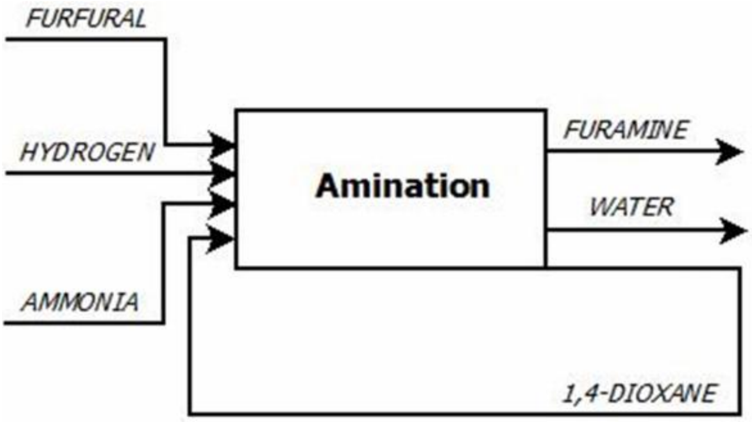


Figure 21: Process of the conversion of Furfural to Furamine

The thermal data and the input and output mass flows of this process are respectively presented in the tables 30 and 31.

Table 30: Thermal data of Furfural to Furamine process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	180.00	25.00	0.001	Hot
2	310.85	25.00	-0.03	Hot
3	92.98	25.00	-0.09	Hot
4	156.14	20.00	-0.36	Hot
5	120.38	119.38	0.01	Cold
6	94.00	93.00	0.002	Cold
7	25.00	180.00	0.35	Cold

Table 31: Mass balances of Furfural to Furamine process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
FURFURAL	water	in	3.89
	furfural	in	1801.21
HYDROGEN	H2	in	37.80
AMMONIA	NH3	in	319.25
WATER	water	out	337.71
FURAMINE	furamine	out	1820.54
	water	out	3.89

Diisocyanate production

Furamine is isolated and is led to undergo a catalytic reaction with acetone for the production of diisocyanate (P=20 atm, T=20℃). Diisocyanate is produced through the reaction:

$$2 \text{ Furamine} + 2 \text{ Acetone} \rightarrow \text{Diisocyanate} + CO_2 + 8H_2$$

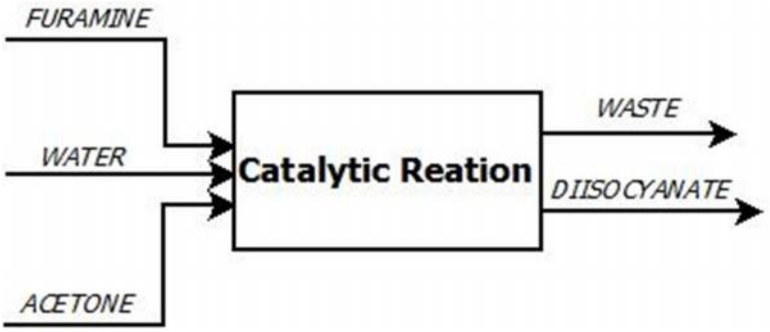


Figure 22: Process of the conversion of Furamine to Diisocyanate(MDI)

The thermal data and the input and output mass flows of this process are respectively presented in the tables 32 and 33.

Table 32: Thermal data of Furamine to Diisocyanate process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	93.33	92.33	-79.56	Hot
2	92.33	25.00	-3.18	Hot
3	337.55	25.00	-0.32	Hot
4	336.55	337.55	82.87	Cold

Table 33: Mass balances of Furamine to Diisocyanate process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
FURAMINE	furamine	in	1820.54
	water	in	3.89
WATER	water	in	4229.23
ACETONE	acetone	in	2045.21
WASTE	H2	out	136.04
	water	out	4233.15
	furamine	out	182.05
	diisocyanate	out	20.85
	acetone	out	1065.33
	CO2	out	371.25
DIISOCYANATE	diisocyanate	out	2090.23

1,2,4-Butanetriol production

Xylose can be also converted in 1,2,4-butanetriol, which is produced by fermentation of xylose under environmental conditions and is then isolated through a series of distillation columns. The xylose residue is recycled in the feed. The basic reaction for this process is indicated below:

Xylose → Butanetriol + CO_2

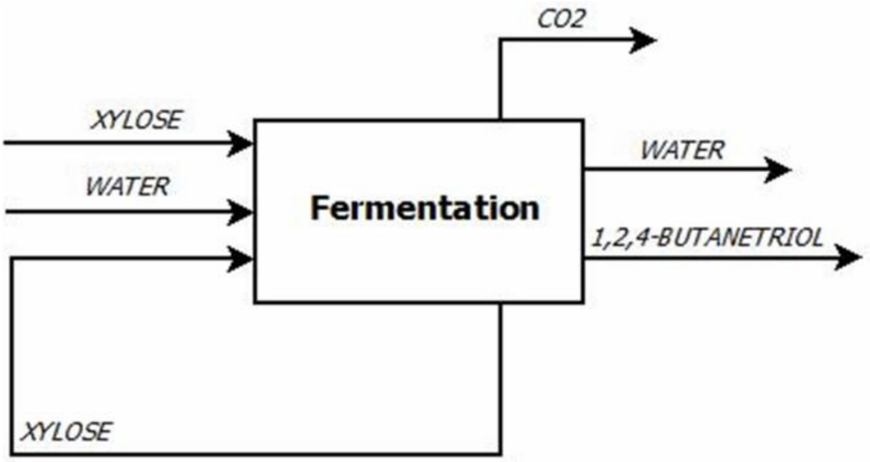


Figure 23: Process of the conversion of Xylose to 1,2,4-Butanetriol

In tables 34 and 35 the thermal data and the input and output mass flows are respectively presented.

Table 34: Thermal data of Xylose to 1,2,4-Butanetriol process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	441.93	20.00	-0.35	Hot
2	84.96	83.96	-306.31	Hot
3	84.88	83.88	-290.97	Hot
4	271.84	20.00	-0.48	Hot
5	440.93	441.93	317.54	Cold
6	270.84	271.84	291.32	Cold
7	-16.68	25.00	6.43	Cold

Table 35: Mass balances of Xylose to 1,2,4-Butanetriol process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
XYLOSE	xylose	in	2875.49
WATER	water	in	149449.33
CO2	CO2	out	703.59
	water	out	57.83
WATER	water	out	149391.49
	CO2	out	139.34
1,2,4-BUTANETRIOL	1,2,4-butanetriol	out	2032.56

Trinitrate production

Lastly, 1,2,4-butanetriol is nitrated in order to be converted in 1,2,4-Butanetriol Trinitrate:

$$\text{Butanetriol} + 3HNO_3 \rightarrow \text{Trinitrate} + 3H_2O$$

Trinitrate is separated from 1,2,4-butanetriol and from the water which is used for the nitration, both of which are recycled to the initial feed.

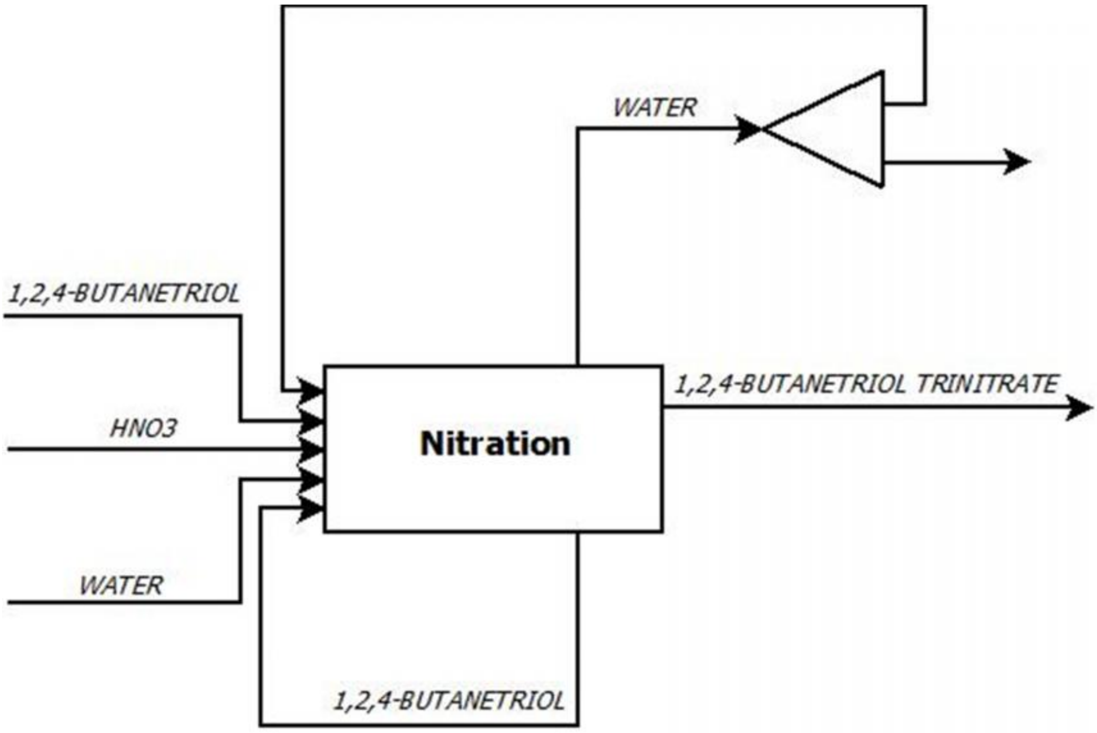


Figure 24: Process of the conversion of 1,2,4-Butanetriol to Trinitrate

In tables 36 and 37 the thermal data and the input and output mass flows are respectively presented.

Table 36:Thermal data of Xylose to 1,2,4-Butanetriol process

No Stream	Tin(℃)	Tout (℃)	Q (MW)	Description
1	98.04	20.00	-0.11	Hot
2	271.84	20.00	-0.02	Hot
3	98.04	25.00	-0.09	Hot
4	201.33	25.00	-0.15	Hot
5	99.04	98.04	-12.29	Hot
6	202.33	201.33	-0.21	Hot
7	201.00	202.00	1.11	Cold
8	270.84	271.84	0.21	Cold

Table 37: Mass balances of Xylose to 1,2,4-Butanetriol process

Stream Name	Layer	Input/Output	Mass Flow (kg/hr)
1,2,4-Butanetriol	1,2,4-butanetriol	in	2032.56
HNO3	HNO3	in	149449.1
WATER	water	out	379.99
	HNO3	out	98.52
TRINITRATE	trinitrate	out	149391.49

7. ECONOMIC DATA

It is also very important for the analysis that is going to follow to know the prices of the intermediates and final products, as well as the auxiliary market prices used in this biorefinery. The market prices of the intermediates and final products are presented in table 38, while the market prices of the auxiliaries are presented in table 39. [36]

Table 38: Market prices of the intermediates and final products in euros/kg

Chemical	Price(US dollars/kg)	Price(Euros/kg)
Oligomers and Activated Carbon	2.8	2.492
Furfural	1.32	1.175
Furamine(3,5-Dimethylisoxazole)	1.5	1.335
Diisocyanate	2.5	2.225
1,2,4-Butanetriol	4.665	4.151
1,2,4-Butanetriol Trinitrate	2.3	2.047
Glucaric acid	1.4	1.246
Adipic acid	2.6	2.314
Nylon-6,6	2.5	2.225
HMF	10	8.899
2,5-FDCA	3.796	3.378
Polyamide	0.99	0.881
Ethylene Glycol	0.9	0.801
PEF	2.5	2.225
Sorbitol	0.615	0.547
Isosorbide	5.2	4.628
PEIF	2.7	2.403

Table 39: Market prices of the auxiliaries used in the processes in euros/kg

Chemical	Price(US dollars/kg)	Price(Euros/kg)
Fresh water	0.001	0.001
Glucose	0.5	0.44
Xylose	2.5	2.20
Ammoniumhydroxide	0.61	0.54
Acetic acid	0.6	0.53
HBR	1.3	1.14
Hydrogen	0.0015	0.0013
NaOH	0.83	0.73
Oxygen	6.27	5.51

Amini	5.2	4.57
Nitrogen	8.5	7.46
Sulfuric acid	0.32	0.28
Hexamethylene	2.75	2.41
Ammonia	0.65	0.57
Acetone	3.065	2.69
Nitric acid	0.45	0.40
Acetonitrile	7.67	6.74
1,3-diazole	9.5	8.34

The investment cost of each process was calculated with the help of the Economic Evaluation add-in of Aspen-Plus V7.2 and it is presented in million euros in table 40.

Table 40: Investment and operating cost of each process in million Euros

Process	**Investment Cost(million Euros)**	**Operating Cost (million Euros/yr)**
CIMV	27.46	56.50
Acivated Carbon+Oligomers	10.08	2.90
Furfural	17.96	17.96
Furamine	8.18	2.84
Diisocyanate	47.66	7.15
1,2,4-Butanetriol	421.75	46.5
Trinitrate	15.16	4.41
Glucaric acid	3.17	0.94
Adipic acid	4.07	0.69
Nylon-66	42.40	0.87
5-HMF	40.29	191.9
2,5-FDCA	36.39	41.99
Polyamide	2.04	1.51
Ethylene Glycol	7.35	2.69
PEF	3.38	1.78
Sorbitol	4.75	1.59
Isosorbide	3.26	1.02
PEIF	5.28	1.62

8. ENERGY INTEGRATION AND COST ANALYSIS WITH OSMOSE

Osmose, the tool which was developed and still is developing in EPFL was used for the individual integration of each chemical path in the biorefinery. The lignin path was not integrated in this program. The paths which have been integrated are shown in figure 24.

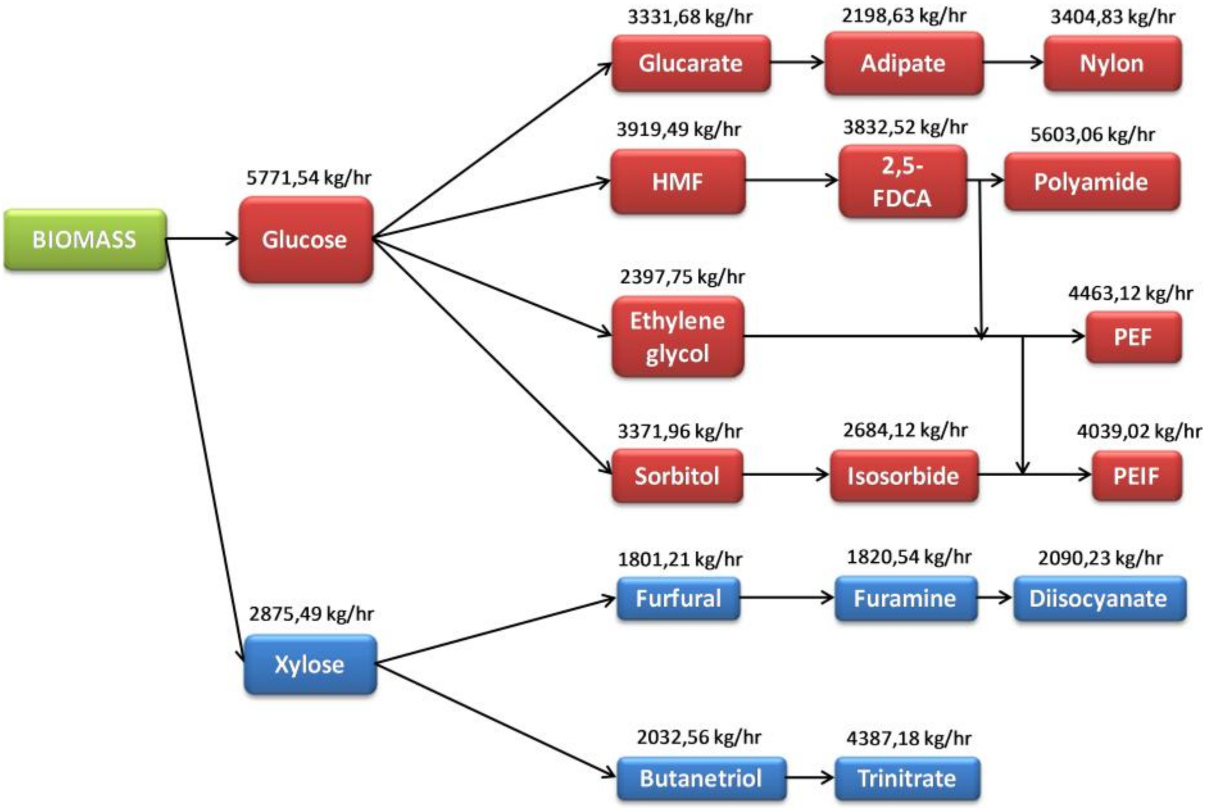


Figure 25: Chemical paths of the biorefinery integrated with the help of osmose

Basically, each path is integrated by assuming that the whole amount of the intermediate products is used for the production of the final products. In that way, the size of the utilities needed to cover the energy needs of the production line for each final product is determined. If the cost of the resources and the income of the products is taken also into consideration, there can be an estimation of the profitability of each chemical path. It is also assumed that the entire amount of the final products can be absorbed from the market. Another important aspect in this analysis is that the CIMV through which biomass is disintegrated in glucose and xylose is not integrated.

In order for osmose to give the expected results, the appropriate input has to be inserted by the user. Before osmose runs, the following variables should be defined:

1) The utilities (hot and cold) which will be applied in the biorefinery.
2) The market prices and the size of the resources (main input and auxiliaries).
3) The market prices and the size of the services (final products and by-products).
4) The thermal data regarding each process as presented in the above chapter (initial temperature, targeted temperature and utility).
5) The mass data regarding each process as presented in the above chapter (input and output of each process)
6) The investment cost of each process as it was estimated in Aspen V7.2. It has to be noted that Osmose, in order to implement the investement cost to the profit which is calculated for each chemical path, it annualizes it based on the estimation that the lifetime of the biorefinery is 25 years and that it produces 8760 hours per year.

The levels of utilities which were applied in the biorefinery are shown in table 41.

Table 41: Levels of utility which are used as input in osmose

Utility	T_{in}(˚C)	T_{out}(˚C)	Default Size (kW)	Cost
Boiler	800	1000	750	1
Cooling (Fresh water)	5	15	100	0.1
Cooling2 (Refrigeration Cycle)	-100	-90	100	0.15

The utilities which were defined are the following:

One boiler with inlet temperature 800 C, outlet temperature 1000 C and a default size of 750 kW, as well as two cooling utilities. The first one was fresh water with inlet temperature 5 C, outlet temperature 15 C and default size of 100 kW. The second one was produced from a refrigeration cycle with inlet temperature -100C, outlet temperature -90C and default size of 100 kW.

According to the thermal data of each process, osmose integrates each chemical path and gives a multiplication factor for each utility applied in each chemical path, which if multiplied with the default size of the utility, gives the demand of the certain level of utility for a certain chemical path. Thus, the multiplication of this factor with the default size defined for each utility, results in the estimation of the actual size of each utility that each path needs. In table 42 you can see the multiplication factors given for each utility and in table 43 the sizes of the utilities which result from these multiplication factors.

Table 42: The multiplication factors for each utility in each integrated chemical path

	Multiplication Factor		
Final Product	**Boiler**	**Cooling**	**Cooling1**
Diisocyanate	85.26	881.13	0
Trinitrate	609.87	6094.94	0
Nylon-66	19.40	232.50	33.39
Polyamide	295.89	978.35	0
PEF	114.04	381.3247	0
PEIF	90.54	297.7209	0

Table 43: The size of the demand of each level of utility for each integrated chemical path

	Size of Utility demands (MW)		
Final Product	**Boiler**	**Cooling**	**Cooling1**
Diisocyanate	63.94	88.11	0
Trinitrate	457.40	609.49	0
Nylon-6,6	14.54	23.25	3.34
Polyamide	221.92	97.84	0
PEF	85.53	38.13	0
PEIF	67.90	29.77	0

As it has been already pointed out, each path is integrated in total, as the only choice that is being given is to produce and sell the final product of each path, and not the intermediates. As a result, each of the grand composite curves which follow includes the thermal data for the sum of the processes which belong in a chemical path. The investment cost of each path is calculated by summing the investment costs of each process included in this certain path. The profit of each chemical path is calculated by abstracting the cost of the resources by the income deriving from the selling of the products and the by-products.

As a result, in order to be able to characterize the production of a final product profitable, the profit has to have a positive value. In table 44, the investment cost and the profit of each path as they were calculated from osmose are presented in million US dollars and million Euros.

Table 44: Investment cost and profit regarding the production of each final product

Final Product	Investment Cost (million US dollars)	Investment Cost (million Euros)	Profit (million US dollars)	Profit (million Euros)
Diisocyanate	0.71	0.63	-2.16	-1.92
Trinitrate	4.2	3.73	-8.56	-7.62
Nylon-66	**0.98**	**0.87**	**11.24**	**9.99**
Polyamide	6.03	5.37	-6.42	-5.71
PEF	2.43	2.16	-6.14	-5.47
PEIF	1.79	1.59	-6.07	-5.40

As you can see on the above table, the only final product which results in positive profit is Nylon-66.

The diagrams presenting the Grand Composite Curve and the Composite Curve of each integrated chemical path are given in Appendix C.

Finally, the energy savings during the integrated production of each final product is shown in table 45.

Table 45: Energy savings for each chemical path after the energy integration

Process	Initial Energy Needs (MW)		Energy Needs after Individual Integration (MW)		Energy Saving (%)	
	Hot Utility	Cold Utility	Hot Utility	Cold Utility	Hot Utility	Cold Utility
Diisocyanate	134,76	137,62	63,94	88,11	52,55	35,98
Trinitrate	616,62	610,97	457,40	609,49	25,82	0,24
Nylon-66	14,54	26,59	11,81	12,52	18,76	41,62
Polyamide	968,54	968,84	221,92	97,84	77,09	89,90
PEF	976,79	973,51	85,53	38,13	91,24	96,08
PEIF	982,97	983,00	67,90	29,77	93,09	96,97

9. ENERGY INTEGRATION AND COST ANALYSIS BY APPLYING THE TRANSSHIPMENT MODEL

In this chapter, the energy integration of each process is going to occur through a different approach based on the transshipment model (Papoulias and Grossman). This time, each process in each path is going to be individually integrated. In addition, different combinations of levels of steams are going to be studied, in order to conclude which is the most cost-effective for this biorefinery. This time, the whole biorefinery is integrated along with the CIMV and the lignin process. Due to the huge amount of data which need to be used for the extraction of the desirable results, the problem was automatized by simulating it in GAMS. The code describing the transshipment model in a GAMS format is given in Appendix B.

After the design of each process in Aspen Plus V7.2 and the estimation of the investment and operating cost with the help of the same program, each process was integrated individually for a DTmin=10˚C.

At first, the program ran with only two utilities as input, the maximum hot and the minimum cold utility needed, in order for the GCC of each process to be designed. Afterwards, the same processes were individually integrated for different combinations of utilities. The levels of utilities which were applied along with their market prices (Douglas, 1988) are shown in the tables 46 and 47 below.

Table 46: The market prices of different levels of hot utilities applied in the processes of the biorefinery

	Low Pressure Steam (LP)	**Price (million Euros/MW/yr)**	**Medium Pressure Steam (MP)**	**Price (million Euros/MW/yr)**	**High Pressure Steam (HP)**	**Price (million Euros/MW/yr)**
Saturation Temperature (˚C)	100	0.0365	180	0.0544	345	0.0641
	120	0.0429	200	0.0596	445	0.0645
	140	0.0451	-		545	0.0648
	160	0.0482	-		-	

Table 47: The market prices of different levels of cold utilities applied in the processes of the biorefinery

	Cold utility	Price (million Euros/MW/yr)
Temperature (°C)	25	0.0191
	0	0.0562
	-10	0.1083
	-15	0.2242
	-30	0.4242

The algorithm which has been composed in GAMS is solved for steady high pressure steam utilities and cold utilities, but for different combinations of low and medium pressure steam utilities. Each combination consists of three utilities. Thus, the possible combinations of utilities are twenty. The size of each utility for each combination is defined with the aim to minimize the cost of the utilities. In the tables below, the total cost of each combination of the utilities in a declining order is presented, as well as the size of the utilities needed to satisfy the energy demands of each process matching the cheapest utility combination. It is important to point out that there was not a solution which included the cold utility of -10°C, so it will not be taken into consideration from now on. The possible utility combinations along with their annual cost are presented in the table 48. It is important to point out that this cost refers to the sum of the utilities used for each occasion. Thus, the three hot utilities and the four cold utilities which are steady in every combination are included in the cost indicated in table 48.

Table 48: Possible utility combinations and their annual cost in an increasing order

Number of Utility Combination	**Utility Combination (°C)**	**Cost (million Euros/MW/yr)**
1	160-120-100	115.086
2	160-140-100	115.220
3	180-140-100	115.248
4	180-120-100	115.264
5	140-120-100	115.301
6	200-140-100	115.372
7	180-160-100	115.506
8	200-120-100	115.514
9	200-160-100	115.535
10	200-180-100	116.344
11	180-160-120	119.638
12	160-140-120	119.648
13	200-160-120	119.667
14	180-140-120	119.676
15	200-140-120	119.800

16	200-180-120	119.885
17	180-160-140	121.367
18	200-160-140	121.396
19	200-180-140	121.463
20	200-180-160	123.967

The most cost-effective combination of the utilities is easily conducted and includes the levels of steam of 160˚C, 120˚C and 100˚C, as well as the steady hot and cold utilities.

Also, the model created in GAMS not only gives the best combination of utilities, but also the optimum way of distributing them according to the needs of each process. In table 49, the optimum way of the distribution of each level of utility in each process is presented.

Table 49: Size of the optimum combination of utilities in MW needed to satisfy the energy demands of each process

Duty (℃)	**545.4**	**445.4**	**345.4**	**160**	**120**	**100**	**25**	**0**	**-15**	**-30**
Process										
1			0.016	34.269			17.823	0.787		
2							3.685	0.567		
3							18.688	2.501		
4	0.087	3.902	3.136	0.01			5.287			1.266
5			3.52	0.0005			2.739	3.323		
6							0.106	0.018		
7		82.871					82.58	0.483		
8	317.54		291.19				591.538			
9			1.316				12.817	0.043		
10							3.081	0.578		
11	0.056	1.244	2.765	6.109	0.001		8.278	0.019	1.632	
12			0.214	0.027			0.04	0.02		
13		0.631	16.589	1.051		717.09	737.145	0.085		
14			62.989		95.08	7.419	32.059	6.912		
15	0.67			0.06	0.11		0.22			
16	2.647		1.985	0.02			3.09	0.128		
17			0.378	0.917	0.065		1.419	0.315		
18	3.872						1.654	0.066		
19		2.872					3.122	0.042		
20			0.419	0.057	0.029	0.093		0.107		

For a more simplified presentation of the results the processes in the table 49 were represented by numbers. In the table 50 which follows, the relevance between the numbers and the processes is indicated.

Table 50: Listing of the processes included in the biorefinery

Number of process	Process
1	CIMV
2	C5-Hydrolysis
3	C6-Hydrolysis
4	Lignin→Oligomers and Activated Carbon
5	Xylose→Furfural
6	Furfural→Furamine(3,5-Dimethylisoxazole)
7	Furamine→Diisocyanate
8	Xylose→1,2,4-Butanetriol
9	1,2,4-Butanetriol→1,2,4-Butanetriol Trinitrate
10	Glucose→Glucaric acid
11	Glucaric acid→Adipic acid
12	Adipic Acid→Nylon-6,6
13	Glucose→HMF
14	HMF→2,5-FDCA
15	2,5-FDCA→Polyamide
16	Glucose→Ethylene Glycol
17	Ethylene Glycol+2,5-FDCA →PEF
18	Glucose→Sorbitol
19	Sorbitol→Isosorbide
20	Ethylene Glycol+2,5-FDCA+Isosorbide→PEIF

Now, the GCC of each process is going to be designed along with the sizes and levels of the optimum combination of the utilities which were presented in table 49. The GCC curves were designed with the help of the “Pinch Analysis Spreadsheet” of ChemE.

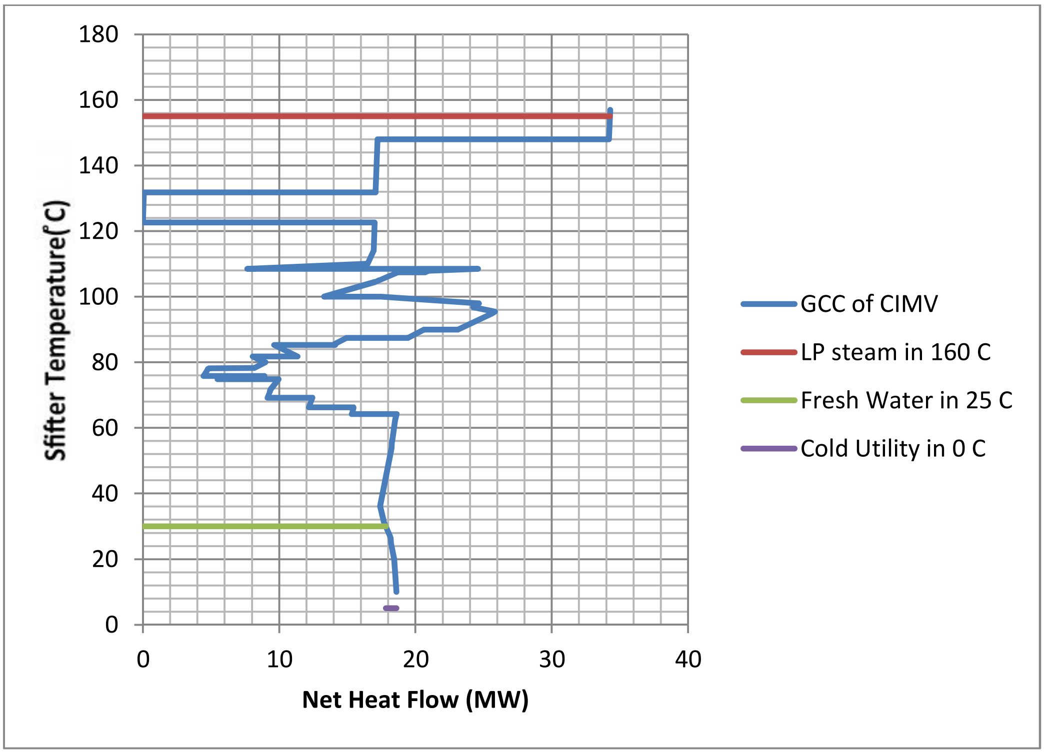


Figure 26: Graph of the Grand Composite Curve and the minimum hot and cold utilities for the CIMV process

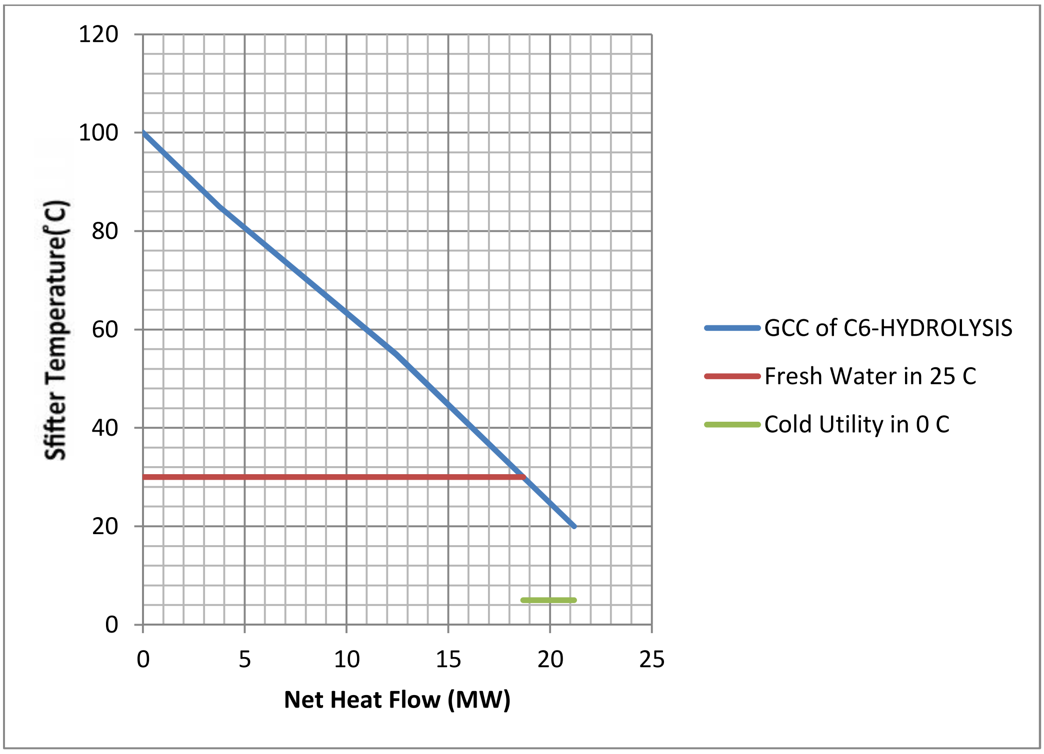


Figure 27: Grand Composite Curve for the C6-Hydrolysis process

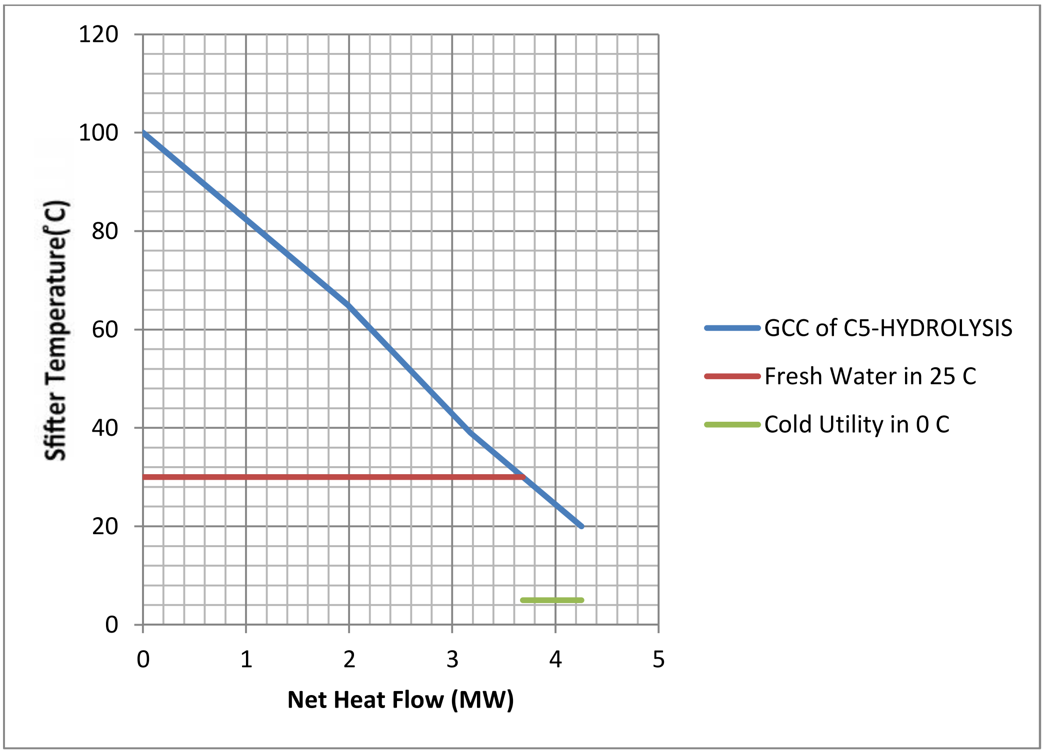


Figure 28: Grand Composite Curve for the C5-Hydrolysis process

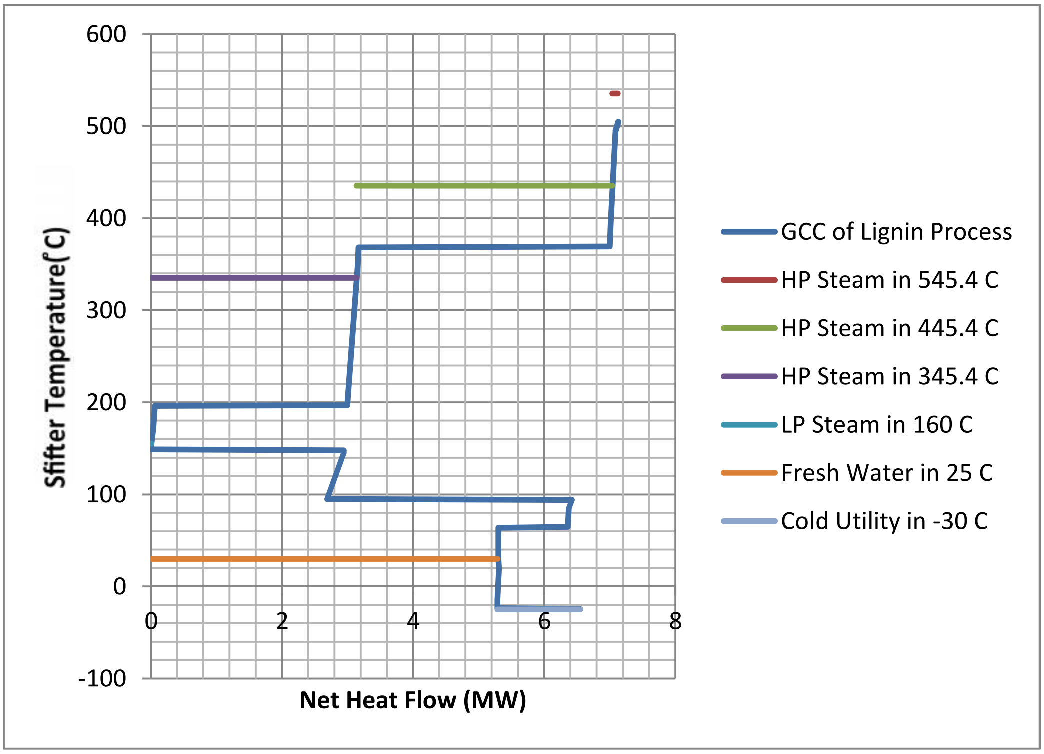


Figure 29: Grand Composite Curve for the Lignin process

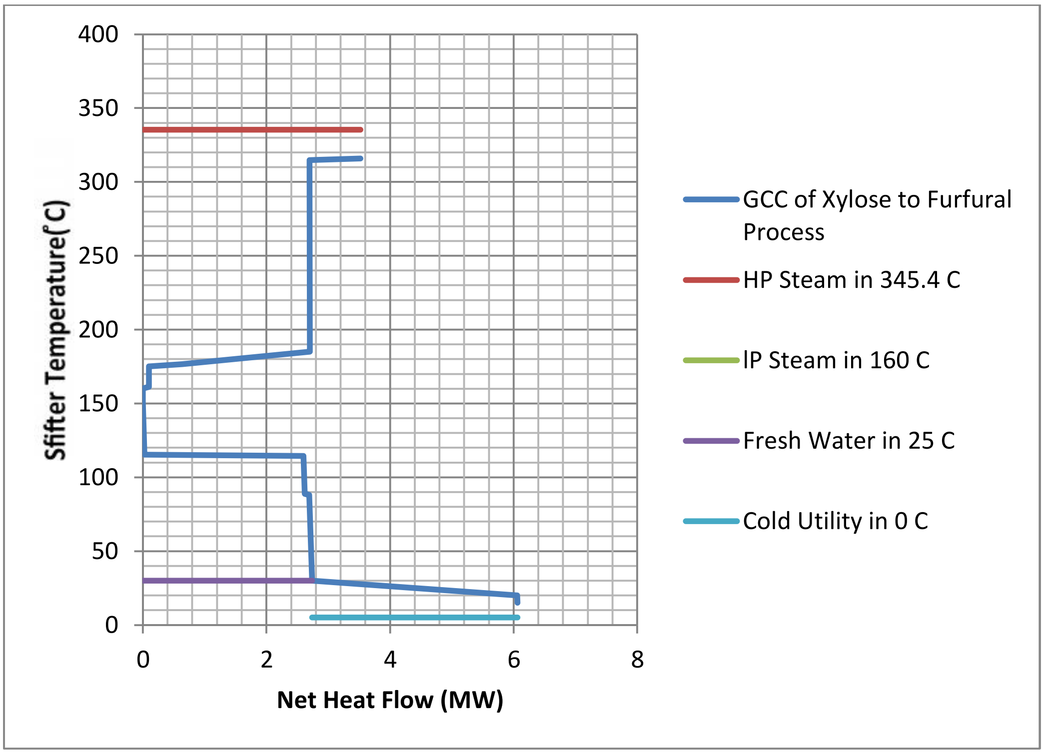


Figure 30: Grand Composite Curve for the Furfural production process

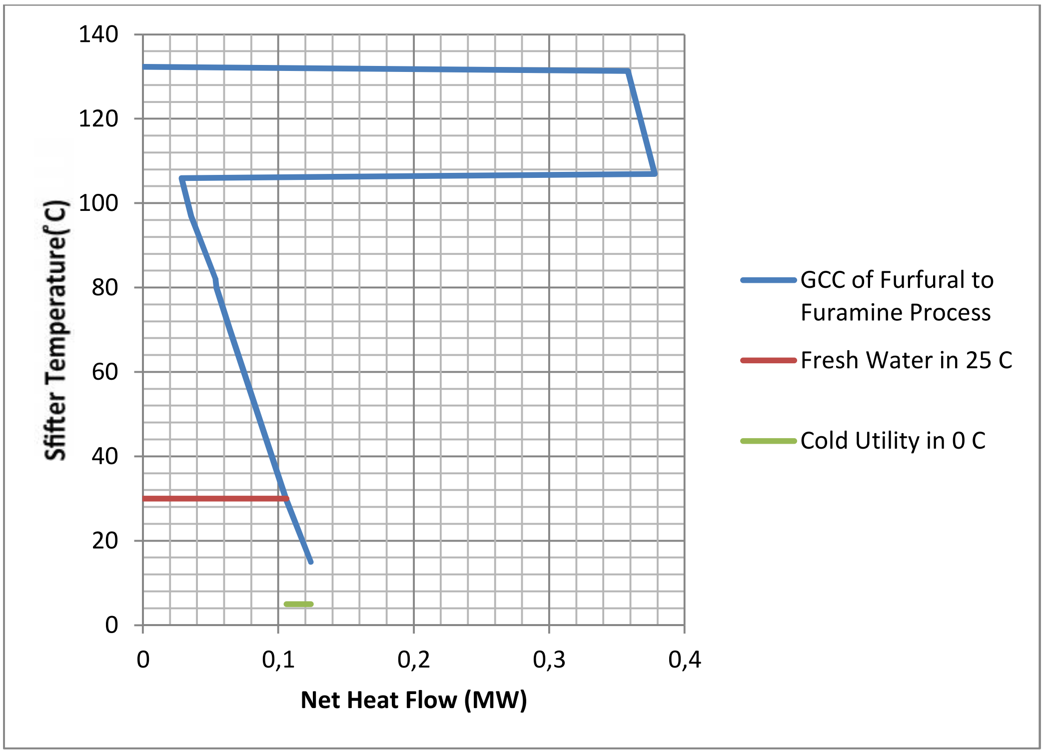


Figure 31: Grand Composite Curve for the Furamine production process

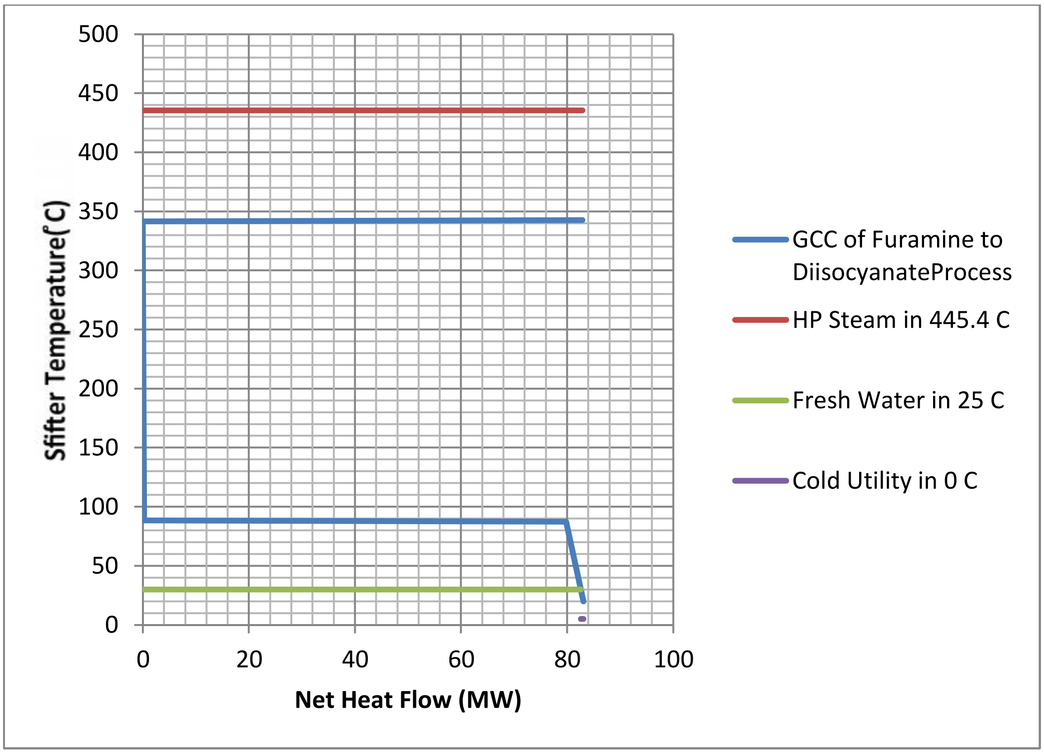


Figure 32: Grand Composite Curve for the Diisocyanate production process

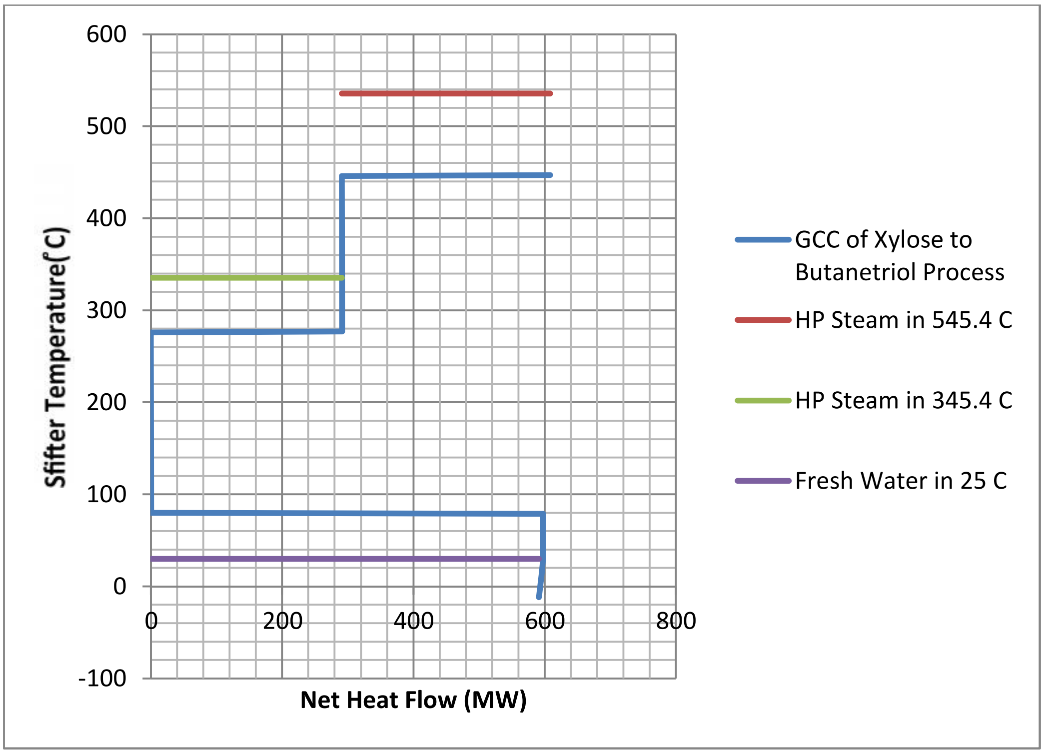


Figure 33 Grand Composite Curve for the Butanetriol production process

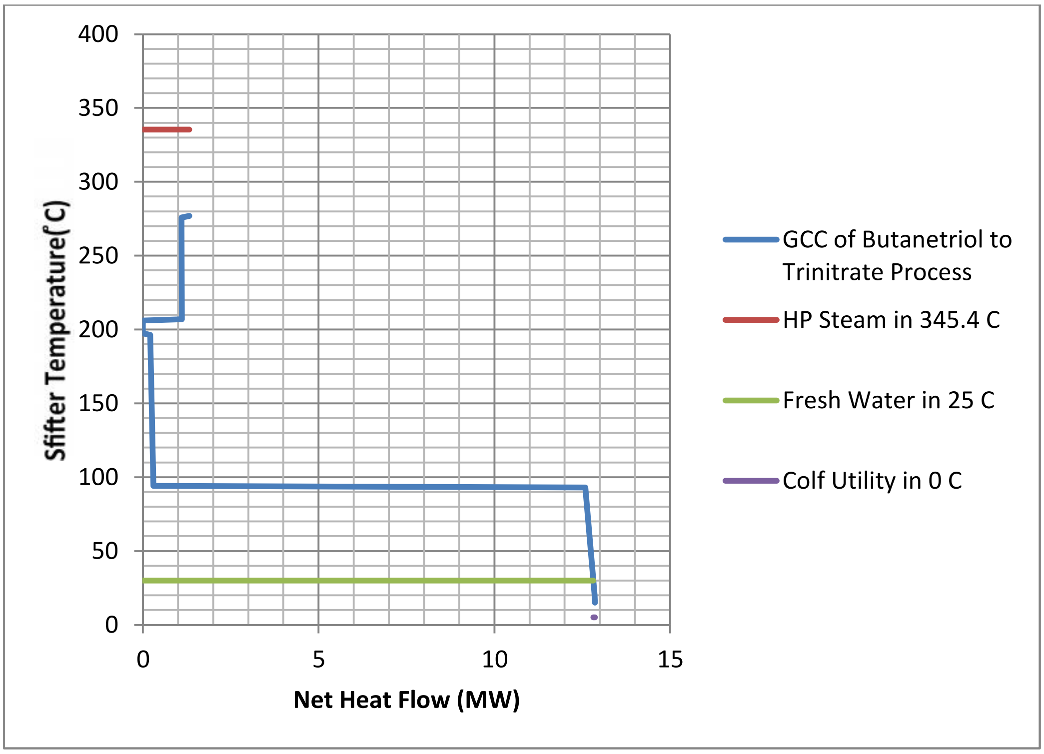


Figure 34 Grand Composite for the Butanetriol to Trinitrate process

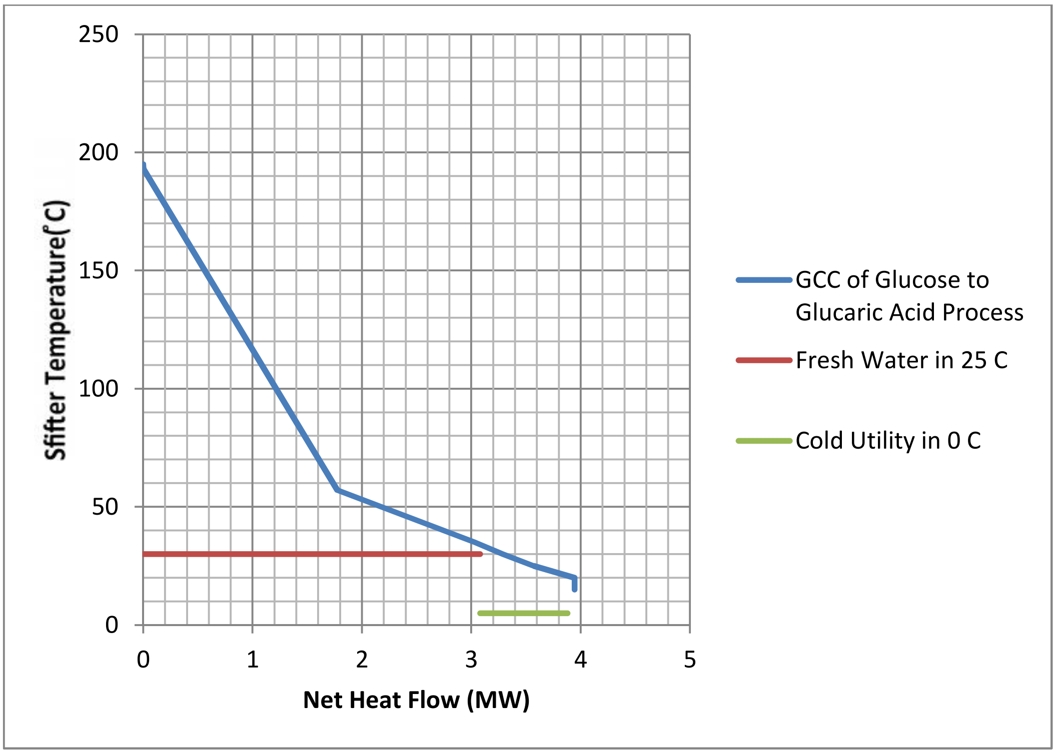


Figure 35: Grand Composite Curve for the Glucaric acid production process

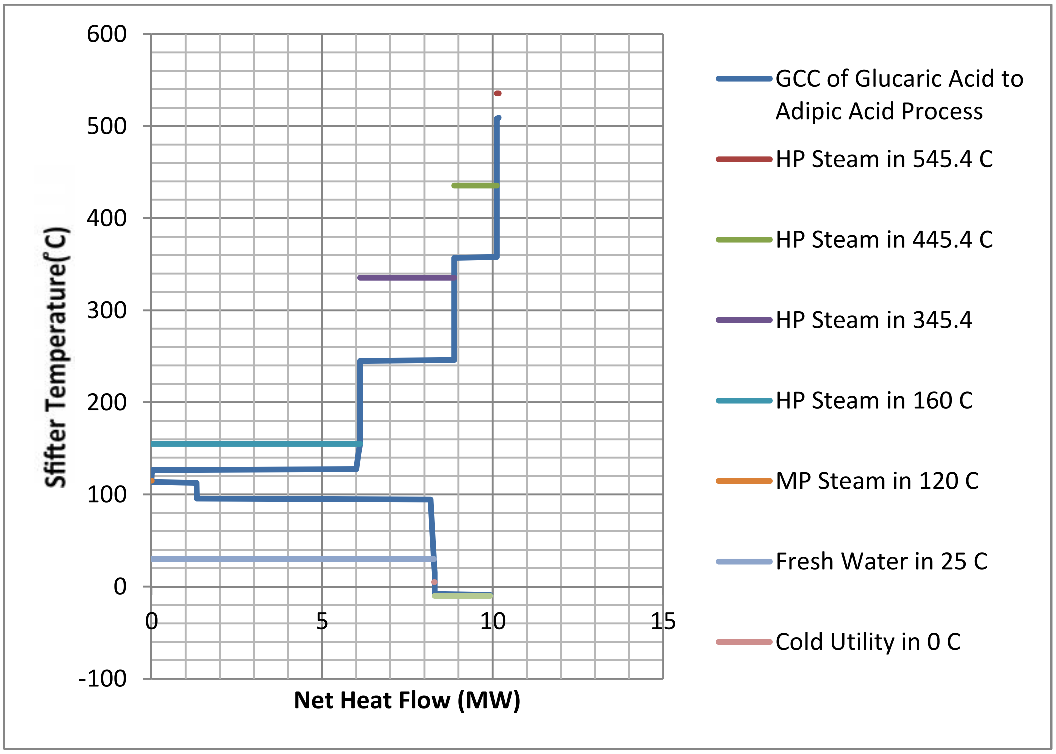


Figure 36: Grand Composite Curve for Adipic acid production process

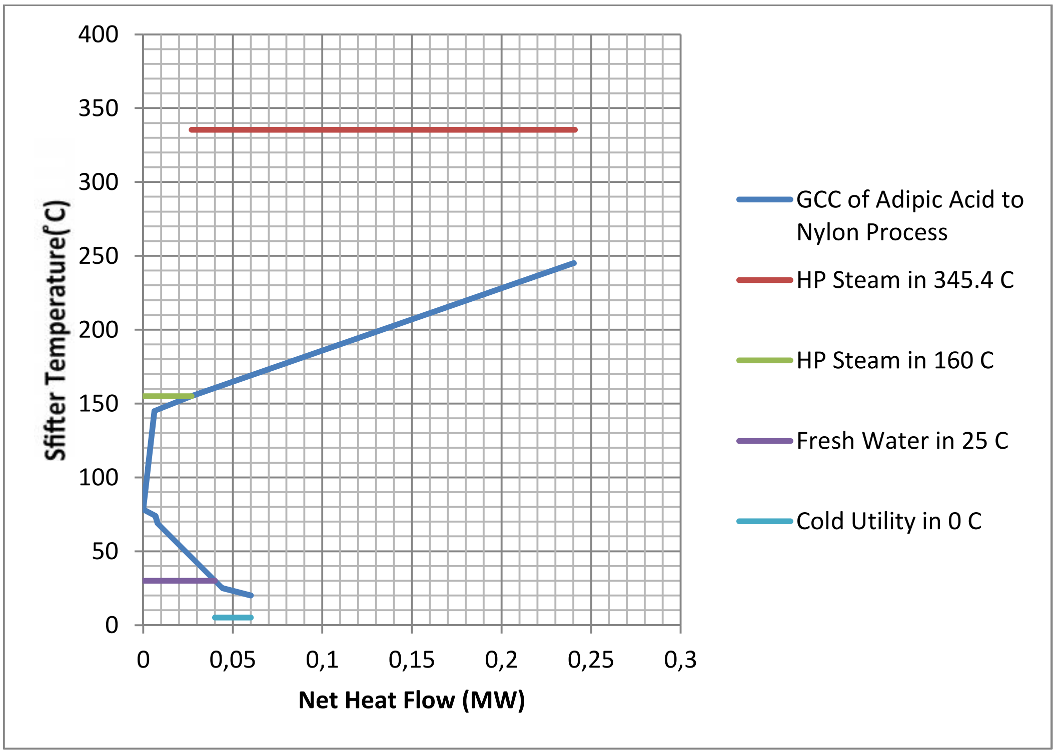


Figure 37: Grand Composite Curve for Nylon-66 production process

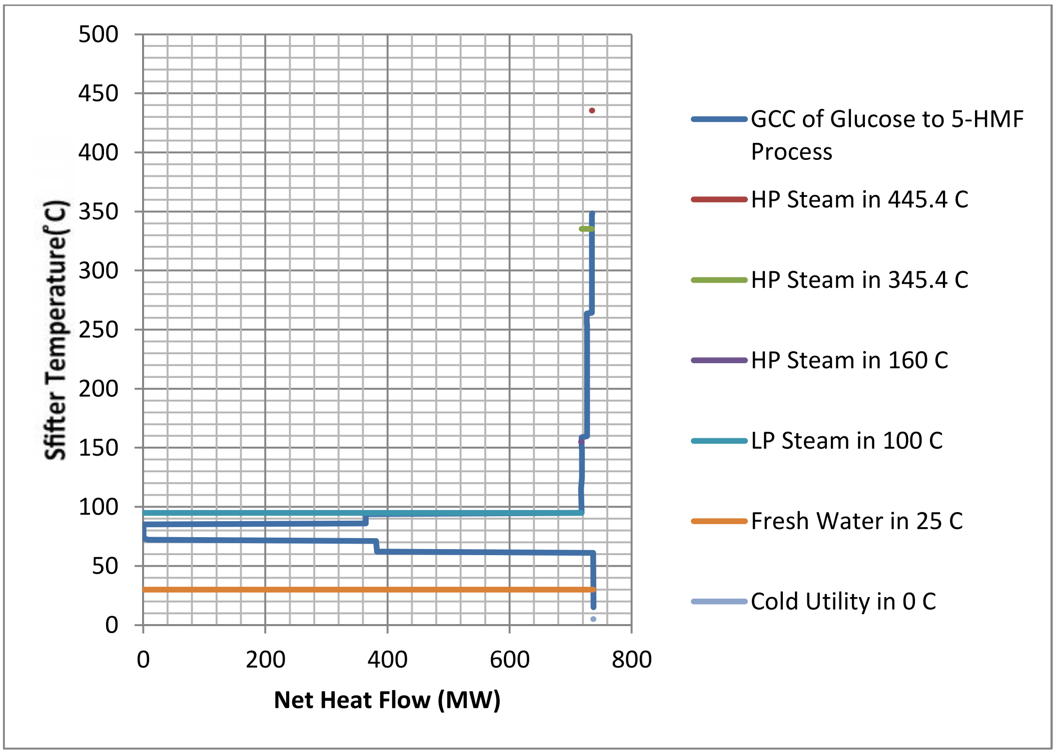


Figure 38: Grand Composite Curve for 5-HMF production process

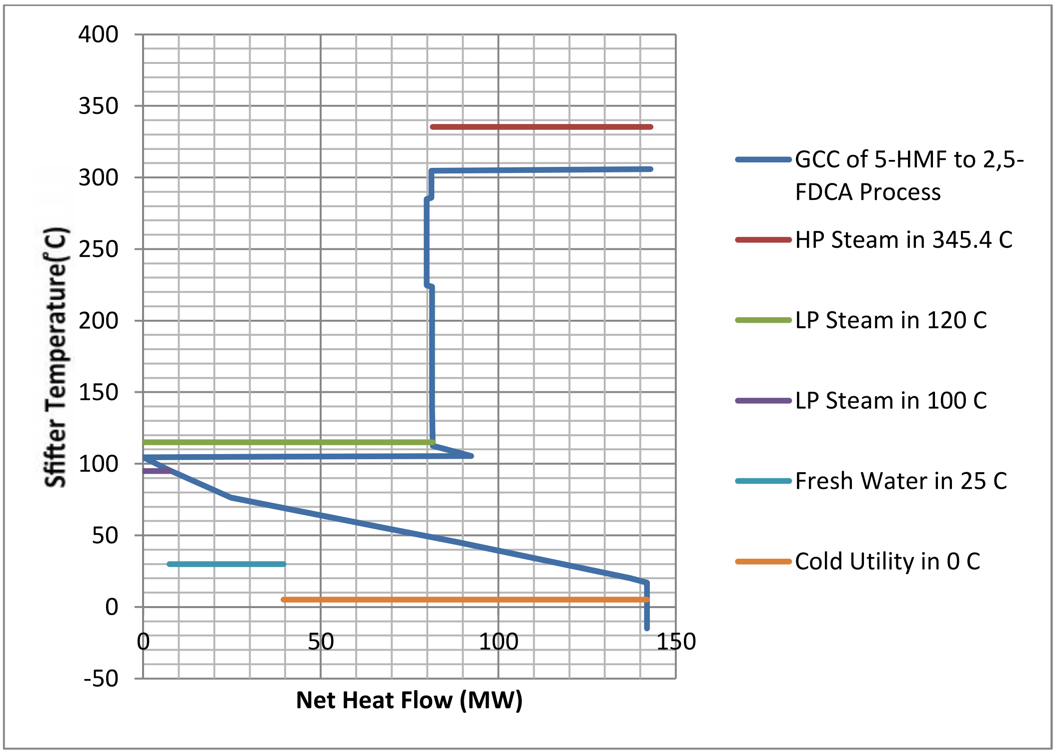


Figure 39: Grand Composite Curve for the 2,5-FDCA production process

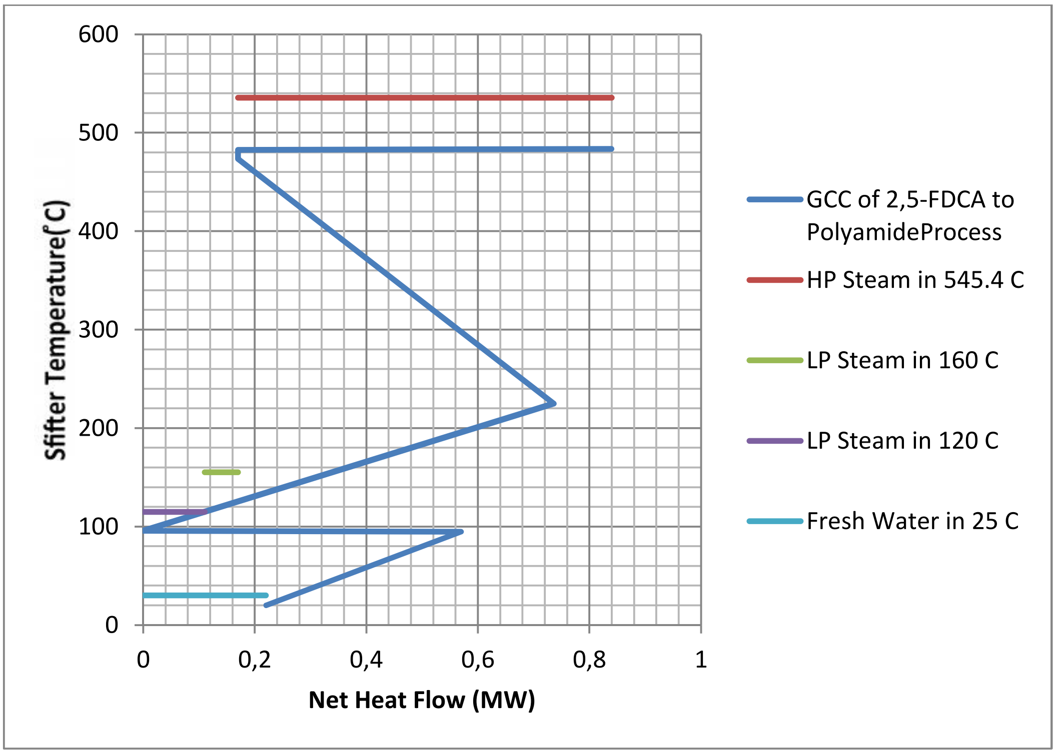


Figure 40: Grand Composite Curve for Polyamide production process

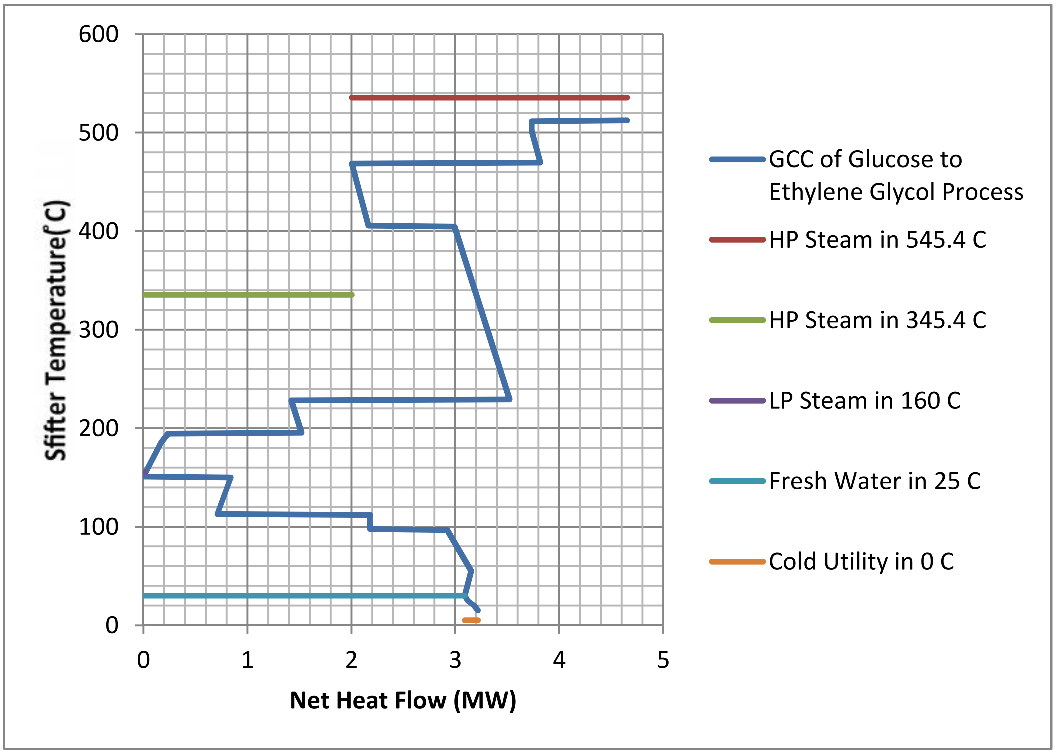


Figure 41: Grand Composite Curve for the Ethylene Glycol production process

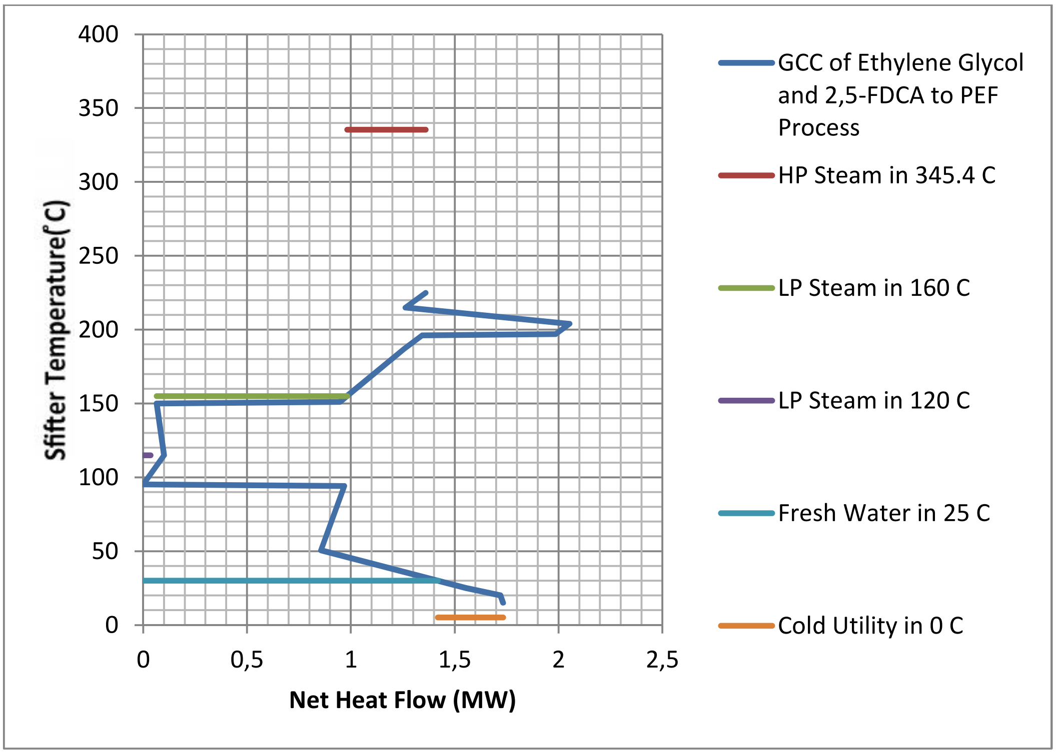


Figure 42: Grand Composite Curve for PEF production process

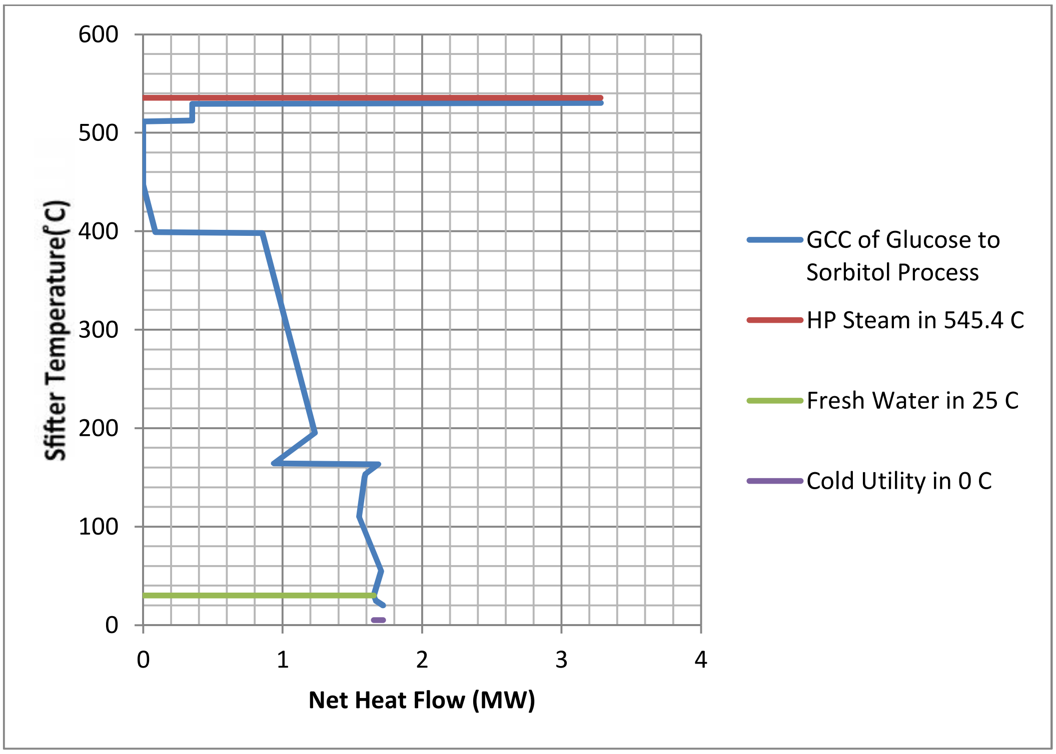


Figure 43 Grand Composite Curve for the Sorbitol production process

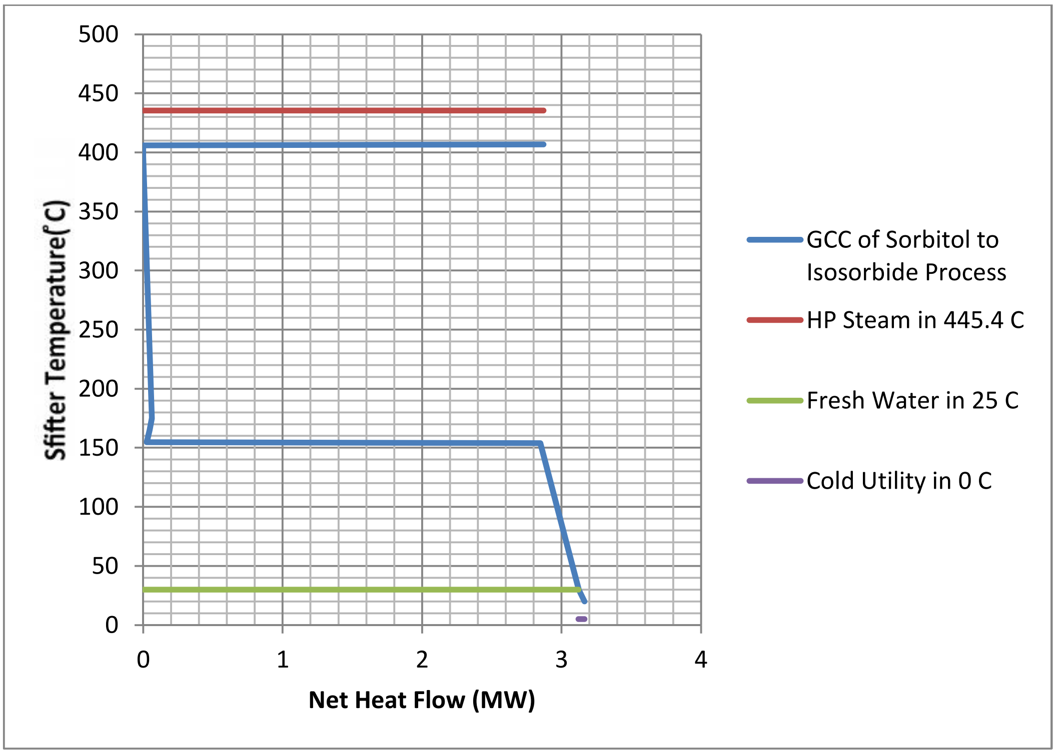


Figure 44 Grand Composite Curve for Isosorbide production process

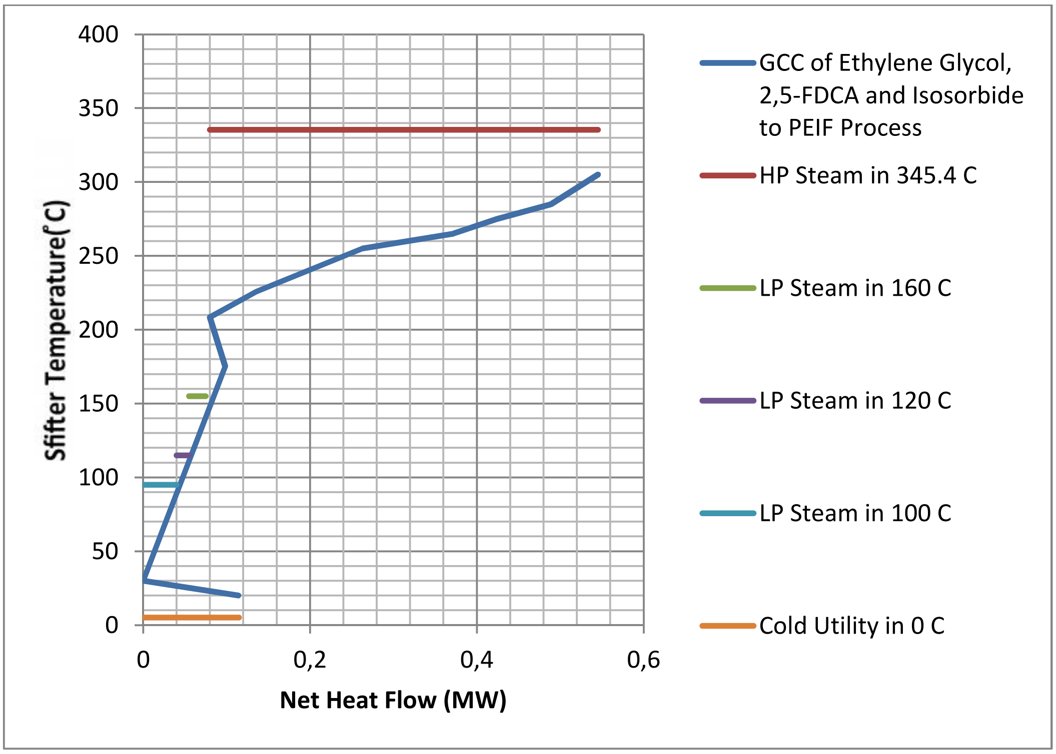


Figure 45: Grand Composite Curve for the PEIF production process

The energy integration of each process by combining a lot of different utility levels resulted in significant energy savings. The hot and cold utility needs before and after the energy integration, along with the energy savings of each process is shown in table 51.

Table 51: Energy savings of each process due to the energy integration

Process	**Initial Energy Needs (MW)**		**Energy Needs after Individual Integration (MW)**		**Energy Saving (%)**	
	Hot Utility	**Cold Utility**	**Hot Utility**	**Cold Utility**	**Hot Utility**	**Cold Utility**
CIMV	101.91	111.68	34.29	44.05	**66.36**	**60.56**
Furfural	51.53	54.07	3.52	6.06	**93.17**	**88.79**
Furamine	0.36	0.49	0.00	0.12	**100.00**	**74.48**
Diisocyanate	89.56	92.23	82.87	83.06	**7.47**	**9.94**
Butanetriol	615.30	598.10	608.73	591.54	**1.07**	**1.10**
Trinitrate	1.32	12.87	1.32	12.86	**0.44**	**0.05**
Oligomers-Activated Carbon	10.19	9.61	7.14	6.55	**29.99**	**31.80**
Glucaric Acid	0.32	3.96	0.00	3.94	**100.00**	**0.44**
Adipic Acid	10.93	11.18	10.01	10.25	**8.44**	**8.25**
Nylon-66	0.57	0.38	0.24	0.06	**57.46**	**84.38**
HMF	745.17	747.04	735.36	737.23	**1.32**	**1.31**
2.5-FDCA	221.06	220.11	142.83	142.83	**35.39**	**35.11**
Polyamide	2.30	1.68	0.84	0.22	**63.51**	**86.90**
Ethylene Glycol	7.78	6.35	4.65	3.22	**40.24**	**49.32**
PEF	2.77	3.14	1.36	1.73	**50.92**	**44.86**
Sorbitol	5.01	3.45	3.28	1.72	**34.48**	**50.10**
Isosorbide	3.16	3.45	2.87	3.16	**9.10**	**8.33**
PEIF	0.78	2.60	0.55	0.11	**29.83**	**95.60**

During the calculations that were made in order to build the table 51, in the CIMV process were included the thermal streams of C5-Hydrolysis and C6-Hydrolysis. This decision was made in the basis that in the real life CIMV process the hydrolysis of the C5 and C6 sugars is implemented in it.

Finally, the energy cost as it was calculated based on the analysis that took place in this chapter and for the optimum combination of utilities along with the investment and operating cost of each process are shown in table 52.

Table 52: Investment, operating and energy cost of each process and total annual cost of each final product in the biorefinery

Process	Annualized Investment Cost(million Euros/yr)	Operating Cost (million Euros/yr)	Energy Cost (million Euros/yr)	Total Energy cost of the final product (million Euros/yr)
CIMV	$18.83*10^{-5}$	56.50	2.63	2.63
Oligomers-Activated Carbon	$2.36*10^{-5}$	2.90	1.09	1.09
Furfural	$3.67*10^{-5}$	17.96	0.47	7.423
Furamine	$9.12*10^{-5}$	2.84	0.003	
Diisocyanate	$16.25*10^{-5}$	7.15	6.95	
Butanetriol	$7.41*10^{-5}$	46.5	50.54	50.87
Trinitrate	$43.13*10^{-5}$	4.41	0.33	
Glucaric Acid	$381.73*10^{-5}$	0.94	0.09	1.19
Adipic Acid	$13.72*10^{-5}$	0.69	1.08	
Nylon-66	$2.87*10^{-5}$	0.87	0.02	
HMF	$3.68*10^{-5}$	191.9	41.41	50.86
2.5-FDCA	$38.37*10^{-5}$	41.99	9.39	
Polyamide	$36.46*10^{-5}$	1.51	0.06	
Ethylene Glycol	$32.94*10^{-5}$	2.69	0.37	51.66
PEF	$1.85*10^{-5}$	1.78	0.12	
Sorbitol	$6.66*10^{-5}$	1.59	0.28	51.37
Isosorbide	$3.06*10^{-5}$	1.02	0.25	
PEIF	$4.30*10^{-5}$	1.62	0.04	

The investement cost was annualized by assuming, like in Osmose, that the biorefinery has an estimated lifetime of 25 years, and it is under full operation for 8760 hours per year. The total energy cost for the production of each final product is calculated by adding the energy cost of each individual process which participates in its production. It has to be noted that for the production of PEF, where 2,5-FDCA is also input, the energy cost of the HMF and 2,5-FDCA process is included. With the same logic, ethylene glycol and 2,5-FDCA are used as input for the production of PEIF, as a result their energy cost will be included in the calculation of the total energy cost for the production of PEIF.

10. CONCLUSIONS AND COMMENTS ON THE RESULTS

In this thesis, a lignocellulosic biorefinery was designed and integrated by using two different approaches. The importance of the development of a biorefinery which uses lignocellulosic feedstock has already been pointed out extensively. The abudance of this kind of feedstock makes this field lucrative for a full extent research. As these chemical paths are in an early development stage, it is very important to start having a more completed image on the cost-efficiensy and sustainability of each process. If these chemical routes are developed completely, the world industry is going to be extremely beneficiated, as many of the final products in this biorefinery can substitute fossil fuel-based materials which cover a considerable size of the market. For example, PEF is already being used instead of the plastic PET efficiently. The results presented in this thesis can be used to get a feeling of the possibilities and the barriers arising during the development of these chemical paths.

Of course, it has to be pointed out that during this simulation of the biorefinery plant there are some deviations from reality. When designing processes in Aspen Plus V7.2, many approximations have to be made regarding the properties of the chemicals and the process conditions. Also, the energy and mass losses which are recorded in a real life biorefinery due to the equipment are not taken into consideration. The most important in this thesis is to get a grip of the cost effectiveness and the amount of energy needed for building these processes.

Osmose – Lua provided us with results regarding the energy cost of the production of each final product, as well as the possible profit that each final product might arise. It is mentioned again that it is assumed that the capacity of the final products can be absorbed from the market and that the whole amount of the intermediates is used for the production of the final product. As it is observed, the only final product which is profitable is Nylon-66. However, after the energy integration the most energy is saved during the production of PEIF and PEF. There is an explanation for that. In order for PEF and PEIF to be produced, more than one intermediates of the biorefinery tree is combined. For the production of PEF, the whole amount of 2,5-FDCA and ethylene glycol is used, whereas for the production of PEIF 2,5-FDCA, ethylene glycol and isosorbide is used. When the chemical path regarding any of these two chemicals is integrated, the production processes of all the intermediates used as resources are integrated in a big Grand Composite Curve.

On the other hand, we have to accept that an approach like this is not completely realistic, as it is impossible in a real life biorefinery for all the streams of a chemical path to be able to exchange energy with one another. There are some restrictions due to the kind of equipment which is being used and the distance between each process of a chemical path. Just because the production of one chemical leads to the production of another, the respective industrial plants are not necessarily located next to one another.

Moreover, as you can see in table 44, the final product with the less damage is diisocyanate. With some adjustments in the utilities or the resources used, it can be the second to reach a positive amount of profit.

During the transshipment method, each process was integrated individually and several combinations of utilities where applied in order to define the most economic one. The cold utilities in 25˚C, 0 ˚C, -15 ˚C and -30 ˚C as well as the high pressure steams in 345˚C, 445˚C and 545˚C were included in all the combinations. The triplet of the low pressure steams which proved to be the most economic included the levels of 100˚C, 120˚C and 160˚C. The cost of the 10 utilities used in total reached 115.086 million Euros/MW/yr. As it can be observed in the table 48, the total energy cost increases significantly each time the lower level of steam increases. The most economic utility combinations are the ones which contain the utility of 100˚C. When the lowest steam level is 120 ˚C the cost increases rapidly by almost 3 million euros. The same happens when 140 ˚C becomes the lowest steam level. The energy cost increases by almost 2 million euros. These changes in the energy cost according to the combination of utilities can be better indicated in the figure 25.

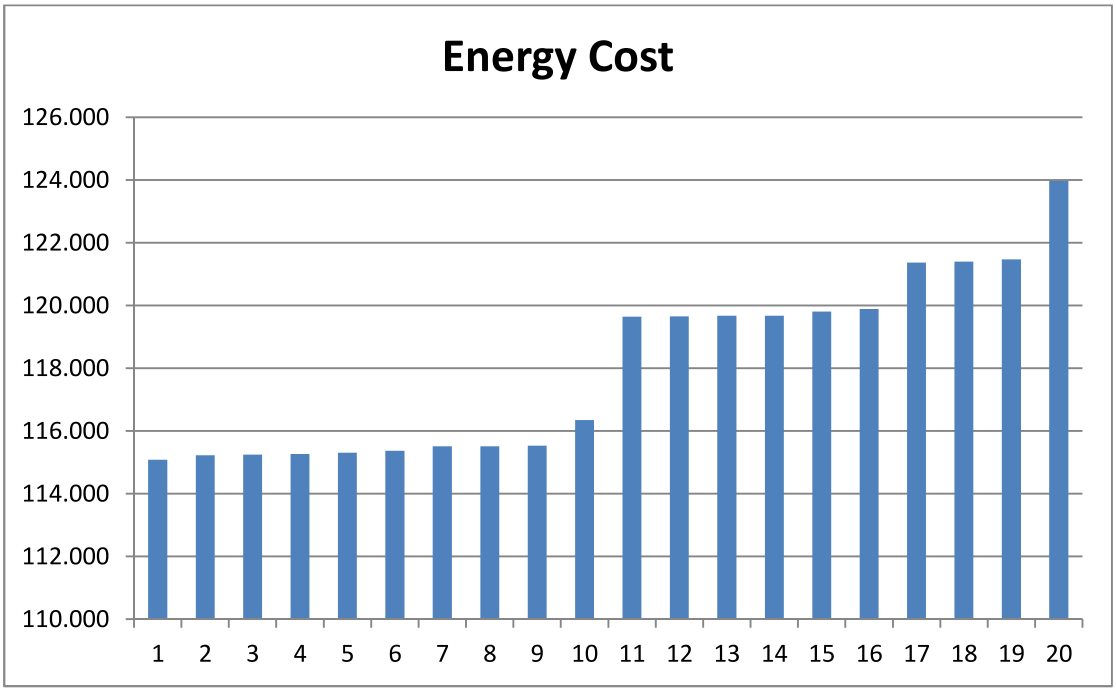


Figure 46: Differentiation of total energy cost according to the combination of utilities

Apart from which combination is the best, the model which was constructed in GAMS gave us the opportunity to know the size of each level of utility for each process. Without this information, it would not be possible to calculate the energy costs as it was described before.

The most energy savings are identified during the production of furfural, furamine and polyamide. On the other hand, during the production of diisocyanate, butanetriol, trinitrate and 5-HMF, the energy savings resulting from the energy integration are quite small. This is confirmed by the large energy cost of the utilities needed to cover the energy need of these processes. In figure 47, there is a schematic presentation of the total energy cost of each final product.

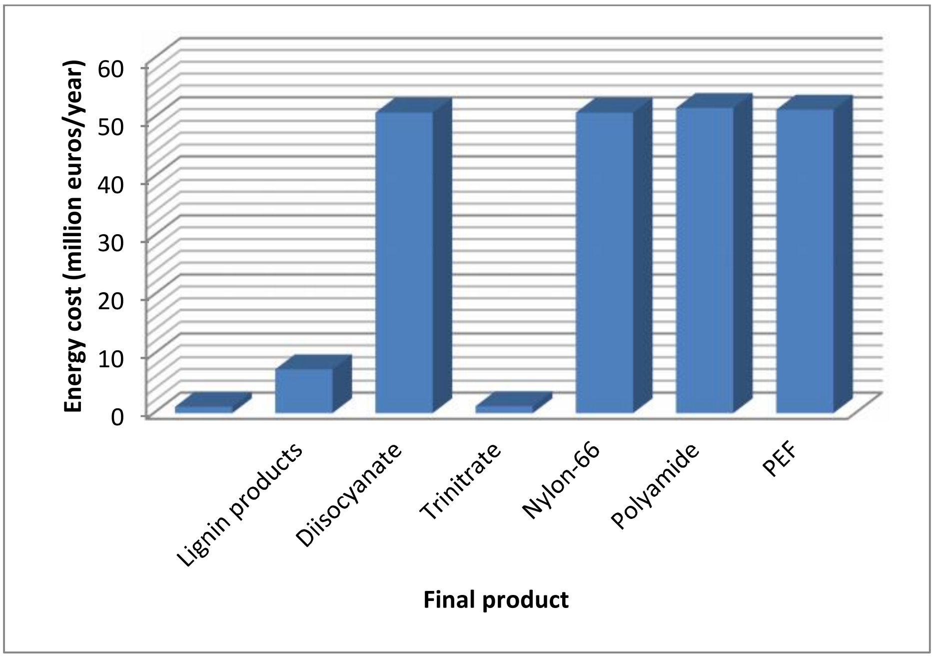


Figure 47: Graph presenting the energy cost for the production of each final product

Additionally, according to table 52, the final product with the less total annual energy cost is nylon-66, the same product which resulted in profit in the results of osmose. Thus, it can safely be deduced by both methods, that the most cost-efficient final product is nylon-66.

Although Osmose is a very handy integration tool, easy to become familiar with, it has one major disadvantage. If the user wants to find the most economic combination of utilities between a series of different levels, he has to make tests by changing the input and then compare the economic results. On the other hand, the model constructed in GAMS based on the transshipment model can do this job automatically. This is a huge advantage, especially when the amount of data is quite big and not easy to handle. Also, as it was already mentioned, the energy integration of a whole chemical path in one grand composite curve is thermodynamically possible, but not realistic.

However, the results provided for the energy integration and the profit of each final product are considered reliable and can be used to make decisions on how to proceed further in the designing of a process. It also offers services which extend to a much wider field, such as the estimation of the environmental impact, information which can be of great use to the designer.

Future Goals

The analysis made until now, provided the possibility to calculate the minimum energy demands of each process, which derive from their individual energy intergration between their streams. However, when a number of processes is included in a larger industrial unit, like the biorefinery, it is possible to integrate the processes between each other.

Usually, in an analysis like this, the heat transfers indirectly from one process to another by using a means of heat transfer, like steam. Practically in every industrial plant production and consuming of steam in different levels of pressure is observed. These levels of pressure are of course specified for each process. Thus, by using an appropriate system, an amount of steam which is produced during a process can be used to cover the energy needs of another, if it has the suitable pressure level.

It is obvious that an approach like this would reduce even more the energy demands and thus the energy cost of the biorefinery. It is a promising expansion of the problem which was studied in this thesis, worthy of attention.

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12. APPENDICES

12.1 Appendix A-Thermal and mass data of CIMV process

Table 53: Capacity of the CIMV process

Capacity (kg/hr)	C5_Output	C6_Output	Lignin
C5	2556	1067	0
C6	243	6493	0
Lignin	0	0	3047.06
Citric acid	3374	0	1474.58
Water	3322	30664	2421.79

Table 54: Thermal data of CIMV process

Stream	Tin (℃)	Tout (℃)	DeltaH (MW)	Description
1	105.0	105.0	4.20	Hot
2	105.0	103.0	8.05	Hot
3	90.5	85.0	3.85	Hot
4	101.8	100.4	2.08	Hot
5	41.1	31.5	1.05	Hot
6	80.0	61.1	0.41	Hot
7	61.0	25.0	1.35	Hot
8	105.0	85.0	8.10	Hot
9	85.0	75.9	0.22	Hot
10	67.5	59	0.25	Hot
11	71.0	15.0	0.98	Hot
12	85.0	85.0	0.00	Hot
13	99.8	82.1	0.41	Hot
14	102.0	100.0	0.01	Hot
15	137.6	85.0	0.06	Hot
16	110.5	71.0	0.89	Hot
17	102.9	80.0	1.05	Hot
18	102.9	100.0	0.09	Hot
19	74.2	74.2	3.3	Hot
20	71.2	71.2	3.3	Hot
21	69.3	69.3	3.3	Hot
22	80.8	80.8	4.5	Hot
23	79.9	79.8	4.5	Hot
24	127.6	127.6	17.0	Hot
25	113.5	113.5	17.0	Hot
26	73.0	105.0	10.96	Cold

27	85.0	85.0	2.49	Cold
28	102.4	102.4	2.00	Cold
29	66.6	90.0	2.90	Cold
30	61.0	90.0	0.99	Cold
31	21.9	73.0	1.09	Cold
32	19.9	85.0	2.12	Cold
33	26.3	85.0	2.35	Cold
34	85.0	109.0	2.50	Cold
35	85.0	99.8	0.35	Cold
36	80.3	99.6	4.62	Cold
37	15.0	151.9	1.18	Cold
38	79.8	99.5	0.32	Cold
39	100.0	100.0	0.01	Cold
40	59.0	60.0	0.02	Cold
41	75.8	102.9	3.28	Cold
42	102.9	105.0	11.54	Cold
43	76.7	76.8	3.3	Cold
44	73.2	73.2	3.3	Cold
45	70.2	70.2	3.3	Cold
46	82.4	82.4	4.5	Cold
47	80.3	80.3	4.5	Cold
48	142.9	142.9	17.0	Cold
49	126.8	126.8	17.0	Cold

Table 55: Thermal and mass data of C5-Hydrolysis

Capital Cost (mil. Euros)	2.610			
Operating Cost (mil. Euros)	1.226			
Capacity of Xylose stream (kg/hr)	**Water**	**Xylose**	**Glucose**	
	1953.90	2875.49	267.30	
Stream	**Tin (℃)**	**Tout (℃)**	**DeltaH (MW)**	**Description**
1	105	25	-4.53785	Hot
2	33.95	60	0.28513	Cold

Table 56: Thermal and mass data of C6-Hydrolysis

Capital Cost (mil. Euros)	4.050			
Operating Cost (mil. Euros)	1.500			
Capacity of Glucose stream (kg/hr)	**Water**	**Xylose**	**Glucose**	
	2089.17	1091.25	5771.54	
Stream	**Tin (℃)**	**Tout (℃)**	**DeltaH (MW)**	**Description**
1	105	25	-20.00914	Hot
2	90	60	-1.18023	Hot

12.2 Appendix B - Individual integration in GAMS

Individual integration in GAMS

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*******************************************************************
Sets
        int temperatures          /1*298/
        k   interval              /1*297/
        i   hot stream            /1*25/
        j   cold stream           /1*24/
        p   number of processes   /1*20/
        m   hot utility           /1*9/
        n   cold utility          /1*11/;
*******************************************************************
Parameter tint(int).thin(p.i).thout(p.i).qhs(p.i).tcin(p.j).tcout(p.j).qcs(p.j);
$libinclude xlimport tint    input.xlsx input!s3:ld4
$libinclude xlimport thin    input.xlsx input!s6:ar26
$libinclude xlimport thout   input.xlsx input!s28:ar48
$libinclude xlimport qhs     input.xlsx input!s50:ar70
$libinclude xlimport tcin    input.xlsx input!s72:aq92
$libinclude xlimport tcout   input.xlsx input!s94:aq114
$libinclude xlimport qcs     input.xlsx input!s116:aq136
*******************************************************************
parameter cs(m) hot utility cost   ;
*ME/ME/yr
cs("1") =0.0648             ;
cs("2") =0.0645             ;
cs("3") =0.0641             ;
cs("4") =0.0596             ;
cs("5") =0.0544             ;
cs("6") =0.0482             ;
cs("7") =0.0451             ;
cs("8") =0.0429             ;
cs("9") =0.0365             ;
*******************************************************************
parameter cw(n) cold utility cost    ;
cw("1")  =0.0596             ;
cw("2")  =0.0544             ;
cw("3")  =0.0482             ;
cw("4")  =0.0451             ;
```

```
cw("5")  =0.0429                ;
cw("6")  =0.0365                ;
cw("7")  =0.0191                ;
cw("8")  =0.0562                ;
cw("9")  =0.1083                ;
cw("10") =0.2242                ;
cw("11") =0.4242                ;
************************************************************************
parameter SK(m) interval that hot  utility is applied
/1 1   . 2 23   . 3 43 . 4 93 . 5 101 . 6 111 . 7 129 . 8 142 . 9 182  /  ;
parameter WK(n) interval that cold utility is applied
/1 82   . 2 98   . 3 102 . 4 126 . 5 136 . 6 159 . 7 275 . 8 286 . 9 288 . 10 291 . 11 297 / ;
************************************************************************
parameter QH(p.i.k).QC(p.j.k) ;
loop(p.
loop((int.k) $ (ord(int)=ord(k) and ord(int)<>card(int)).
      loop(i.
            if( (tint(int)<=thin(p.i) and tint(int+1)>=thout(p.i)).
               QH(p.i.k) = qhs(p.i)/(thin(p.i)-thout(p.i)) * (tint(int)-tint(int+1))  ;
            );
      );
      loop(j.
            if( (tint(int)<=tcout(p.j) and tint(int+1)>=tcin(p.j)).
               QC(p.j.k) = qcs(p.j)/(tcout(p.j)-tcin(p.j)) * (tint(int)-tint(int+1))  ;
            );
      );
);
);
************************************************************************
positive variables R(p.k).QS(p.m).QW(p.n) ;
variables          cost            ;
*************************************
Equations cascade.obj              ;
*************************************
R.fx(p.k) $ (ord(k)=card(k)) = 0    ;
*************************************
*QS.fx(p.m) $ (ord(m)<>1) = 0 ;
QS.fx(p."2") = 0 ;
QS.fx(p."3") = 0 ;
QS.fx(p."4") = 0 ;
```

```
QS.fx(p."5") = 0 ;
QS.fx(p."6") = 0 ;
QS.fx(p."7") = 0 ;
QS.fx(p."8") = 0 ;
QS.fx(p."9") = 0 ;
******to fix the utilities that you do not want.
*QW.fx(p.n) $ (ord(n)<>card(n))= 0 ;
QW.fx(p."1") = 0 ;
QW.fx(p."2") = 0 ;
QW.fx(p."3") = 0 ;
QW.fx(p."4") = 0 ;
QW.fx(p."5") = 0 ;
QW.fx(p."6") = 0 ;
QW.fx(p."7") = 0 ;
QW.fx(p."8") = 0 ;
QW.fx(p."9") = 0 ;
QW.fx(p."10") = 0 ;
*********************************************************************
cascade(p.k)..    R(p.k-1) + sum(i. QH(p.i.k)) + sum(m $ (ord(k)=SK(m)). QS(p.m))
=e=
            R(p.k)   + sum(j. QC(p.j.k)) + sum(n $ (ord(k)=WK(n)). QW(p.n))  ;

obj..       cost =e= sum((p.m). cs(m)*QS(p.m)) + sum((p.n). cw(n)*QW(p.n))     ;

*********************************************************************
Model HINT /all/              ;
Solve HINT using lp minimizing cost ;
*********************************************************************
display QS.l. QW.l ;
*********************************************************************
$libinclude xldump R.l input.xlsx results!a1
*********************************************************************
```

12.3 Appendix C- Curves extracted from Osmose - Lua

Diisocyanate

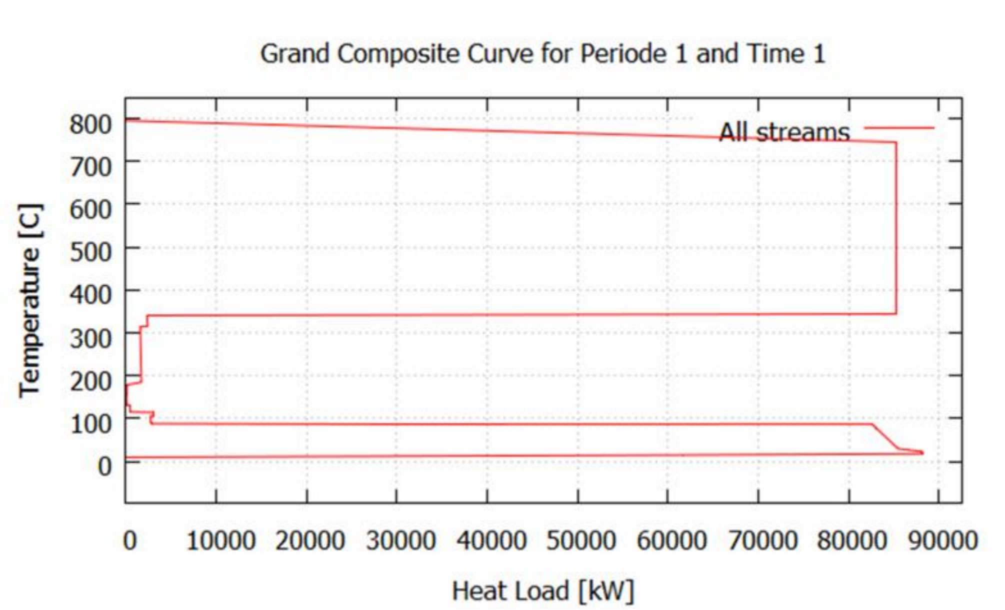

Figure 48: Grand Composite curve of the Diisocyanate production process

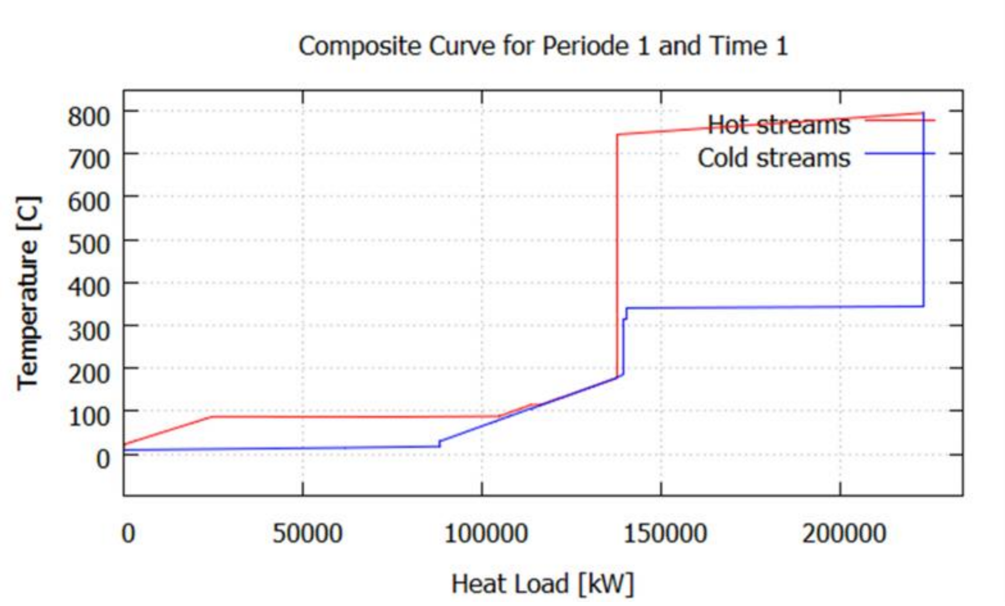

Figure 49: Composite curve of the Diisocyanate production process

Trinitrate

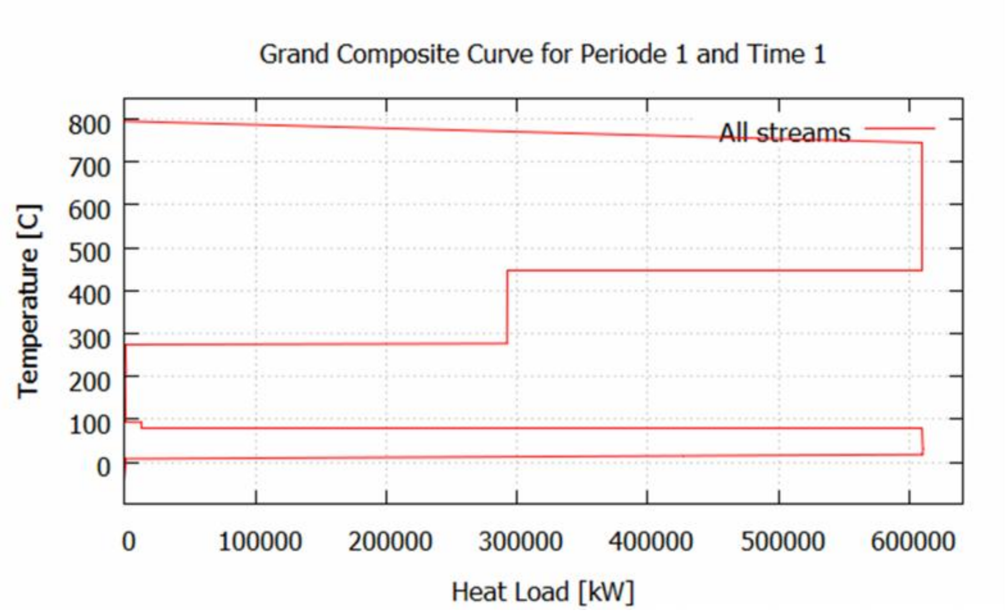

Figure 50: Grand Composite curve of the Trinitrate production process

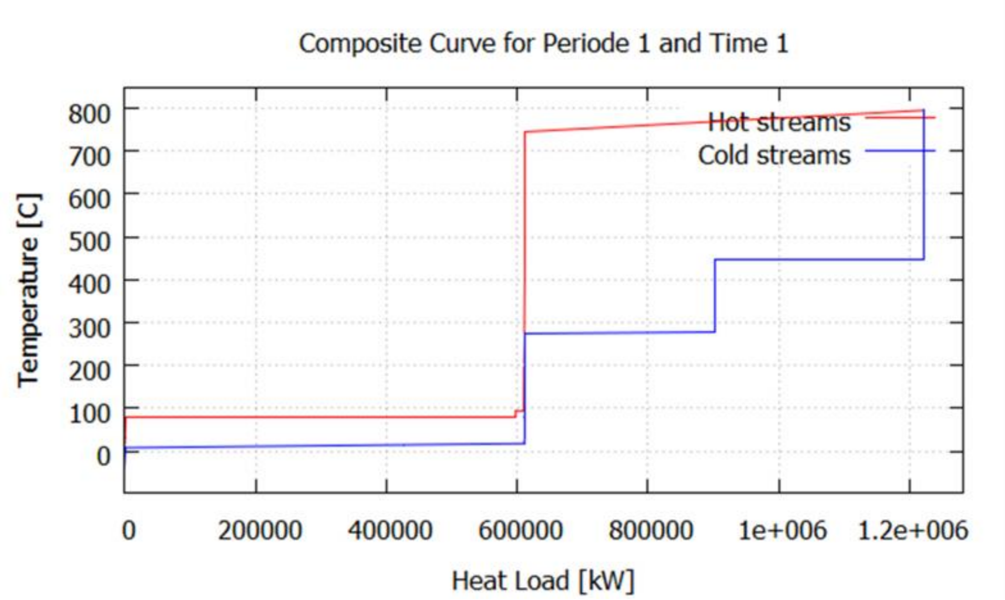

Figure 51: Composite curve of the Trinitrate production process

Nylon-66

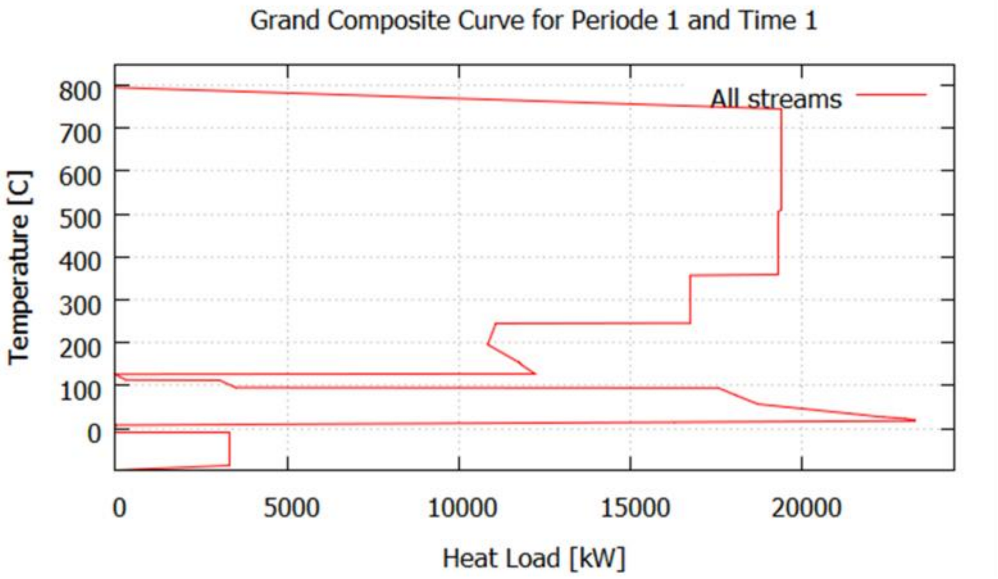

Figure 52: Grand Composite curve of the Nylon production process

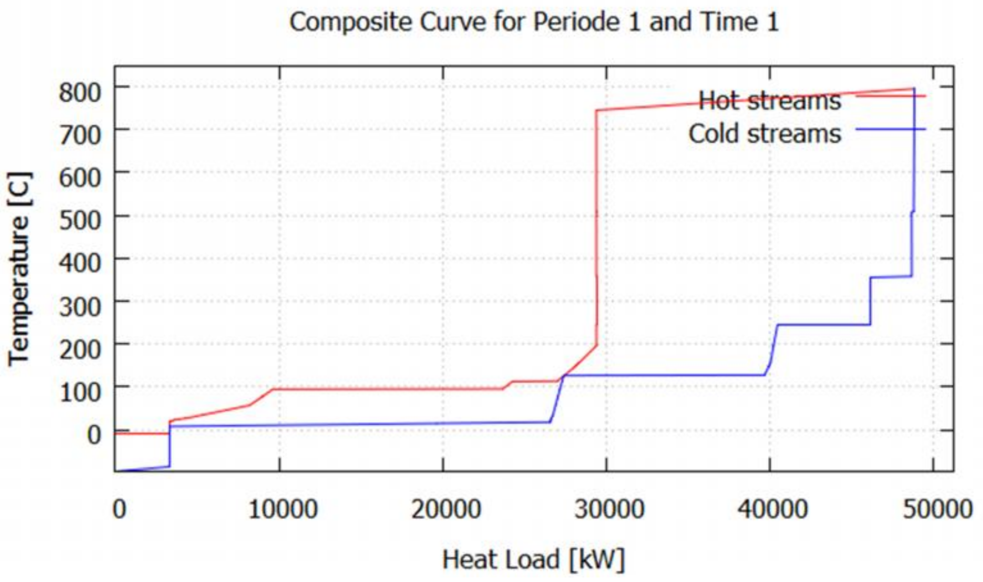

Figure 53: Composite curve of the Nylon production process

Polyamide

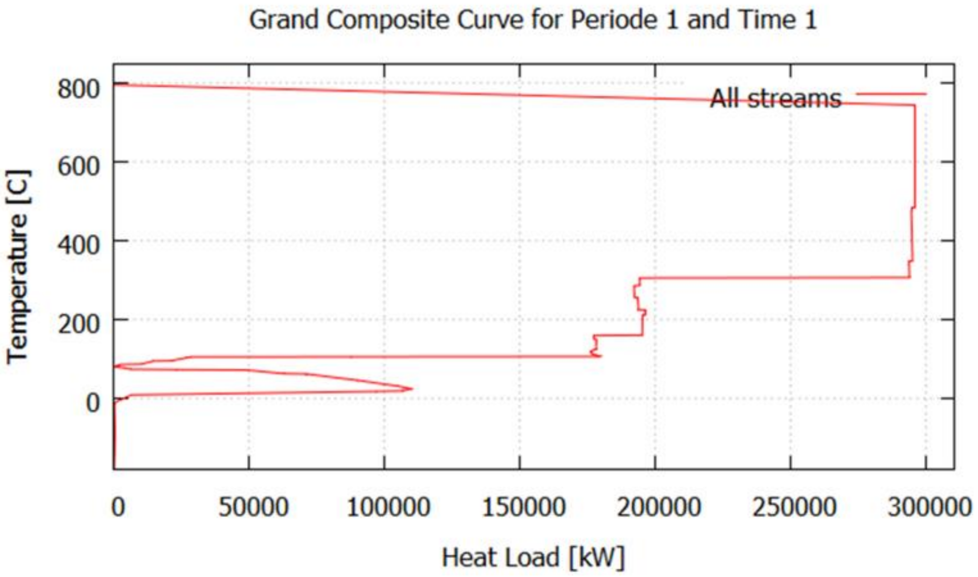

Figure 54 Grand Composite Curve of the Polyamide production process

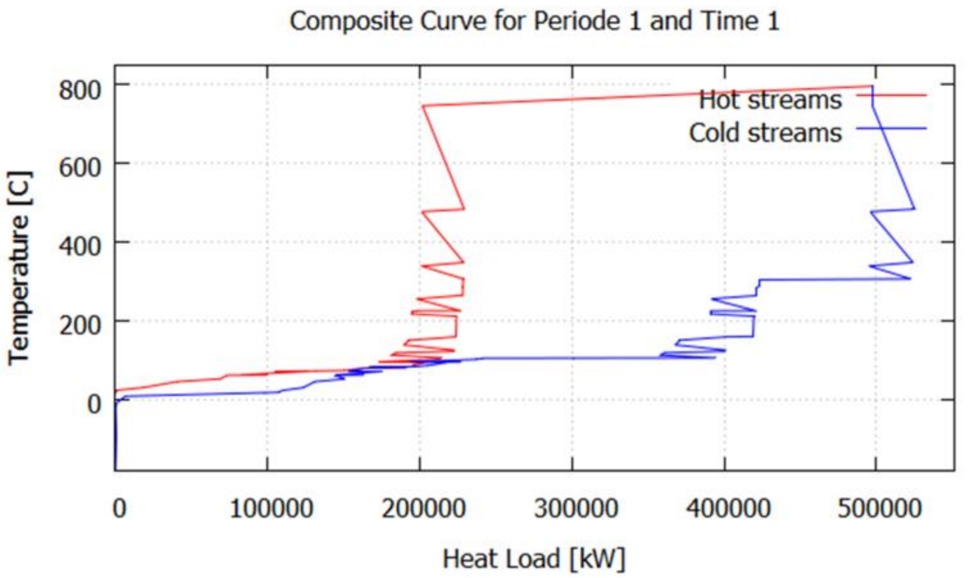

Figure 55: Composite curve of the Polyamide production process

PEF

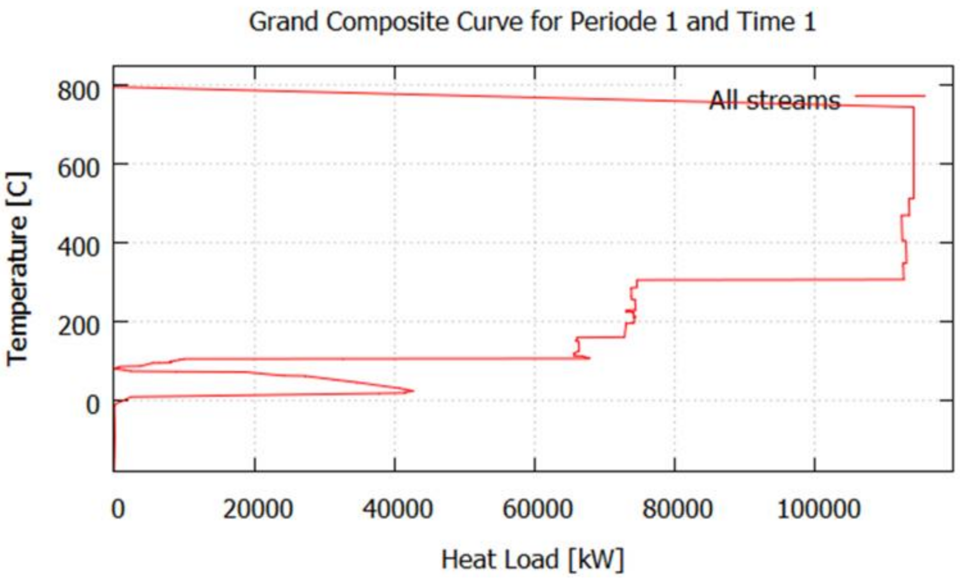

Figure 56: Grand Composite curve of the PEF production process

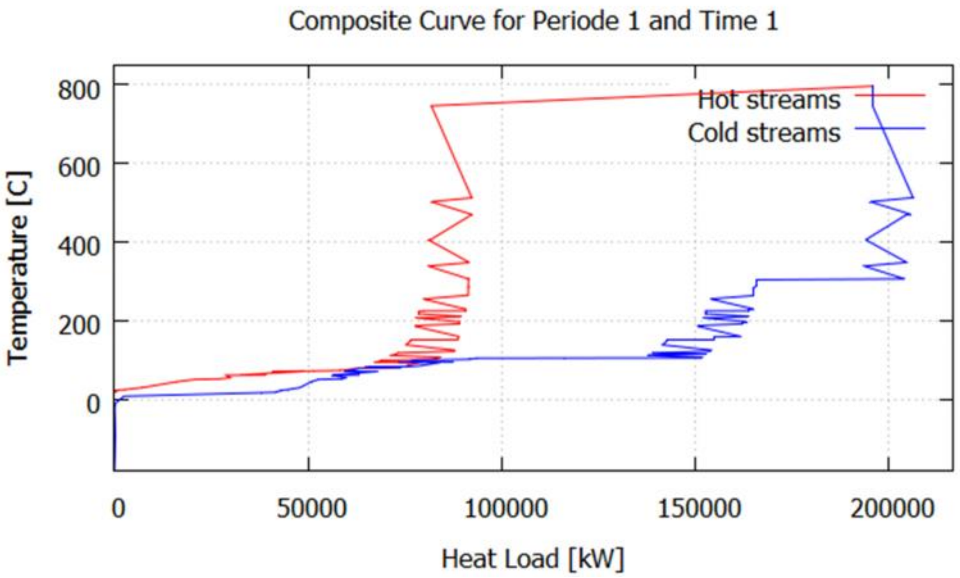

Figure 57: Composite curve of the Nylon production process

PEIF

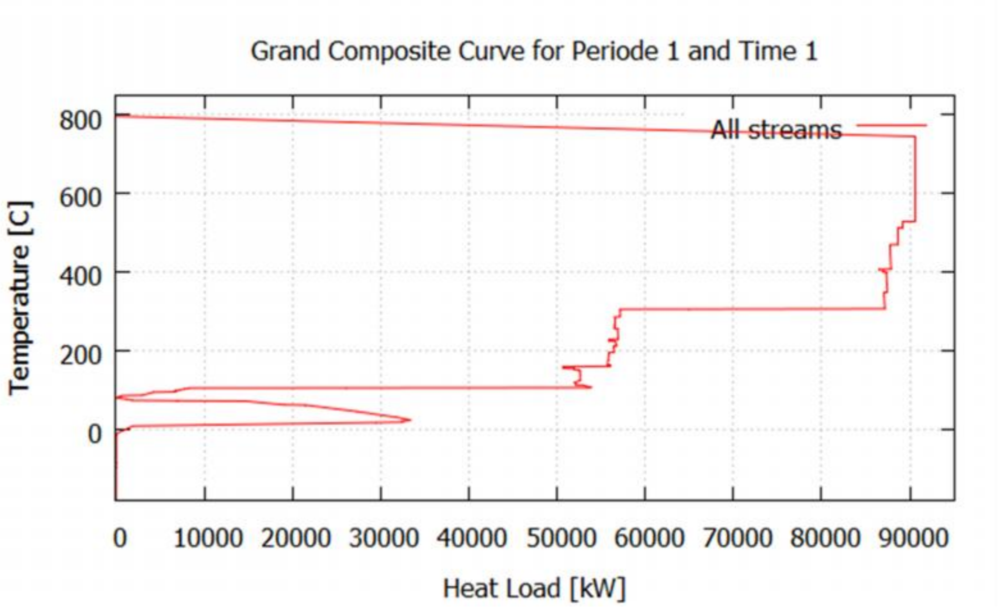

Figure 58: Grand Composite curve of the PEIF production process

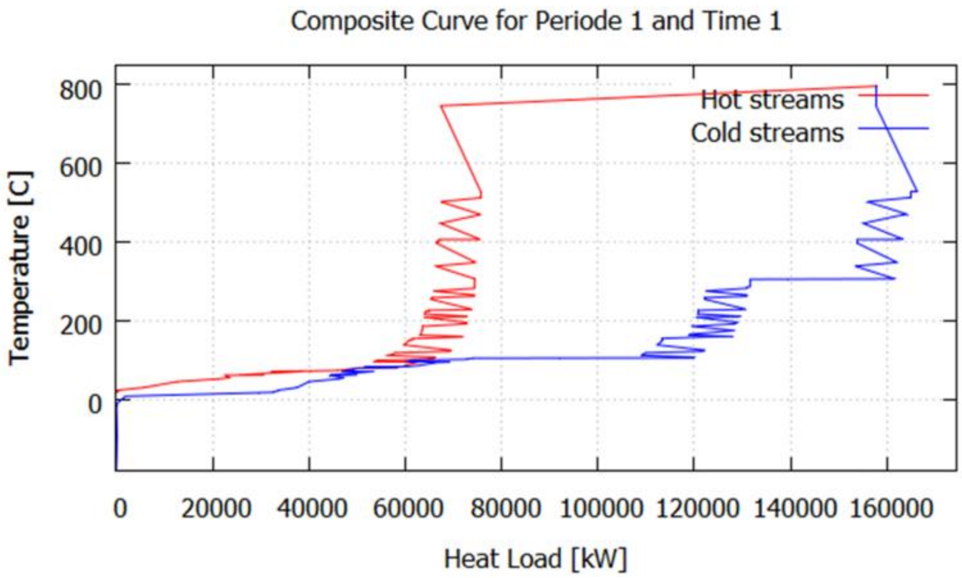

Figure 59: Composite curve of the PEIF production process