

Life Cycle Assessment of platform chemicals

(phenolic compounds, solvent, soft and hard plastic precursors)

from fossil and lignocellulosic biomass scenarios

MASTER THESIS. MARTIN GALLARDO*

ABSTRACT

One of the challenges of our time is the substitution of the existing fossil based economy by a green economy within the framework of sustainable development of our society. Biomass, especially from lignocelluloses, is a promising solution for the substitution of fuels, energy, chemicals and materials from fossil sources in a so called "Biorefinery". The production of biochemicals presents higher mass and carbon theoretical efficiency, and it seems an interesting alternative to provide a renewable path for globally and widely demanded platform chemicals like phenols, solvents (Acetone), soft plastic precursor (Polyethylene) and hard plastic precursor (Polypropylene).

In this report, the environmental loads associated to the production of biochemicals (Phenolic compounds, Acetone, PolyHydroxyButyric Acid and Polylactic Acid) from lignocellulose biomass scenarios (Poplar and Eucalyptus) are evaluated and compared to the petrochemical equivalents. Life Cycle Assessment Methodology and the latest Global Warming Potential Indicator that accounts biogenic greenhouse gas effect related to the rotation period of the feedstock along the entire carbon cycle are used along this study.

Biochemicals production could contribute to possible reductions between 37% and 48% on greenhouse gas emissions for the functional unit when taking into account the entire carbon cycle and not only from cradle to gate. Also, up to 80% fossil fuel can be saved while ecotoxicity indicators present much lower values for biochemicals production. PHB seems to be the most environmentally friendly of all the biochemicals, and phenolic compounds the worst. But there are some trade-offs; biochemicals may increase other impact categories such Eutrophication and Acidification, but also Human toxicity, Photochemical Oxidant Formation and Particulate Matter Formation. Last but not least, water depletion is a fundamental issue involved, being substantially higher for biochemicals, even when irrigation of certain wood species may not occur. Decrease of fertilizers and irrigation, new solutions for disposal, treatment and recycling of ash and gypsum, increase of yields and production, energy efficiency techniques and a cleaner electricity mix, could bring the production of biochemicals to an status where they are dramatically better in all impact indicators if all the stakeholders on the life cycle of the biochemicals (Agriculture and Industry sectors, research institutions, policy makers and final customers) get involved.

1 INTRODUCTION AND AIM

1.1 Background

Environmental sustainability is set as one of the Millennium Development Goals by the United Nations (U.N, 2005). From the environmental point of view, anthropogenic causes, like burning petroleum derived fuels and products, are modifying the carbon cycle once we are releasing CO₂ rapidly to the atmosphere from carbons sequestered hundreds of millions years before; hence, some unexpected consequences can be derived of it, like a greenhouse effect on a planetary scale. This is called "Anthropogenic Climate Change".

It is widely accepted by the scientific community and most of the countries and organizations across the world, and it implies a change in the policies of those countries that agreed on the Kyoto Protocol (Kyoto Protocol, 1997). One of the most capable approaches for the achievement of the Environmental sustainability target is the green economy concept, which "*is low carbon, resource efficient and socially inclusive. In a green economy, growth in income and employment should be driven by public and private investments that reduce carbon emissions and pollution, enhance energy and resource efficiency, and prevent the loss of biodiversity and ecosystem services*" (UNEP Green Economy Report, 2011). One of the most promising resources to mitigate climate change is the use of biomass, since it is an effective way of producing a variety of fuels, energy (heat and power) and materials (from wood based elements to biochemicals) decreasing CO₂-emissions (Cherubini, 2010).

* Corresponding author. Tel.: + 47 94260143. E-mail address: martigal@stud.ntnu.no (M. Gallardo).
Supervisors: Anders H. Strømman and Francesco Cherubini. Industrial Ecology, Department of Energy and Process Engineering, Norwegian University of Science and Technology, (NTNU), NO-7491 Trondheim, Norway
Ingeniería Industrial. Universidad Carlos III de Madrid (UC3M).
14th June 2011.

We can define Biomass as abbreviation given to any organic matter of recent origin (then, not fossil) which was derived from animals, plants, fungi and bacteria as a result of the conversion process photosynthesis. Just by taking a look at the European Union Directives biomass should play an important role in the future as part of the solution for a scenario without fossil derived energy and materials since biomass is abundant and accessible resource on the Earth and it can be renewable if well managed (UE Biomass Action Plan, 2005). This approach to substitute petroleum (oil and gas) products is called “biorefinery” (Cherubini, 2010; Demirbas, 2010; Kamm et al, 2006).

1.2 Biorefinery systems

Although the biorefinery feedstock can be provided from different kinds of biomass, in the last years some studies have noticed the potential of lignocellulose (composed mainly by cellulose, hemicelluloses and lignin) for biorefinery purposes. (Cherubini, 2010; FitzPatrick et al, 2010 Hamelinck, 2005; Kamm et al, 2006; Michels, 2010). In-depth studies about crop and wood residues, short rotation wood, Poplar and Eucalyptus production and their ecological implications have been made with the intention of providing lignocellulose to the production of fuels and combined heat and power. (Cherubini, 2010; Da Costa Sousa, 2009; Guest et al, 2010; Karacic, 2005; González-García, S. et al., 2009).

The production of biochemicals from lignocellulose (Phenolic compounds, Acetone, PolyHydroxyButyric Acid and Polylactic Acid) that are able to substitute petrochemicals (Phenols, Acetone, Polyethylene and Polypropylene) is one the feasible scenarios for a biochemical oriented biorefinery in a mid-term perspective. Within this framework, it has been pointed out that the biochemical oriented biorefinery presents the highest theoretical efficiency in carbon and mass terms (Cherubini, F. and A. H. Strömman (2010) and it is interesting from the energetic point of view since we can obtain also biofuels (mainly pyrolytic oil and charcoal) from the waste streams that can be used to cover, at least partially, our energy needs at plant. Different common chemicals from biomass feedstock had been already identified in the previous years. (Haveren et al, 2008; Marshall and Alaimo, 2010; U.S PNNL/NREL, 2004).

It has been already researched life cycle assessment of the biorefinery concept that includes a chemical oriented approach (Cherubini and Jungmeier, 2009), even out of the biorefinery concept, other environmental studies have been made about fermentation of sugars into bioplastics: PHA (Harding et al, 2007) and PLA production (Dornburg, 2006; Groot and Borén, 2010; Vink et al, 2003, Vink et al, 2010), but still they are focused on energy consumption and CO₂ mitigation, mostly carrying out CO₂ accounting starting from the CO₂ sequestration on soil.

This lack of a Full-LCA of a biochemical oriented biorefinery for the substitution of the most important petrochemicals seemed to be a relevant and interesting study for this thesis. This topic, related to lignocelluloses biomass and biorefineries LCA, satisfied the interest of the Industrial Ecology department at NTNU, where this thesis was entirely developed.

1.3 Selection of biochemicals

Petroleum derived resources, like oil and gas, are essential for today’s human society, as 84 million barrels of petroleum derivatives are consumed every day (IEA, 2007), of which 7.8% is converted into petrochemicals. (OECD/IEA, 2005). The Port of Rotterdam is responsible for 4-5% of the total world production of base chemicals (Haveren et al, 2007). Using their data we can estimate an annual production volume of around 300 million tonnes worldwide of petrochemicals. From them, Benzene, ethylene and propylene are massively used in products of our daily life (APPE). In total Benzene, Propylene and Ethylene accounts for around 250 million metric tons and growing, most of the petrochemical production in the world and its possibilities as precursors are multiple and well known, for example, in the production of **Phenols**, **Polypropylene** and **High Density Polyethylene (HDPE)** respectively, which are very interesting and demanded petrochemicals. We have added **Acetone** to our study, for two main reasons, its importance as solvent in multiple processes in the industry, and for the fact of being co-product in the cumene-phenol process.

What we want is a product that has similar properties to act as a platform chemical coming from renewable sources and present environmental advantage. There are two main ways to produce equivalent platform

chemicals to those from fossil derived sources: Arriving to the same chemical structure or finding a chemical that can perform the same duties. In our case, acetone from bioethanol is a clear example of the first strategy, since ethanol fermentation, even from lignocellulose, is a well known process (Lynd, 1996; Olsson, 1994; Stenberg, 1999). There is still interest and current research on developing more efficient processes for 2nd generation bioethanol (Hamelinck et al, 2004; Pfromm, P.H, 2008; Wingren, 2008; Zhu and Pan, 2010). A new path to acetone has been lately patented (Masuda et al, 2011). Polylactic Acid and PHA are examples of the second one. *“Polylactic acid is a promising plastic substitute. PLA is a bio-based, biodegradable polymer with much potential as raw material for food packaging because of its mechanical properties, because its strength, PLA can be fabricated into fibres, films and rods that are fully biodegradable (lactic acid, CO₂) and compostable, having degraded within 45-60 days”* (Kamm et al, 2006). Being renewable, biodegradable and flexible to produce shapes are clear advantages. Studies have revealed also the interesting thermo-mechanical properties of the PLA (Madhavan Nampoothiri et al, 2010). On the other hand, PLA production is a costly and high energy intensive process. It is already produced from corn by Nature Works (United States) and from sugarcane by Purac (Europe/Malaysia). PHB (Poly Hydroxy Butyric acid) is an environmental degradable (to compost) material belonging to the PHA (Poly Hydroxy Alkanoates) family. PHB, and especially P3HB, seem to deliver similar properties than those from Polyethylene. (Kamm et al, 2006). With a theoretical yield of 75% and a fermentation yield of 98%, PHB is a renewable and biodegradable alternative to petrochemicals (European Bioplastics organization), and its main advantage is to be able to be fermented from hemicelluloses (Ramsay et al, 1995; Lopes et al, 2009) being this approach more profitable, but showing lower thermal stability and excessive brittleness upon storage (Huey, C.S., 2006). It is already commercially available from sugar cane (Biocycle, Brazil). Phenolic resins are in between previous approaches since phenolic compounds contain the type phenol, but they are still a potential substitute of petro derived phenols (Kamm et al. 2006). There are several methods (Effendi et al, 2008), but pyrolysis of lignin into pyrolysis oil (Basu, 2010; Gayubo et al, 2010) prior to phenols extraction seems to be an adequate approach (Brehmer et al, 2009; Cherubini and Ulgiati, 2010; Ekerdt, J. G., 2010; Pakdel et al, 1992; Pandey, M. P., & Kim, C. S., 2011;

Pinto, P.C.R. & Borges, E.A., 2011). Some of the advantages that present the production of phenolic compounds are the increase of mass and carbon efficiency in the biorefinery (Mass and Carbon goes to products instead of being burnt) and possible environmental advantages (González-García, 2010), but it yields low quantities (Pandey and Kim, 2011).

Considering that the substitutes can perform the same duties and sometimes surpass performance, we can conclude that the selection proposed is a reasonable approach for the substitution of petrochemicals in a biochemical oriented biorefinery in a mid-term perspective.

2 METHODOLOGY

2.1 LCA Methodology

“Life Cycle Assessment is a technique [...] compiling an inventory of relevant inputs and outputs; and interpreting the results of the inventory and impact phases in relation to the objectives of the study” (International Organization for Standardization). According to the environmental management standards it can be summarized as a tool to assess the environmental impacts of product systems and services, accounting for the emissions and resource uses during the production, distribution, use and disposal of a product (Hertwich, E.G, 2005). The review from Rebitzer and coauthors about LCA is a very spread and solid explanation of the LCA and ISO 14:000 methodology (Rebitzer, G. et al., 2004). The importance of the LCA perspective is to obtain a holistic understanding of the environmental aspects associated with a service or product delivered from a system (Strømman, 2008). The consequence of understanding the relationships within the entire life cycle and the environment make LCA a solid and relevant environmental tool that allows us to transcribe its implications in a clearer way for policy makers and industry leaders (European Commission 6th Environmental Action Programme, 2001; European Topic centre on sustainable consumption and Production; Finzbeiner, 2006).

2.2 Goal of the study and LCA parameters

The objective of this study is to understand deeper the environmental performance of the substitution of petrochemicals by biochemicals from lignocellulose in order to provide a better insight of the processes involved, its related impacts and where potential improvements can be achieved.

The functional unit is “1 unit of platform chemicals composed by:

- 1 kilogram of phenol (Phenols or Phenolic compounds).
- 1 kilogram of solvent (Acetone).
- 1 kilogram of soft plastic precursor (Polyethylene or PHA).
- 1 kilogram of hard plastic precursor (Polypropylene or PLA)”.

The Carbon Cycle follows the indications for the biogenic Global Warming Potential lately researched (Cherubini et al., 2011). For LCIA (Life Cycle Impact Assessment), ReCiPe Method (Hierarchical perspective) was chosen for Impact Assessment, selecting ten most relevant indicators to show the main results. Software used was the LCA GUI Software developed at Industrial Ecology at NTNU (Norwegian University of Science and Technology). Wherever possible the Life Cycle Inventory includes relevant and consistent data obtained from petrochemical companies, the rest is based on the EcoInvent Database (EcoInvent) and scientific sources. Exergy allocation for the cumene-phenol plant, and Energy allocation for waste streams combustion. No further specific allocations. No explicit cutoff criteria. All available weight information is processed. The results were compared to the EcoInvent database for petrochemical

productions, and other scientific papers and references in the discussion part.

2.3 System boundaries and location

- WTG: Well to Gate for petrochemicals. Delivery unit: 1 kg of phenols, 0.63kg of acetone, 1 kg Polyethylene and 1 kg Polypropylene
- FTG: Field to Gate for biochemicals. Input unit: 1 kg dry lignocellulose (Poplar or Eucalyptus).

It is not include any end-of-life scenario in which the sub products of these platform chemicals are disposed, incinerate or recycled due to the wide range of sub products and the variability of assumptions, but on the other hand, a carbon cycle approach is considered when dealing with carbon accounting.

Regarding location, Spain was considered to be representative scenario for substitution of petrochemicals. Spain, as large importer of crude oil for its economy, it is highly dependent from fossil based resources. On the other hand, Spanish agriculture sector has been traditionally important for the economy. The amount of agriculture residues from different crops is a potential source of lignocellulosic material for the production of biochemicals in Spain.

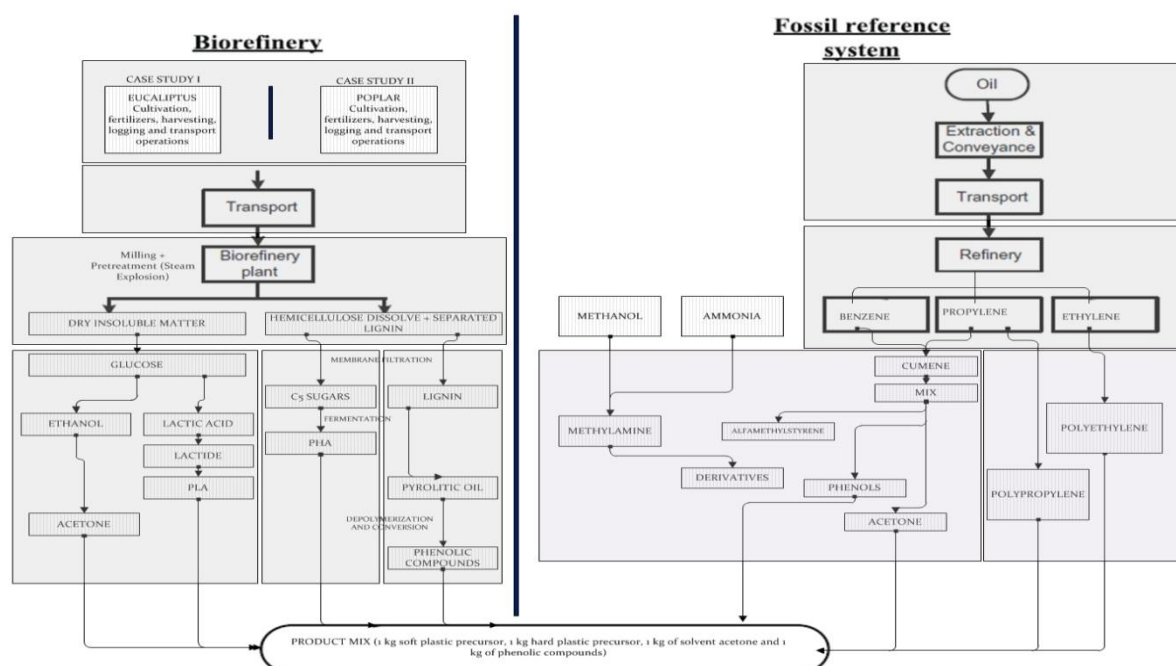


Figure 1: Flow diagram of both scenarios

2.4 Biogenic Global Warming Potential Indicator

A “Cradle to Gate” approach seemed to be unequal to the scenarios, being quite favorable to the petrochemicals since most of their carbon remains from the feedstock into the products of the functional unit. This meant that we were taking into account most of the carbon for biochemicals before gate and few of the carbon for petrochemicals till the same point, leaving apart external CO₂ emissions related to the production process. But also, the greenhouse gas effect of biogenic CO₂ emissions due to the delay on uptake by the biomass. We need to compare the entire carbon cycle without compromising our system boundaries for the reasons stated before. We will use a method to evaluate the greenhouse gas effect of this biogenic CO₂ (Cherubini et al., 2011), considering that oxidation of all biogenic C takes place within one year after the harvesting of the feedstock.

3 CASES AND LIFE CYCLE INVENTORY

3.1 Biomass scenario

For our cases two main lignocelluloses sources are considered: Poplar (44.70 % Cellulose, 18.55 % Hemicellulose, 26.44 % Lignin, rest made of ash, derivatives and other components) and Eucalyptus (49.5% Cellulose, 27.71 % Hemicellulose, 13.07% Lignin, rest made of ash, derivatives and other components). Heating value is assumed to be similar than softwood for both, 19.3MJ/kg (Cherubini and Strømman, 2010). A reference value of 1% of biomass input converted to ash when combusted and sent to a sanitary landfill is taken (Guest, 2010), assumed to be filtered from hydrolyzate in pretreatment effluent and rectified to 0.9 % to be coherent with our pretreatment and wastewater assumptions. Data about energy usage, herbicides and fertilizing, operation and emissions for 1 kg of dry feedstock produced were taken from scientific literature (Anon, 2003; Delucchi and Lipman 2003; Fan, J. et al., 2011; IPCC, 2006; Gonzalez-Garcia, S. et al., 2009) and can be found in the complete report. Water needed for growing a Populus SRF crop is lower than the consumption of other irrigated crops, as corn, that can compete for the same lands in the Mediterranean area (Sevigne, E. et al., 2011); hence, we will consider that the poplar population can manage without more water than the received from the annual precipitation. The total energy input of this phase is around 1MJ per kg of dry biomass (Eucalyptus). (González-García, S. et al.,

2009; Miranda, I., 2001). Wood as biotic resource is included and the occupation of forest intensive was calculated from the density and annual productivity (11.3 m³/ha) for Eucalyptus, and it was also applied for Poplar. Transportation is modeled as “Transportation service. High load trucks. 28tn lorry” from Ecoinvent database with a value of a 0.130 tkm (tons per kilometer), which is 1 kg delivered 65 km and trip back (130km) of the lorry, consistent with other studies (EcoInvent. Biomass Report). For the pretreatment, mechanical and chemical treatment (Steam Explosion) will be used since it is one of the most used methods in the industry, being successfully applied to several types of lignocelluloses biomass (Da Costa Sousa, 2009; Zhu, J.Y. and Pan, X.J., 2010). It operates “*Spruce 2-10mm wood chips. 5 minutes at 215°C, SO₂=3% in two steps: Step I 2 minutes at 190°C; SO₂=3% and step II 5 min at 210°C SO₂=0%. L/W*” (Zhu, J.Y. & Pan, X.J., 2010). Then pressure is explosively released. The “Liquid to solid ratio” is 1, which means that we need 3% in the liquid fraction, which it is the same as the solid. No recovery of acid (sulphur dioxide) applied, but the alkaline chemicals needed to neutralize the hydrolyzate (Da Costa Sousa et al, 2009) were neglected, this could lead to lower emissions on the pretreatment stage. Consumption of energy per kg dry biomass input is 1.79 MJ heat and 0.18 MJ of electricity, which include chipping (Zhu, J.Y. & Pan, X.J., 2010). Comparing our study with the Ecoinvent process of ethanol from wood where it stated that the respective consumption of electricity and heat per ton of chips over the stage of pre hydrolysis amount to 13.5 kWh and 987 MJ of heat (EcoInvent. Bioenergy Summary Report), which is 0.0486MJ of electricity (27% of our value) and 0.987MJ of heat (54.9% of our value). A membrane filtration is able to separate the hemicellulose (mainly xylose) (Knutsen and Davis, 2004 ;Persson, T. et al., 2010). The dry fraction can be washed and separated into lignin and cellulose. Part of this cellulose, around 10%, must be taken for the bacteria cultivation prior to fermentation, while the other 90% of it goes to saccharification to be converted into glucose, although this can be done in a so called “SSF” or “Simultaneous Sacharification and Fermentation”. Glucose is separated in two equal streams, one for fermentation of polylactid acid and one for ethanol prior to acetone.

For the production of phenolic compounds it has been estimated 75% pyrolysis oil from lignin, a mix of

different chemical compounds having an average phenol content of 32.3%, which can be recovered at an efficiency of 50% (Cherubini, F. & Jungmeier, G., 2009). For the energy input from lignin to aromatics, we follow the estimations of Brehner and coauthors (Brehner et al, 2009). We had to convert their values due to the fact that the conversion rate of their study was 18.5%, while we were using 12.18%, and they were referred to lignin input, but not output. Data only includes requirements inputs from lignin and energy, being 16.22 MJ of heat and 0.59 MJ of electricity per kg of phenol. No capital or other materials considered for the process or the pyrolysis equipment. No waste during the process which is consistent with our mass balance, which gives the waste stream a calorific value for self supply of heat.

For acetone we need to produce ethanol (96%). Also Brehner and coauthors when replacing petrochemicals study the process from fermentation sugars to ethanol, giving C6 sugars (glucose) and C5 sugars (xylose) conversion rate (%) for standard and recent system, and the electric and thermal energy required (Brehner et al, 2009). We have converted their values to fit our study where sugars fermentate into CO₂ (48%) and ethanol (52%), with a yield of 85% and energy consumption of 11.74 MJ of heat and 1.04 MJ of electricity. No wastewater treatment considered as main outputs are water and carbon dioxide. No water

consumption is given in the study, though Kansas State estimates “2.85 gallons of water per gallon of ethanol, produced assuming zero liquid discharge and otherwise current industrial practice data” (Pfromm, P.H., 2008). Therefore, water consumption is estimated on 15.39kg/kg ethanol. For modeling the path from ethanol to acetone we have used the U.S Patent number US 21011/0015445 published on January 20, 2011 and registered by Masuda and coauthors, in which they present a technique for producing acetone in a high yield from hydrated ethanol derived from biomass, without requiring a large amount of energy: “Hydrated ethanol derived from biomass is heated to a reaction temperature of 400°C or higher in the presence of a Zr-Fe catalyst, thereby producing acetone” (Masuda et al, 2011). The value of water was calculated by using the solution composition and ethanol recovery rates. The energy consumption was calculated by the energy required to bring the solution to the operation point and estimating no residual energy recovered, finally being estimated on 6.21 MJ of heat. Due to the efficiency of the process an amount of 0.43 kg/kg acetone of waste streams is produced, of which 0.142kg is CO₂ and 0.286kg is ethanol. Ethanol is not recycled and it is sent to the waste stream to provide heat for the process.

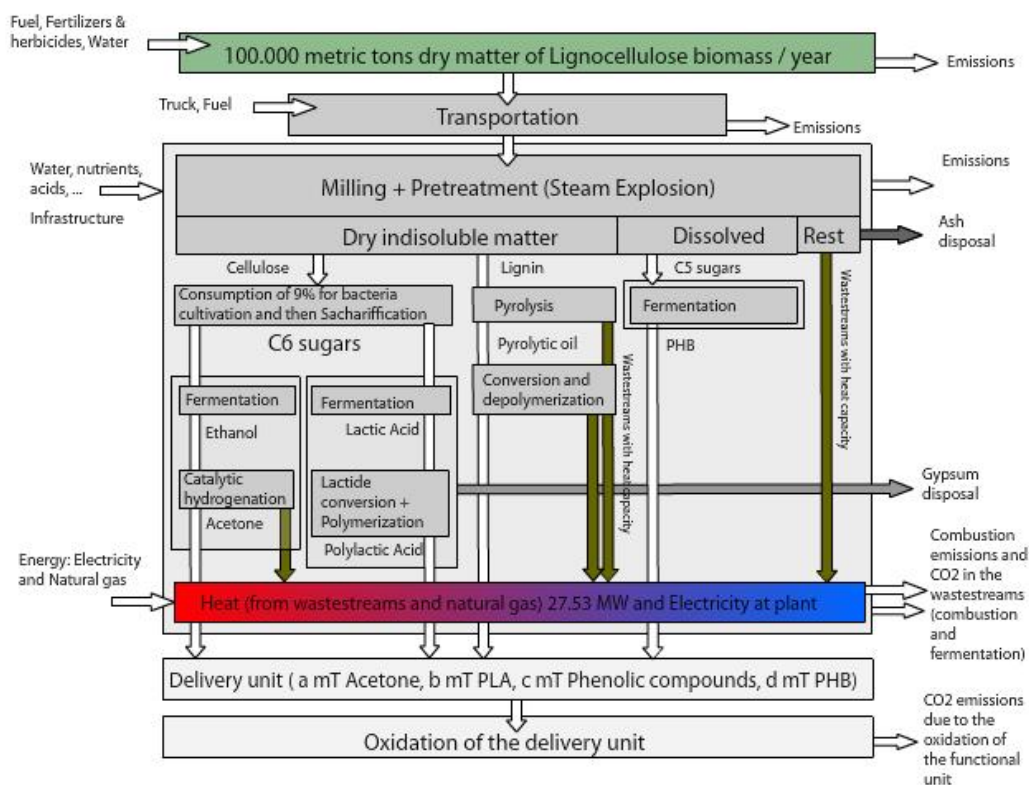


Figure 2: Detailed lignocellulose cases flow sheet

We will use the hemicelluloses as carbon source for Poly hydroxy butyric acid production (Ramsay et al, 1995; Lopes et al, 2009). The production includes other nutrients in the seed media (organism, carbon source, water, nutrients and salts) and fermentation media (carbon source, water, nutrients and salts) plus enzymes in a series of steam sterilization, fermentation reactors, centrifugations and other processes like spray drying and wastewater treatment (Harding et al, 2007). Regarding the production of enzymes, an LCA carried out by Novozymes presents some data about emissions linked to the production of their enzymes (Nielsen, P.H. et al, 2006). Energy consumption is 14.8 MJ of heat and 3.94 MJ of electricity per kg of PHB. More specific data about inputs and direct emissions can be found in the complete report.

For the production of Polylactic acid from Glucose we use the values of energy consumption given of a commercial plant (Vink et al, 2003) that we split into 85% Thermal energy and 15% Electricity, following other studies (Dornburg et al, 2006; Groot and Borén, 2010; Gruber and O'Brien, 2002). Finally an energy consumption of 12.66 MJ of heat and 2.23 MJ of electricity per kg of lactic acid, and 10.88 MJ of heat and 1.92 MJ of electricity per kg of Polylactic acid is estimated. Waste streams and energy consumptions related to other operations and supplies are not taken into account. Water is estimated from the graphs in the study to be around 30 kg per kg of Polylactid acid. 1 kg of dry gypsum is generated per kg of PLA (Dornburg et al, 2006), which is disposed to sanitary landfill.

Energy content of the waste streams was calculated neglecting calorific value of bacteria cells, ash and gypsum (disposed), ... It was assumed 17.37 MJ/kg for the pretreatment residue, a little lower than feedstock calorific value due to the ash. Rest of pyrolysis: 80% charcoal (31.8MJ/kg) + 20% gas (9.2MJ/kg) = 27.28 MJ/kg and 22.5 MJ/kg for the pyrolysis oil not transformed into phenolic compounds (Pakdel et al, 1992). 27.3 MJ/kg for the Ethanol that was not converted into acetone. The energy balance results that 7.77 MJ/kg dry biomass and 4.92 MJ/kg dry biomass input are available for the case of Poplar and Eucalyptus respectively. Meanwhile, our process requires 7.24MJ of heat and 1.1 MJ of electricity per kg dry biomass input for the case of Poplar, and 7.93

MJ of heat and 1.26MJ of electricity for the case of Eucalyptus.

This means that for the case of the poplar we could theoretically cover the demand of heat in plant as we have supposed, but technically we should achieve efficiency in the boiler of around 93%, and we have modeled our boiler (For burning charcoal and pyrolysis oil) with an efficiency of 85% following the indications of the study of green electricity production based on bio-oil co firing in a natural gas fired power station when burning this mix (Biomass Technology Group, The Netherlands). Eucalyptus cannot even cover this demand theoretically due to its lower lignin content. We will then need to supply heat from natural gas (grid) at the facility to match our needs.

- Heat from waste streams (self-supply)
- Heat from outside (natural gas from the grid): EcoInvent database

Our system handles 100000 tons/year, at a rate of 8000 hours/year working hours, gives us 12500 kg/hour, which is the feed rate. We have to provide energy for the worst case, Eucalyptus, which needs 7.93MJ of heat/kg dry biomass. Multiplying by the feed rate we get 9115 MJ/hour or 27.53 MW. Components of the boiler for pyrolysis oil would be: 1 component / (total useful energy in lifetime) per useful energy unit. A scaling factor of 0.7 was applied as effect of the high level of energy production.

Values of emissions per MJ followed the Combined Heat and Power study at NTNU (Guest, 2010) for "*Heat from waste streams (self-supply)*", which used the GEMIS v4.5 database process: "*Small scale CHP: 'woodgas-aCFB-wood-wastes-A 1/2-ICE-cogen 1 MW – 2010/gas'*". Methane emission factor has a very small contribution to the overall greenhouse gas impact (despite the characterization factor is much higher) and it will be neglected since we are considering the whole carbon cycle as CO₂ for the climate change indicator, on the other hand, carbon monoxide is included since it has a important contribution on other indicators such human toxicity.

The last step is modeling the electricity mix of Spain using the report by the Spanish Electric Network "Red Eléctrica Española" for the year 2009 (REE, Annual Report 2009).

It is considered 30 years as operation and capital time for all the processes and their respective annual

volumes starting from 100000 metric tons of dry lignocellulose and applying each absolute yield.

All assumptions and values of inputs and emissions can be found in the complete report, where also the quality and robustness is discussed.

3.2 Petrochemicals

In the Spanish background the petroleum extraction occurs in North of Africa, mainly Argelia, and then, transportation by pipeline (oil) and carrier (LNG) to Huelva, in the south of Spain, where the refinery and petrochemical facilities of CEPSA, S.A. are located. When the crude oil arrives to the refinery is heated in the distillation tower and cracked into different hydrocarbon chains. From heavy naphtha we can extract aromatic components, so called BTX (Benzene, Toluene and Xylene) which contains usually between seven and eight carbon molecules. The gas phase provides ethane and propane, from where we can arrive to ethylene (process such cracking, naphtha steam of hydrocarbons or from LPG) and propylene (dehydrogenation of propane) respectively. The Petrochemical plant of Palos de la Frontera is located only 3km from the refinery of La Rábida, and connected by pipeline. The cumene phenol process or Hock process is an industrial process for developing phenol and acetone from benzene and propylene. Cumene also is converted into cumene hydroperoxide prior to become Phenol and Acetone (Weber and Weber, 2010). We use data from "The Polimeri Europa Cumene-Phenol Processes" (Meyers et al, 2005). The two facilities for the production of Polyethylene and Polypropylene are considered to be located beside the petrochemical plant. Polymerization of ethylene is a widely used process (University of Washington). Similarly to the polymerization of ethylene, polymerization of propylene uses a reactor in which the propylene and the catalyst produce polypropylene. The catalyst used are Ziegler-Natta Catalyst, usually based on Titanium (TiCl₄) or Magnesium (MgCl₂), that are activated with special co catalyst containing organo aluminium compound such as Al (C₂H₅). The two most important technological characteristics of all supported catalyst are high productivity and high a high fraction of the crystalline isotactic polymer they produce at 70-80°C under standard polymerization conditions. As we have seen, various catalysts (catalyst and co catalyst) are needed in the production of polyethylene and polypropylene. The preparation of Titanium tetrachloride from Titanium oxides TiCl₄ is

formed by passing chlorine over a mixture of coke and Titanium dioxide at 800°C. The source of Titanium dioxide is ilmenite, which can contain a 42% of Titanium dioxide in mass. The catalysts needed are produced in the petrochemical plant of Tarragona (Spain) that belongs to the company BASF.

Also, data gathered includes very small quantities of other substances like Acid drainage, Solid and terrain polluted. That was model as a process: disposal, refinery sludge, 89.5% water, to sanitary landfill. Inert residues: Mud from effluents, mud from raw water, non useful metals, urban inert material, Isolation materials, Fluorescents tubes and Hg bulbs, clean plastics, others. Urban and others: Organic urban waste, construction waste, ink cartridges, normal batteries, light packages, electrical/electronic waste

All assumptions and values of inputs and emissions can be found in the complete report, where also the quality and robustness is discussed.

3.3 Carbon cycle in biomass scenarios

Once the rotation period has been defined we obtain the Global Warming Potential for it following the FIRF factor for CO₂eq in 100 years horizon, which is 0.08. Per 1 kg of dry biomass, which is our starting point for the delivery unit, we have 0.494 kg of C. All of this carbon will be combusted or oxidized within one year from the harvest of the lignocellulose biomass. The combustion/oxidation of this carbon follows the formula: $1\text{ C} + \text{O}_2 = 1\text{ CO}_2$. Molar weight of Carbon (C) = 12 gr/mol. Molar weight of Molecular Oxygen (O₂) = 2·16 gr/mol = 32 gr/mol. Molar weight of Carbon Dioxide (CO₂) = 12 gr/mol + 2·16 gr/mol = 44 gr/mol. $0.494\text{ (kg C)} \cdot (44\text{ gr/mol}) / 12\text{ (gr/mol)} = 1.81\text{ kg CO}_2\text{ per kg dry biomass}$. Due to the delay on uptake by biomass growth according to GWPbio: $1.81\text{ kg CO}_2\text{ per kg dry biomass} \cdot 0.08\text{ kg CO}_2\text{eq/kg CO}_2 = \underline{\underline{0.145\text{ kgCO}_2\text{eq per kg dry biomass}}}$.

The characteristics (Name, formula, molecular weight, carbon content, kg production for 1 kg dry lignocellulose input and share of kgCO₂eq) of the product mix are:

- PLA (C₃H₆O₃) (90g/mol) (0.4 kgC/kg) (0.0761 kg) (0.0089 kgCO₂eq)
- PHA (C₄H₈O₃) (104 gr/mol) (0.4615 kgC/kg) (0.742 kg) (0.01 kgCO₂eq)
- Acetone (C₃H₆O) (58 gr/mol) (0.62 kgC/kg) (0.566 kg) (0.01 kgCO₂eq)

- Phenol (C_6H_5O) (152 gr/mol) (0.63 kgC/kg) (0.322 kg) (0.0059 kgCO₂eq)
- Waste streams (0.5) (0.76) (0.1096 kgCO₂eq)

Per kg of waste streams (not taking into account bacteria cultivation, around 5%) the value is 0.15521, and for MJ of waste streams combusted (though some of this CO₂ belongs to fermentation processes) it is 0.0166. We proceeded analogously for the Eucalyptus Case.

3.4 Carbon Cycle in the Petrochemical scenario

Assuming 0.84 kg of C per 1 kg of crude oil, 0.82 per kg C of VGO (Vacuum gas oil) and 0.8571 per kg of ethene gas (Multineer refining characteristic brochure). In our case we remember that VGO is supposed to be equivalent to Natural gas. All of this carbon will be combusted or oxidized within one year from the extraction of the oil and gas. The combustion/oxidation of this carbon follows the formula: $1\text{ C} + \text{O}_2 = 1\text{ CO}_2$. Molar weight of Carbon (C) = 12 gr/mol. Molar weight of Molecular Oxygen (O_2) = $2 \cdot 16\text{ gr/mol} = 32\text{ gr/mol}$. Molar weight of Carbon Dioxide (CO_2) = $12\text{ gr/mol} + 2 \cdot 16\text{ gr/mol} = 44\text{ gr/mol}$.

For each of the components of the feedstock is:

- Crude Oil: $0.84\text{ kg C} \cdot 44\text{ gr/mol} / 12\text{ gr/mol} = \mathbf{3.08\text{ kg CO}_2\text{ per kg crude oil}}$. $2.31\text{ kg of crude oil} \cdot 3.08\text{ kg CO}_2\text{ per kg crude oil} = \mathbf{7.24\text{ kg CO}_2\text{eq}}$
- Vacuum gas oil: $0.82\text{ kg C} \cdot 44\text{ gr/mol} / 12\text{ gr/mol} = \mathbf{3.00\text{ kg CO}_2\text{ per kg vacuum gas oil}}$. $0.612\text{ kg of VGO} \cdot 3.00\text{ kg CO}_2\text{ per kg VGO} = \mathbf{1.84\text{ kg CO}_2\text{ eq}}$
- Ethene Gas: $0.857\text{ kg C} \cdot 44\text{ gr/mol} / 12\text{ gr/mol} = \mathbf{3.14\text{ kg CO}_2\text{ per kg ethene gas}}$. $1.11\text{ kg ethene gas} \cdot 3.14\text{ kg CO}_2\text{ per kg VGO} = \mathbf{3.48\text{ kg CO}_2\text{eq}}$

Total = 12.58kgCO₂eq

4 RESULTS AND DISCUSSION

4.1 Life Cycle Stages

Over the cradle to gate study, the lifecycle inventory calculations indicate, for example, that for most impact categories the pretreatment phase is a

critical process of the production of biochemicals, since it deals with the initial input in the biorefinery. But using structural path analysis methodology we can note down that those impacts are related to the assumption of capital, more in detail, copper extraction, use and disposal in the facility. Cultivation, forest operations and transportation show a moderate contribution to most of the impacts except agricultural land occupation and eutrophication. Phenols are not presented in the graphic because there were model just attending their energy needs, which are represented stand alone. Electricity is an important contributor to several impact categories, especially taking into account that the energy needs in the facility are mainly heat. Import and combustion of natural gas to cover the rest of the heat is not very prominent in the poplar case, since all the heat demand is almost covered, but still we can appreciate a significant impact on fossil and ozone depletion. Disposal of ash filtrated from the sludge has a tremendous impact on freshwater and marine eutrophication, while disposal of gypsum from polylactic acid production contributes significantly to particulate matter formation and acidification. Pyrolysis oil and phenol production are not present since their impacts are just associated with energy consumption.

For the Climate Change Indicator we can observe that the carbon content in the feedstock (CO₂ combustion and CO₂ oxidation) only accounts for an overall 20% of the global CO₂eq along the entire process (16.84% for combustion and 5.4% for oxidation after use), where CO₂ contribution of heat from wastestreams (30.2%) is due to dinitrogen monoxide. The share of this contribution can change substantially due to the GWP factor used when assuming other rotation period, for example, one year rotation period would reduce these values almost to zero, while more than the assumed 20 years horizon would increase substantially the contribution for combustion and oxidation stages.

Freshwater ecotoxicity indicator is formed by disposal of sulfidic tailing from the building demolition (31.99%), pulp plant dismantling (14.81%) and disposal of lignite/coal mining from coal extraction (13.53%/12.91%). Eutrophication indicators as commented are a consequence of ash disposal (>70%) on both cases. Human toxicity is a product of the disposal of sulfidic tailings for the building demolition (46.24%), lignite+coal in the electricity mix (10.14% + 9.6%) and ash disposal

Impact by processes for Biochemicals per kg dry biomass input

Case Poplar (32.2 gr phenols, 56.6 gr acetone, 76.2 gr PLA, 74.2 gr PHB)

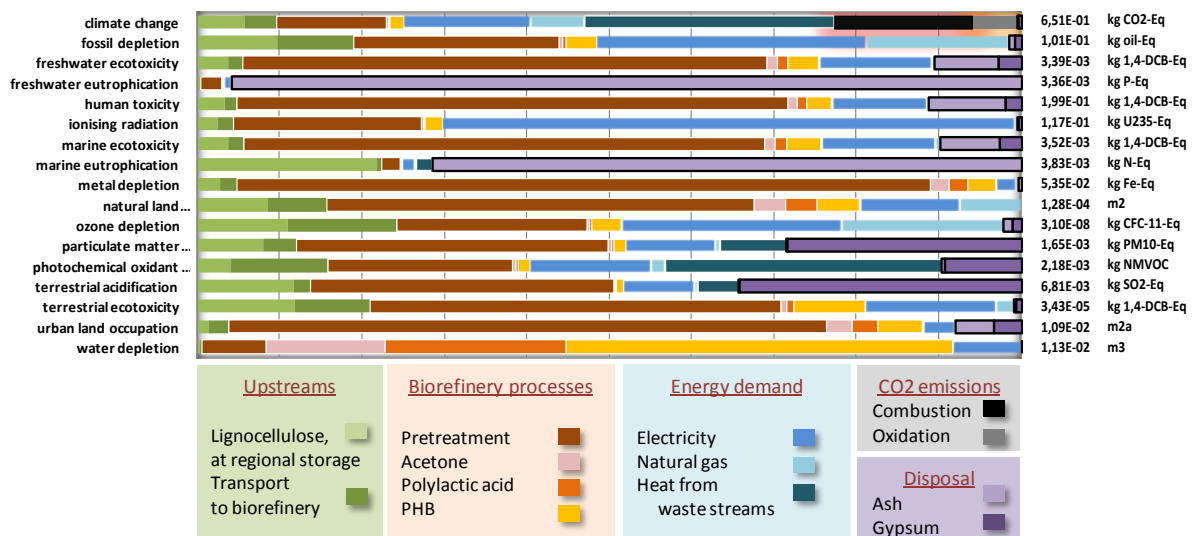


Figure 3: Impacts for the delivery unit of biochemicals (Poplar Case) from field to gate including CO₂ emissions along the entire carbon cycle.

(9.2%). Similar behavior presents marine ecotoxicity indicator. Particulate matter formation is a sum of the impact provoked by disposal of gypsum (28%), production of sulphur dioxide for steam explosion (17%), heat from waste streams (8.12%), burning of hard coal in the electricity mix (8.09%). Meanwhile, Heat from waste streams and wood transportation are main contributors of photochemical oxidant formation, 33.45% and 9.8% respectively, followed by coal in the electric mix (9.2%). Terrestrial acidification indicator is a sum of the disposal of gypsum (34%), and production of sulphur dioxide (20.7%), being the third in importance phosphorus in soil (9.2%). Terrestrial ecotoxicity has as main contributor drilling waste due to gas production (18%), followed by disposal of wood (12.09%). We could also comment that the urban land occupation indicator is covered by biorefinery facility for pretreatment, equivalent to a pulp plant (63.44%), and all fermentation processes, equivalent to an ethanol fermentation plant (8.5%), being the third component landfill (2.9%).

In the Eucalyptus Case we can appreciate that the lignocellulosic production has much more importance than before in the life cycle. This is due to our fertilizing and irrigation assumptions. The second thing we can observe is the increase of impact on diverse categories of the natural gas combustion. This is logical since Eucalyptus has lower lignin content; therefore less available energy in the waste streams.

4.2 Main Results

The results of the comparison revealed that the biochemical system achieves a reduction between 37% and 48% on greenhouse gas emissions for the functional unit when taking into account the entire Carbon Cycle. Contribution to the climate change indicator from petrochemicals are 21.42 kgCO₂eq (of which 7.62 kgCO₂eq from well to gate), 11.1 kgCO₂eq for biochemicals from Poplar (of which 10 kgCO₂eq from field to gate) and 13.4 kgCO₂eq from Eucalyptus (of which 12.8 kgCO₂eq from field to gate). Production of biochemicals presents higher CO₂eq emissions, but products, co products and waste containing carbon from both fossil (higher carbon content) and biomass usually oxidize or combust not later than after one year of use, and this contribution, usually neglected, is fundamental to understand the beneficial effect of biomass derived products on climate change mitigation, which is also linked to the rotation period of the feedstock and the composition of the lignocellulose biomass.

In the table 1 we can find the results of our study for the functional unit for ten different indicators, sorted in the table in four categories:

- Climate change and Fossil depletion
- Water bodies and water depletion
- Human toxicity and air emissions
- Terrestrial impacts

Table 1
Result of the environmental profile of the functional unit for ten different impact categories

Impact category	Unit	Petro chemicals	Biochemicals from Poplar	Biochemicals from Eucalyptus
Climate change	kg CO ₂ -Eq	7.62E+00	1.06E+01	1.30E+01
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	2.14E+01	1.12E+01	1.36E+01
Fossil depletion	kg oil-Eq	8.21E+00	1.75E+00	3.96E+00
Water depletion	m3	2.40E-02	1.63E-01	8.76E-01
Freshwater ecotoxicity	kg 1,4-DCB-Eq	1.92E-01	6.25E-02	9.04E-02
Freshwater eutrophication	kg P-Eq	2.68E-03	6.55E-02	6.62E-02
Human toxicity	kg 1,4-DCB-Eq	1.67E+00	3.70E+00	4.33E+00
Particulate matter formation	kg PM10-Eq	8.13E-03	2.79E-02	2.88E-02
Photochemical oxidant formation	kg NMVO-C	2.87E-02	3.75E-02	4.61E-02
Terrestrial acidification	kg SO ₂ -Eq	2.50E-02	1.14E-01	1.05E-01
Terrestrial ecotoxicity	kg 1,4-DCB-Eq	3.12E-03	6.22E-04	1.31E-03

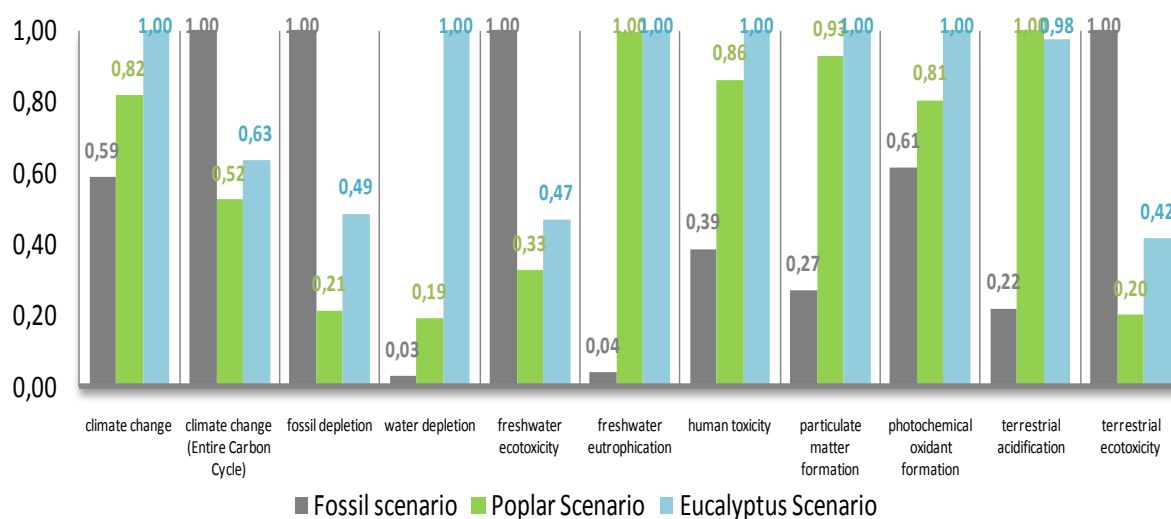


Figure 4: Normalized impact in ten relevant indicators for the different scenarios

4.3 Benchmarking

After disaggregating the functional unit into the different chemicals for benchmarking, we have found that the phenol production both from fossil and biomass is the most pollutant one, while soft plastic precursor (Polyethylene and PHB) present better environmental performance.

4.4 Mitigation approaches

Despite the environmental drawbacks of the biochemical production, a set of mitigation approaches

Biochemicals production could reduce fossil depletion between 50% and 80% since we do not use fossil resources as feedstock, just to provide its part in the electricity mix of Spain and the rest of the heat demand that the waste stream is not able to cover, important when our feedstock has low lignin content. Other improvements are visible in the indicators related to ecotoxicity (freshwater and terrestrial ecotoxicity) but the production of biochemicals also involves some trade-offs. Freshwater Eutrophication and Acidification potential Impacts of the biochemicals are significantly higher than the petrochemical equivalents, mainly due to the disposal of filtered ash from pretreatment and gypsum from Polylactic acid. Water depletion is a function of irrigation procedures, but the Poplar Case (no irrigation) already spends around 140 liters of water more than the petrochemical equivalents in production processes. Human Toxicity, Particulate Matter and Photochemical Oxidant formation also present worse values than petrochemicals.

like scaling up to the actual production of pulp and paper industry (from 100000 metric tons year to 400000 metric tons years) (Borregaard LCA Report), increasing energy efficiency up to 20%, purchasing all the electricity from wind power and a shorter rotation period (could decrease the climate change indicator up to 22%, which is an additional advantage over petrochemicals of around 11%, although other environmental drawbacks of such a substitution are not considered in this study) could decrease at least 50% the environmental impacts on 10 out of 16 Impact Indicators, including Climate Change, Fossil

and Ozone depletion and Human toxicity and Ecotoxicity (Marine, freshwater and terrestrial) potential.

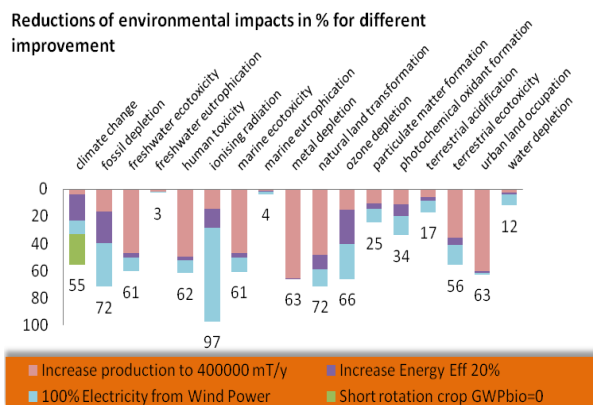


Figure 5: Response of the Impact indicators to possible mitigation approaches (Poplar Case): Scaling up, Energy efficiency, Cleaner electricity and Shorter rotation period.

Dealing with CO₂

CO₂ accounting issues deserves a special section since our methodology for CO₂ accounting differs from other studies does not take into account the biogenic contribution of biomass oxidation. Since most of the carbon from the petroleum feedstock remains in the products, it makes sense that the carbon dioxide emission when the products, whatever petro derived product is, is oxidized (indistinctly how it is oxidized), releases a substantial amount of CO₂. For the case of biochemicals we have “oxidized” most of the carbons (around 70%) in fermentation processes or

combustion to provide heat for the facility, and the others will be oxidized after its use.

The time horizon for oxidation of products, both fossil and bio based were considered one year. Having as reference Polylactic acid (Groot and Borén, 2010), the time frame of CO₂ emission to atmosphere would suit this assumption for the case of incineration (<1month), anaerobic digestion (<1month) and composting (>6month), when landfill (>10years) or recycling scenarios 2-10 years) and were not considered in our study.

On the other hand, some of these plastics (and its carbon) could be incinerated generating other kind of emissions apart of CO₂ that are harmful, and not taken into account whereas all the possible emissions of the combustion of waste streams are accounted for biochemicals and oxidation of some of the bio based products releases just water and CO₂ (PLA and PHB compost processes). This assumptions seemed to be enough representatives for our scenarios.

Following the carbon cycle, first to the ocean, and in a twenty years horizon back (rotation period used was 20 years, a sustainable forest management practice which provide high yield in long term and not exhaust the soil) to the biomass feedstock, this CO₂ will contribute to a greenhouse effect in the atmosphere during its time on it.

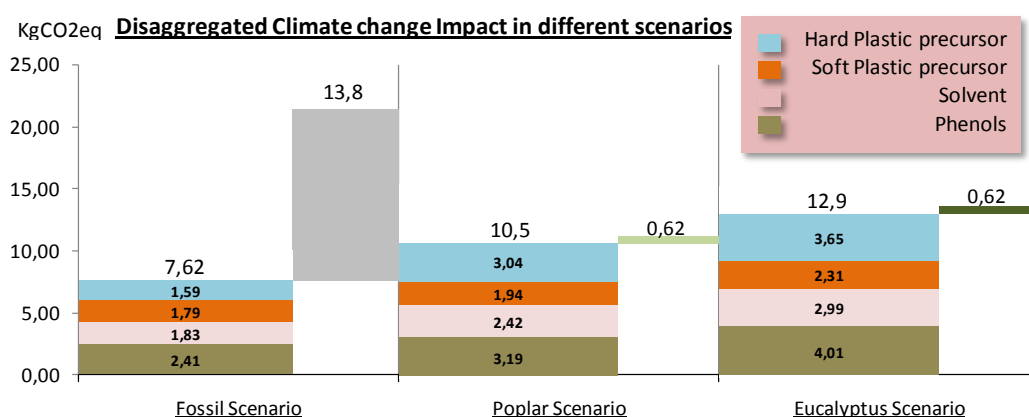


Figure 6: CO₂eq emissions for each component of the functional unit from cradle to gate (left column of each scenario) and from gate to grave (right column of each scenario)

In order to ensure the reliability of our study we have compared our values for soft and hard plastics precursor with previous literature.

Nature Works study of PLA was reviewed by the authors in 2010 (Vink et al, 2010), disaggregating more the results of their previous scientific paper

(Vink et al, 2003). They estimates that the GHG emissions for processes are 3.18 kgCO₂eq / kgPLA (Corn production 0.37 kgCO₂eq (11.6%), 0.36 kgCO₂eq Dextrose, 1.53 kgCO₂eq lactic acid and 0.92 kgCO₂eq polymer), only 2 kgCO₂eq / kgPLA with CO₂ sequestration. In our case we have values ranging from 3.04 to 3.65 and kgCO₂ without

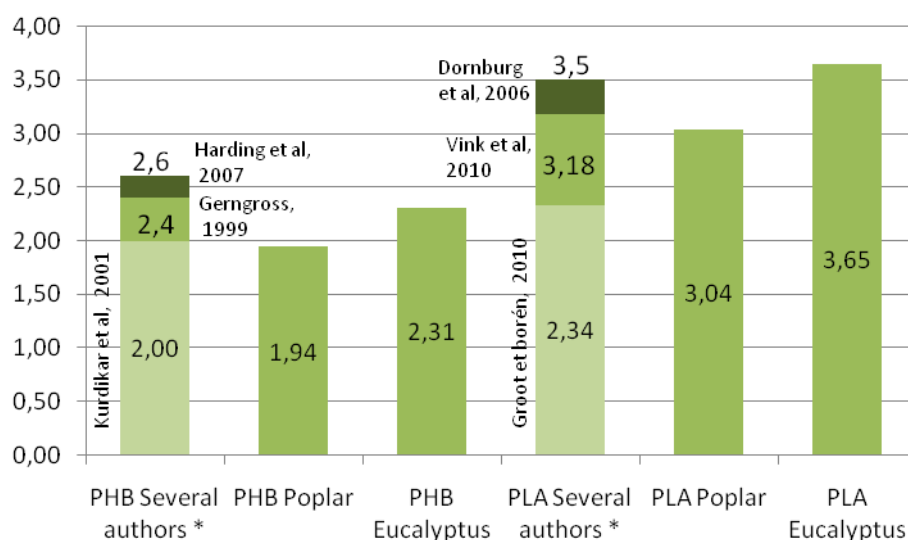


Figure 7: GHG emissions of soft and hard plastic precursor. Cradle to Gate.

taking into counting sequestration but *Cradle To Gate* (between 5-10% of this value is due to the feedstock from lignocellulose, logically a bit lower than the value of 11.6% of the corn production impact).

The minimum CO₂ process emissions of PHB are is 2.34 kgCO₂eq / kg polymer (Groot and Borén, 2010), while for short rotation wood it seems a much higher value, around 3.5 kgCO₂eq / kg polymer than from wheat straw, around 1.5 kgCO₂eq / kg polymer (Dornburg et al, 2006).

It is confirm that PHA production could have lower impacts than PLA production (Kurdikar, 2001; Gerngross Harding et al, 2007), being our results very close to previous research. Values for phenols and acetone from renewable sources were not found. An initial estimation is to compare the values for vanillin (phenolic compound) and ethanol from the biorefinery Borregaard in Norway (Borregaards LCA) with our phenolic compounds and acetone respectively. Vanillin shows a GHG emission impact of 1.13 kgCO₂eq / kg, while our phenols are much higher, 3.19 kgCO₂eq / kg phenols for Poplar and 4.01 kgCO₂eq / kg phenols for Eucalyptus. Ethanol has a climate change impact of 0.335 kgCO₂eq / kg ethanol, while our acetone ranges from 2.24 and 2.99 kgCO₂eq / kg phenols. Such a difference can be a consequence of allocation methods, CO₂ accounting, or overestimation of heat and electricity demand in our cases. Our yield is also very low and possible synergies among processes, like heat recovery, were not considered.

Our study estimates that the energy consumption of biochemicals is 214.14 MJ/Functional unit, 77% of that consumed by petrochemicals (277.07 MJ/Functional unit), being consistent with the values given for PLA, where 54MJ/kg were required to produce PLA from corn, that being compared to the 73.37 MJ/kg needed for the production of Polypropylene (Plastics in Europe) gives us a ratio of 73.5%, which is very similar than ours. It is very important to note down that this energy includes the energy in the feedstock, being the one of the oil (around 45 MJ/kg) much higher than biomass (around 20 MJ/kg). This is an important statement; per functional unit, biochemicals require more process energy than petrochemicals.

5 CONCLUSIONS

5.1 Recommendations for research, policy makers and industry leaders

For the scientific community a more detailed research on the Nitrogen and Phosphorus life cycle must be an area of interest. Authors suggest different values so these implications may have been underestimated. New combustion technologies of pyrolytic oil and charcoal, as well as waste streams, must be researched, accompanied by environmental studies. A further study of the implications of the end-of-life cycle is needed. Recycling rates for phenol and acetone were not taken into consideration, while bioplastics (PLA, PHB) are mainly biodegradable (Carbon Dioxide + Water). A Techno-economic performance of the multiple output approach presented could be consider, since the facility can

adapt to different kind of lignocellulosic biomass, and can prioritize the production of some of the products. The possibility of using some of the infrastructure for multiple processes could be interesting.

When arriving to industrial processes, new pretreatment technologies could reduce cost and environmental impacts. Also, substitution of bacteria fermentation by enzymes could increase production levels and decrease the CO₂ emissions in the production phase, although the climate change along the entire carbon cycle would be same (time horizon of combustion/compostage is less than one year). Gypsum is the main waste of Polylactic acid production, recycling of gypsum for substituting mined gypsum could be interesting from the economic and environmental point of view. At the same time, ash land filling must be re think. 1% of the production is land filled ash, with non neglectable environmental impacts. Efficiency of the systems should be evaluated as potential economic and environmental improvement. Integration of renewable energies in the production could be consider, like wind for the production of electricity in plant (which is low compared to the heat consumption), and solar concentration tubes for the production of steam (which is highly demanded). This is a possible approach especially in southern countries like Spain. In terms of scaling up, investment should not be scarce; arriving to the same production volume of actual pulp and paper (or reconversion of these ones) would reduce substantially the environmental impact per kg of biochemicals.

Decision and Policy making bodies cannot neglect that the biorefinery concept (bioenergy, biofuels, and biochemicals/biomaterials) is one of the anchors of the new green economy, and lignocellulosic biomass must be one of the sources to fuel it. But further implications of the technology related to social, environmental and economic burdens should be understood. Achieving better environmental performance before moving forward at the same time as keeping high incentives and sector attractiveness should be the main objectives. In the light of this, subsidizing product might not be very efficient, whereas reseach support, awarding environmentally friendly practices, innovation and breakthrough technologies, promoting start-ups and regulating the waste management of biochemicals production should be used as possible actuation guidelines.

Last, but not least, we must highlight the role of forest management. Reduction of fertilizing, proper rotation periods and recollection efficiency must be achieved for a long term sustainability of the lignocellulosic biomass. Governments tend to subtract priority from agriculture and silviculture departments, but including this issue in their agenda could bring potential benefits from the environmental point of view and sustainability of the sector.

5.2 Colophon

The environmental profile of biochemicals could contribute to climate change mitigation, fossil independence and a decrease on toxicity potential on ecosystems. Decrease of fertilizers and irrigation, increase of yields, new solutions for disposal, treatment and recycling of ash and gypsum and development of the approaches exposed to mitigate the other environmental drawbacks of its profile, such energy efficiency techniques or cleaner electricity, could bring the production of biochemicals to an status where they are dramatically better in all impact indicators if all the stakeholders on the life cycle of the biochemicals (Agriculture and Industry sectors, research institutions, policy makers and final customers) get involved.

Acknowledgments

The author would like to thank his supervisors on this thesis Anders Hammer Strømman and Francesco Cherubini. Also, CEPISA, S.A for the collaboration in the petrochemical life cycle inventory.

References

Scientific Articles/Patents

- Anon. (2003). Agricultural Phosphorus and Eutrophication Second Edition Agricultural Phosphorus and Eutrophication Second Edition. *Environmental Protection*, (September).
- Brehmer, B., Boom, R. M., & Sanders, J. (2009). Maximum fossil fuel feedstock replacement potential of petrochemicals via biorefineries. *Chemical Engineering Research and Design*, 87(9), 1103-1119. doi: 10.1016/j.cherd.2009.07.010.
- Butnar, I., Rodrigo, J., Gasol, C. M., & Castells, F. (2010). Life-cycle assessment of electricity from biomass: Case studies of two biocrops in Spain. *Biomass and Bioenergy*, 34(12), 1780-1788. Elsevier Ltd. doi: 10.1016/j.biombioe.2010.07.013.
- Cherubini, F., & Strømman, A. H. (2011). Life cycle assessment of bioenergy systems: State of the art and future challenges. *Bioresource technology*, 102(2), 437-

51. Elsevier Ltd. doi: 10.1016/j.biortech.2010.08.010.
- Cherubini, F. and A. H. Stromman (2010). "Production of Biofuels and Biochemicals from Lignocellulosic Biomass: Estimation of Maximum Theoretical Yields and Efficiencies Using Matrix Algebra." *Energy & Fuels* 24(4): 2657-2666.
- Cherubini, F. & Jungmeier, G., (2009). LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. *The International Journal of Life Cycle Assessment*, 15(1), pp.53-66. Available at: <http://www.springerlink.com/index/10.1007/s11367-009-0124-2>.
- Cherubini, F. (2010). The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management*, 51(7), 1412-1421. Elsevier Ltd. doi: 10.1016/j.enconman.2010.01.015.
- Cherubini, F., & Ulgiati, S. (2010). Crop residues as raw materials for biorefinery systems – A LCA case study. *Applied Energy*, 87(1), 47-57. Elsevier Ltd. doi: 10.1016/j.apenergy.2009.08.024.
- Cherubini, F. et al. (2011). CO₂ emissions from biomass combustion for bioenergy: atmospheric decay and contribution to global warming. *GCB Bioenergy*, p.no-no. Available at: <http://doi.wiley.com/10.1111/j.1757-1707.2011.01102.x> [Accessed March 26, 2011].
- Costa Sousa, L. da, Chundawat, S. P. S., Balan, V., & Dale, B. E. (2009). "Cradle-to-grave" assessment of existing lignocellulose pretreatment technologies. *Current opinion in biotechnology*, 20(3), 339-47. doi: 10.1016/j.copbio.2009.05.003.
- Curran, M. A. (2007). "Co-product and input allocation approaches for creating life cycle inventory data: A literature review." *International Journal of Life Cycle Assessment* 12: 65-78.
- Delucchi MA, Lipman T (2003) A Lifecycle Emissions Model (LEM): lifecycle emissions from transportation fuels, motor vehicles, transportation modes, electricity use, heating and cooking fuels, and materials. Appendix C: emissions related to cultivation and fertilizer use. Institute of Transportation Studies, University of California, Davis, CA, USA
- Demirbas, A. (2010). "Biorefinery Technologies for Biomass Upgrading." *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 32(16): 1547-1558.
- Dornburg, V., Faaij, a, Patel, M., & Turkenburg, W. (2006). Economics and GHG emission reduction of a PLA bio-refinery system—Combining bottom-up analysis with price elasticity effects. *Resources, Conservation and Recycling*, 46(4), 377-409. doi: 10.1016/j.resconrec.2005.08.006.
- Effendi, a, Gerhauser, H., & Bridgwater, a V. (2008). Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renewable and Sustainable Energy Reviews*, 12(8), 2092-2116. doi: 10.1016/j.rser.2007.04.008.
- Eggeman, T., & Elander, R. T. (2005). Process and economic analysis of pretreatment technologies. *Bioresour technology*, 96(18), 2019-25. doi: 10.1016/j.biortech.2005.01.017.
- Ekerdt, J. G., Jia, S., Cox, B. J., Guo, X., & Zhang, Z. C., (2010). Decomposition of a phenolic lignin model compound over organic N-bases in an ionic liquid. *Holzforschung*, 64(5), 577-580. doi: 10.1515/HF.2010.075.
- Fan, J. et al. (2011). Life cycle assessment of electricity generation using fast pyrolysis bio-oil. *Renewable Energy*, 36(2), pp.632-641. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0960148110003186> [Accessed January 12, 2011].
- Finkbeiner, M., Hoffmann, R., Ruhland, K., Liebhart, D., & Stark, B. (2006). Life Cycle Management (Subject Editor : Gerald Rebitzer) Application of Life Cycle Assessment for the Environmental Certificate of the Mercedes-Benz S-Class. *International Journal*, 11(4), 240 - 246.
- FitzPatrick et al. (2010). A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value added products.
- Gayubo, a G. et al., (2010). Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation. *Journal of Chemical Technology & Biotechnology*, 85(1), pp.132-144. Available at: <http://doi.wiley.com/10.1002/jctb.2289>
- Gerngross, T.U. (1999). Can biotechnology move us towards a sustainable society? *Nat. Biotechnol.* 17, 541–544.
- Gonzalez-Garcia, S. et al. (2009). Evaluation of forest operations in Spanish eucalypt plantations under a life cycle assessment perspective. *Scandinavian Journal of Forest Research*, 24(2), pp.160-172. Available at: <http://www.informaworld.com/openurl?genre=article&doi=10.1080/02827580902773462&magic=crössref||D404A21C5BB053405B1A640AFFD44AE3>
- González-García, S. et al. (2009). Environmental impact assessment of total chlorine free pulp from Eucalyptus globulus in Spain. *Journal of Cleaner Production*, 17(11), pp.1010-1016. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0959652609000584>
- González-García, S. et al. (2009). Environmental impacts of forest production and supply of pulpwood: Spanish and Swedish case studies. *The International Journal of Life Cycle Assessment*, 14(4), pp.340-353. Available at: <http://www.springerlink.com/index/10.1007/s11367-009-0089-1>
- González-García, S., Feijoo, G., Heathcote, C., Kandelbauer, A., & Moreira, M. T. (2010). Environmental assessment of green hardboard production coupled with a laccase activated system. *Journal of Cleaner Production*, 19(5), 445-453. Elsevier Ltd. doi: 10.1016/j.jclepro.2010.10.016.
- Groot, W. J., & Borén, T. (2010). Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. *The International Journal of Life Cycle Assessment*, 15(9), 970-984. doi: 10.1007/s11367-010-0225-y.
- Gruber P,O'Brien M. (2002). Polylactides “NatureWorks TM PLA. In: Doi Y,Steinbu’chel A,editors. Biopolymers in 10 volumes,volume 4,polyesters III applications and commercial products. Weinheim: Wiley-VCH; 2002 [ISBN 3-527-30225-5]. p. 235–49

- Hamelinck, C., G. Hooijdonk, et al. (2005). "Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term." *Biomass and Bioenergy* 28(4): 384-410.
- Hamelinck et al. (2004) Production of FT transportation fuels from biomass; technical options, process analysis and optimization, and development potential. (2004). *Energy* 29 (2004) 1743-1771].
- Harding, K. G., Dennis, J. S., Blottnitz, H. von, & Harrison, S. T. L. (2007). Environmental analysis of plastic production processes: comparing petroleum-based polypropylene and polyethylene with biologically-based poly-beta-hydroxybutyric acid using life cycle analysis. *Journal of biotechnology*, 130(1), 57-66. doi: 10.1016/j.biotech.2007.02.012.
- Haveren, J. v., E. L. Scott, et al. (2008). "Bulk chemicals from biomass". *Biofuels, Bioproducts and Biorefining* 2(1): 41-57.
- Heijungs, R. & Guinée, J.B., 2007. Allocation and "what-if" scenarios in life cycle assessment of waste management systems. *Waste management (New York, N.Y.)*, 27(8), pp.997-1005. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/17408944>
- Hertwich, E.G. (2005) *Life Cycle Approaches of sustainable consumption: A critical review*. *Environ Sci Technol*. 2005 Jul 1;39(13):4673-84.
- Huey, C.S. (2006). Polyhydroxybutyrate (PHB) production from cafeteria wastes under anoxic and aerobic conditions in sequencing batch reactor. <http://www.efka.utm.my/thesis/IMAGES/3PSM/2006/4JKAS/PARTS1/chiangsheahueyaa010073d06ttt.pdf>
- Karačić, A. (2005). Production and Ecological Aspects of Short Rotation Poplars in Sweden. *Ecology*.
- Knutsen et Davis (2004). Cellulase retention and sugar removal by membrane ultrafiltration during lignocellulosic biomass hydrolysis. *Applied biochemistry and biotechnology* [0273-2289] yr:2004 vol:114 iss:1 pg:585 -599.
- Kurdikar, D., Paster, M., Gruys, K.J., Fournet, L., Gerngross, T.U., Slater, S.C., Coulon, R. (2001). Greenhouse gas profile of a plastic derived from a genetically modified plant. *J. Ind. Ecol.* 4 (3), 107-122.
- Lopes, M.S.G., Rocha, R.C.S., Zannotto, S., Gomez, J.G.C. & Silva, L.F.d. (2009). "Screening of bacteria to produce polyhydroxyalkanoates from xylose", *World Journal of Microbiology & Biotechnology*, vol. 25, no. 10, pp. 1751-1756.
- Lynd LR. (1996). Overview and evaluation of fuel ethanol from cellulosic biomass: technology, economics, environments and policy. *Annual reviews, Energy and Environment* 1996; 21; 403-65)
- Madhavan Nampoothiri, K., Nair, N. R., & John, R. P. (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresour technology*, 101(22), 8493-501. Elsevier Ltd. doi: 10.1016/j.biortech.2010.05.092.
- Marcela, B. et al. (2005). Producción de Poly-β por *Ralstonia eutropha* ATCC 17697. *Universitas Stuttgart*, 10(1), pp.45-54.
- Marshall, A.-L., & Alaimo, P. J. (2010). Useful products from complex starting materials: common chemicals from biomass feedstocks. *Chemistry (Weinheim an der Bergstrasse, Germany)*, 16(17), 4970-80. doi: 10.1002/chem.200903028.
- Masuda, T., Tago, T., Hirokazu, T., & Yanase, T. (2011). Process for producing acetone from bioethanol. US Patent 2011/0015445 A1.
- Miranda, I. (2001). Provenance and site variation of wood density in *Eucalyptus globulus* Labill. at harvest age and its relation to a non-destructive early assessment. *Forest Ecology and Management*, 149(1-3), pp.235-240. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0378112700005600>.
- Nielsen, P.H., Oxenbøll, K.M. & Wenzel, H. (2006). Cradle-to-gate environmental assessment of enzyme products produced industrially in denmark by novozymes A/S. *The International Journal of Life Cycle Assessment*, 12(6), pp.432-438. Available at: <http://www.springerlink.com/index/10.1065/lca2006.08.265.1>.
- Olsson, L. (1994). Ethanol Production from lignocellulosic Materials: Fermentation and On-line Analysis. Lisbeth Olsson. University of Lund. 1994.
- Pakdel, H. (1992). Vacuum pyrolysis of lignin derived from steam-exploded wood. *Biomass and Bioenergy*, 3(1), 31-40. doi: 10.1016/0961-9534(92)90017-K.
- Pandey, M. P., & Kim, C. S. (2011). Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chemical Engineering & Technology*, 34(1), 29-41. doi: 10.1002/ceat.201000270.
- Persson, T. et al. (2010). Fractionation of process water in thermomechanical pulp mills. *Bioresour technology*, 101(11), pp.3884-92. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/20137925>
- Pinto, P.C.R. & Borges, E.A. (2011). Insights into Oxidative Conversion of Lignin to High-Added-Value Phenolic Aldehydes. , pp.741-748.
- Pfromm, P.H. (2008). The Minimum Water Consumption of Ethanol Production via Biomass Fermentation. *The Open Chemical Engineering Journal*, 2(1), pp.1-5. Available at: <http://www.bentham-open.org/pages/content.php?TOCENGJ/2008/00000002/0000000001/1TOCENGJ.SGM>.
- Ramsay, J.A., Aly Hassan, M.-C., Ramsay, B.A. (1995). Hemicellulose as a potential substrate for production of poly(β-hydroxyalkanoates) Ecole Polytechnique de Montreal, Succursale 'centreville', C.P. 6079, Montreal, Que. H3C 3A7, Canada Canadian Journal of Microbiology Volume 41, Issue SUPPL. 1, 1995, Pages 262-266
- Rebitzer, G. et al. (2004). Life cycle assessment part 1: framework, goal and scope definition, inventory analysis, and applications. *Environment international*, 30(5), pp.701-20. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/15051246>.
- Sevigne, E. et al. (2011). Water and energy consumption of *Populus* spp. bioenergy systems: A case study in Southern Europe. *Renewable and Sustainable Energy Reviews*, 15(2), pp.1133-1140. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S136403211000403X>
- Stenberg, K. (1999). Ethanol from softwood. Process Developments based on Steam Pretreatment and SSF. Kersting Stenberg. Lund University. 1999.
- Vink, E. (2003). Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. *Polymer Degradation and Stability*, 80(3), 403-419. doi: 10.1016/S0141-3910(02)00372-5.

- Vink, E. T. H., Davies, S., & Kolstad, J. J. (2010). The eco-profile for current Ingeo polylactide production. *Industrial Biotechnology*, 6(4).
- Weber, Manfred, & Weber, Markus. (2010). Phenolic Resins: A Century of Progress. (L. Pilato, Ed.), Chapter II 9-24. Berlin, Heidelberg: Springer Berlin Heidelberg. doi: 10.1007/978-3-642-04714-5.
- Wingren, A., Galbe, M., & Zacchi, G. (2008). Energy considerations for a SSF-based softwood ethanol plant. *Bioresource technology*, 99(7), 2121-31. doi: 10.1016/j.biortech.2007.05.058.
- Zhang Q, Chang J, Wang T, Xu Y (2007). Review of biomass pyrolysis oil properties and upgrading research. *Energ Convers Manage* 48:87–92
- Zhu, J.Y. & Pan, X.J. (2010). Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation. *Bioresource technology*, 101(13), pp.4992-5002. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/19969450>.

Research Reports/Other sources

- Gallardo, M. (2010). Lignocellulosic Biorefinery Model: Efficiencies of different approaches for the production of biofuels and biochemicals. Specialization course Report. December 2010. Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU), Trondheim – Norway.
- Guest, G., Bright, R. M., Cherubini, F., Michelsen, O., & Strømman, A. H. (2010). Life Cycle Assessment of Bio-fuelled Combined Heat and Power Plants — Centralized vs Decentralized Deployment Strategies Case study Summarized. *Energy*. Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU), Trondheim – Norway.
- Michels, J., & Wagemann, K. (2010). The German Lignocellulose Feedstock Biorefinery Project. Biofuels, Bioproducts and Biorefining, 4(3), 263-267. doi: 10.1002/bbb.216. <http://doi.wiley.com/10.1002/bbb.216>
- Strømman, A.H. (2008). Methodological Essentials of Life Cycle Assessment. Class notes of the course TEP 4223 Life Cycle Analysis and Eco-Efficiency at Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU), Trondheim – Norway.
- Stromman, A. H. and Solli, C. (2008). "Applying Leontief's price model to estimate missing elements in hybrid life cycle inventories". *Journal of Industrial Ecology* 12(1): 26-33.

Books

- Basu, P. (2010). Biomass Gasification and Pyrolysis: Practical Design and Theory (377 pages) ISBN:9780123749888
- Kamm, B., Gruber, P. R. and Kamm, M. Eds. (2006), "Biorefineries - Industrial Processes and Products; Status Quo and Future Directions", 2006, Wiley-VCH Verlag GmbH & Co., Weinheim.
- Meyers et al. (2005). Handbook of Petrochemicals Production Processes. McGraw-Hill, NY, p 14.45, 2005.

Data from Companies

- Borregaard** <http://www.borregaard.com/>
Commissioned Report: Life Cycle Assessment of cellulose, ethanol, lignin and vanillin from Borregaard, Sarpsborg. Phase II. Ostfold Research. Applied Research in Environmental Protection and Business and Regional Development (Modahl, I.S, Brekke, A, Raadal, H.L). 2009.
<http://ostfoldforskning.no/engelsk/publication/life-cycle-assessment-of-cellulose-ethanol-lignin-and-vanillin-from-borregaard-sarpsborg--580.aspx>
- CEPSA, S.A.** Environmental Declaration ISO 14001:2004 Refinery La Rábida
http://www.cepsa.com/recursos_cepsa/iniciativas/DM/DMRabida/2010/index.htm
- Petrochemicals Palos de la Frontera**
http://www.cepsa.com/recursos_cepsa/iniciativas/DM/DMPalos/2009/1.htm
- Multineer Engineering.**
 Multineer refining characteristic brochure
- Yarn and fibers.** Benzene Report 2011
<http://www.yarnsandfibers.com/textile-pricewatch/benzene-price-trends-reports.html>

Reports from Institutions/Governments

- Association of Petrochemicals Producers in Europe (APPE)**
<http://www.petrochemistry.net/>
- Biomass Technology Group, The Netherlands**
 B.M. Wagener et al. BIO-OIL AS NATURAL GAS SUBSTITUTE IN A 350 MW POWER STATION. B.M. Wagener, J. H. Florijn, E. Gansekoete, R.H. Venderbosch, BTG Biomass Technology Group BV Pantheon 12, 7521 PR Enschede. The Netherlands
<http://www.btgworld.com/uploads/documents/BTG%20Paper%20Bio-oil%20as%20natural%20gas%20substitute.pdf>
- EcoInvent BioEnergy and Biomass reports**
<http://www.ecoinvent.org/documentation/reports/>
- European Bioplastics organization**
<http://en.european-bioplastics.org/>
- European Union.** European Environmental Agency (1997). Life cycle assessment. A guide to approaches, experiences and information sources. *Environmental Issues series. No6.*. 1997.
- European Union.** 6th Environment Action Programme. 2002-2012
http://europa.eu/legislation_summaries/agriculture/environment/l28027_en.htm
<http://ec.europa.eu/environment/newprg/intro.htm>
- European Union.** European Topic centre on sustainable consumption and Production
<http://scp.eionet.europa.eu/themes/lca>
- European Union Biomass Action Plan.** Commission of the European Communities. Brussels, 7.12.2005. COM (2005) 628 final].
- International Energy Agency (IEA).** World Energy Outlook. Paris: International Energy Agency 2007
- International Energy Agency (IEA).** Task 42 about biorefineries.
- Sonnenberg, A., Baars, J., & Hendrickx, P. (n.d.). *Breeding Challenges in the Button Mushroom IEA Bioenergy Task 42 Biorefinery.*
- International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD).**
Chemical and petrochemical sector. Potential of Best practice Technology. Saygin et al. OECD/IEA. 2009.
- IPCC.** (2006) Guidelines for national greenhouse gas inventories. Volume 4: Agriculture, forestry and other land use

International Organization for Standardization. ISO 14000 series

http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?csnumber=31807

Kyoto Protocol. (1997)

<http://unfccc.int/resource/docs/convkp/kpeng.html>

United Nations Millenium Goals Report 2005-2010
<http://www.un.org/millenniumgoals/enviro.html>

United Nations Environmental Programme (UNEP). Green Economy Report: *Towards a Green Economy. Pathways to sustainable and poverty eradication (a synthesis for policy makers)*.
http://www.unep.org/greenconomy/Portals/88/documents/ger/GER_synthesis_en.pdf

University of Washington

http://faculty.washington.edu/finlayso/Polyeth/Group_B/themer.html

Spanish Electric Network (REE: Red Electrica Española)

<https://demanda.ree.es/demandaEng.html>
http://www.ree.es/sistema_electrico/pdf/infosis/Inf_Sis_Elec_REE_2009_ElSectorElectrico.pdf

US Department of Energy [PNNL/NREL] 2004

Top Volume Added Chemicals from biomass. I-Results of Screening for potential candidates from sugars and synthesis gas.

Plastics in Europe

<http://www.plasticseurope.org/plastics-sustainability/life-cycle-thinking.aspx>

Reports from Consultancy Companies

SRI Consulting

<http://www.sriconsulting.com>

GLG Consulting Group

<http://www.glgroup.com/>

Global Industry Analysts, Inc

<http://www.strategyr.com/>

Pré Consultants. ReCiPe Method

<http://www.pre.nl/>

Companies mentioned

BioCycle Brazil

<http://www.biocycle.com.br/site.htm>

Nature Works

<http://www.natureworksllc.com/>