



Green chemistry metrics for Safe and Sustainable-by-design chemicals: The case of renewable amines

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Abstract

Safe and Sustainable-by-design chemicals are an increasingly important topic in early-stage chemical process development. This study evaluates two pyrolysis production pathways in the early stage for renewable aniline, an important platform chemical for producing polyurethane and other industrial and pharmaceutical purposes. The sustainability assessment is performed at an early stage of process development, with the used data obtained from existing literature, as no experimental proof of concept has been performed yet. A selection of green chemistry indices is employed to perform a mass-based comparative analysis of the environmental impacts of these pathways. Applying the Safe and Sustainable by Design (SSbD) framework and green chemistry metrics, this research aims to identify the advantages and disadvantages of both pathways. For aniline production, the biomass pathway yields significantly more waste than the polyurethane pathway due to the organosolv extraction of lignin, despite the higher selectivity towards aniline, a more mass-efficient reaction and lower separation mass intensity. When liquid pyrolysis products (LPPs) are regarded as the desired product, the biomass pathway still yields more waste due to the lignin extraction than the polyurethane pathway, despite higher selectivity to liquid products rather than biochar and gases. When the organosolv extraction of lignin is omitted from the biomass pathway, it becomes significantly less mass-intensive. The performance in the green chemistry indices significantly increases regardless of the desired product. However, due to the incompleteness of the data, several rough assumptions had to be made, which led to significant simplifications and uncertainties in the data and, thus, the analysis. Scope definition regarding the process and weighing of the applied indices significantly influence the applicability of engineering systems in both pathways of this study.

Preface

Before you, the bachelor project report 'Green chemistry metrics for Sustainable and Safe-by-design chemicals: The case of renewable amines' is presented. This bachelor thesis was written as part of the graduation requirements of the Bachelor of Science in Chemical Engineering at the University of Groningen. The project was designed, developed, and completed between April and July 2024.

Performing a sustainability assessment as conducted in this project was still novel to me after finishing all other courses in the bachelor's program. Therefore, the project was challenging to get into but ultimately taught me a lot about the field of sustainable chemistry and process design.

I want to express my gratitude to Paraskevi Karka for the opportunity to do this project and for her guidance and support throughout the project. My gratitude extends to Fadhli Fadhli for his immense support and guidance regarding this project's existing relevant processes and literature. In both, I have found invaluable discussion partners who significantly aided in the development of this project.

I hope you enjoy reading the report.

Stijn Wiersma
4 July 2024

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1 Introduction

1.1 The evolution of green chemistry and Safe and Sustainable By Design

Rapid development in the chemical industry has significantly increased our prosperity and living standards. However, due to the finiteness of resources and the environmental impact of production and consumption, challenges arise in sustaining the current way of living [1]. Currently, the depletion of the Earth's natural resources occurs more rapidly than the resource replenishment [2]. Therefore, significant changes must be implemented to develop more sustainable processes and products to decrease environmental impact while sustaining the current prosperity. Sustainable development was first introduced in 1987 in the Brundtland Report of the United Nations. As defined in the report: '*development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs*' [3]. This definition leads to two clear prerequisites: (i) Natural resources should be extracted and used at rates that do not unacceptably deplete supplies over the long term. (ii) Waste should be generated at rates no higher than can be readily assimilated by the natural environment [4]. To assist the growing interest in minimum

impact chemistry, or 'green chemistry' as introduced in the early 1990s [5], the American Chemical Society (ACS) introduced the 12 Principles of green chemistry Table 1, published initially by Anastas and Warner [6]. It forms a fundamental, qualitative guideline for improving the nature of a product and its production where the objective is reducing environmental and human health impact. Various dimensions are covered in the descriptions. Reducing environmental impact is described by principles (i),(ii),(v),(vi),(vii),(ix),(x) and (xi). Whereas the remaining principles are directed predominantly towards decreasing human health impact. Quantitative measurements were also developed next to qualitative assessment of chemical processes. Two of the early developed metrics are the (i) E(nvironmental)-factor and (ii) Atom-Economy (AE) [7][8]. The E-factor measured the mass ratio of waste to the desired product. In contrast, AE divided the molar mass of the desired product by the sum of the molecular masses of all reactants and other products produced in the stoichiometric equation. The AE is particularly beneficial when assessing waste production of a production pathway without performing any experiments, whereas a correct E-factor calculation requires mass data from the process. However, as definitions of 'waste' and 'desired products' have room for manipulation, the E-factor has shortcomings. Nonetheless, the E-factor and AE have brought about a great motivation in considering waste generation in both industry and academia [4]. Developing further metrics to assess more specific characteristics has been an ongoing process. Metrics like the Reaction Mass Efficiency (RME) and Carbon Efficiency (CE) indicate, like the AE, the amount of raw material needed. If, besides the raw materials, reagents also have to be considered, metrics like Reaction Mass Intensity (RMI) or Effective Mass Yield (EMY) may be more appropriate [9]. A tailored assessment can be performed by choosing appropriate metrics for a specific process. Over time, many frameworks have been developed to

assess various chemical processes' environmental and human health aspects. One of the most used tools for assessing the environmental impact of a specific process is the Life Cycle Assessment (LCA). It has specifically been designed to consider the entire life cycle of a product, from obtaining necessary starting materials to its end-of-life treatment. LCA consists of four stages: (i) definition of the goal and scope, (ii) inventory analysis (LCI), (iii) impact assessment (LCIA), and (iv) interpretation. All stages of the LCA can be performed at various levels of detail, depending on the scope of the study [4]. As LCA comprises all stages of a product and its production, a significant amount of data is necessary to fulfil all stages of the assessment. This leads to one of its most significant pitfalls: completeness in scope comes at the price of simplification and uncertainties in the used data [10]. More holistic frameworks have gained global attention

as well. The Planetary Boundaries concept [11], which originally quantifies seven different processes that regulate the Earth system's stability and resilience, signifies the need for living within the Earth's ecological boundaries. That is also one of the objectives of the European Union (EU) Green Deal, which aims to support a more sustainable future and to implement the United Nations' agenda 2030 [12][13]. For this goal, a series of actions were outlined in the Chemicals Strategy for Sustainability (CSS) [14][15]. One of those actions was adaptation of the Safe and Sustainable By Design (SSbD) framework, developed by the Joint Research Centre. The SSbD framework is a '*holistic approach that integrates safety, circularity and functionality of chemicals, materials, products and processes throughout their entire life cycle, minimizing their environmental footprint*'. Like LCA, the application of the SSbD framework consists of four steps: (i) hazard assessment, (ii) assessment of human health and safety aspects in production, (iii) assessment of human health and environmental aspects in final application (iv) environmental sustainability assessment Figure 1. An optional fifth step consists of a Socio-Economic assessment. Like the fifth step, the framework in its entirety is a voluntary, iterative guideline to use and can be adapted to fit the practitioner's specific

goal. It goes beyond traditional frameworks as it comprises safety-based integration in addition to life cycle-based considerations from early (design) stages up until end-of-life treatment [16]. This means besides environmental aspects like preventing leaks, spills, fires, explosions, equipment malfunction, over-pressures, over-temperatures, corrosion, metal fatigue, and similar conditions in chemical process facilities are taken into account [17].

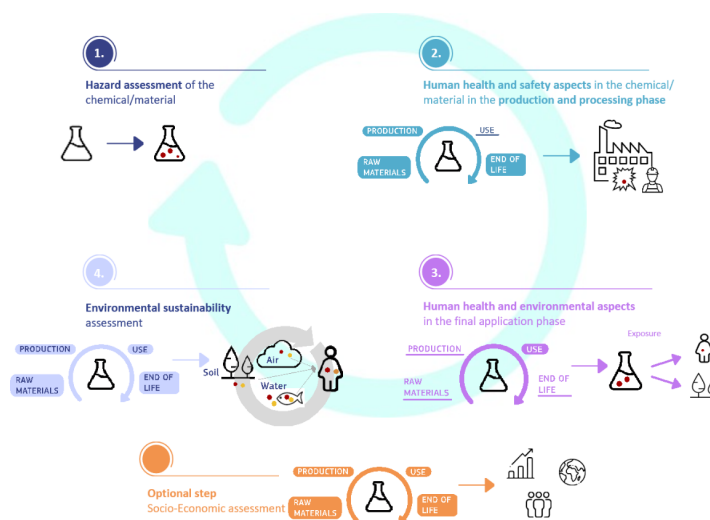


Figure 1: The four steps of the Safe and Sustainable By Design framework [14]

When innovative processes and products are developed, early-stage assessment is essential to uncover the limitations and difficulties involved in the process prematurely. By applying green chemistry metrics to assess the process as a whole or within a specific process boundary, characteristics of the process regarding environmental or human health impact can be recognised and taken into account. In this manner, possible undesired aspects of a process can possibly be prevented, decreasing environmental and human health impact. The SSbD framework methodology assists in performing this assessment. By following the SSbD framework and using green chemistry indices, comparisons between two processes can also be performed to indicate the advantages and disadvantages of the production pathways.

1.2 Background of assessed processes and products

In this project, two production pathways of renewable amines will be assessed in terms of their environmental impact. As the SSbD framework suggests, this assessment is performed early in the process development. As the assessed processes have yet to be experimentally performed in their entirety, all data had to be obtained from the literature. A target compound had to be appointed to make an equitable comparison between the

two assessed pathways. As both reactions yield aniline, a well-known useful chemical, it has been appointed the target chemical for both pathways. Aniline is a widely used bulk chemical which is mostly used for the synthesis of methylene diphenyl di-isocyanate (MDI), which is the precursor for polyurethane. Moreover, aniline is also used regularly in producing pharmaceuticals, dyes and other polymers [18]. Currently, aniline is produced industrially through two processes: (i) catalytic hydrogenation of nitrobenzene and (ii) amination of phenol with ammonia. However, nitrobenzene and phenol are produced from benzene [19], which is in its place obtained mostly from fossil feedstock currently [20]. As reducing fossil fuel reliance aids in reaching the sustainability goals, having a renewable aniline production pathway is of great interest. However, besides aniline, all liquid pyrolysis products (excluding water) (LPPs) could also be considered useful. Therefore, separate assessments have been performed to indicate the advantages and disadvantages of both processes when the desired product is 1 kg of aniline or when the desired product is 1 kg LPPs. This project aims to

perform a comparative study on the environmental impact of both pyrolysis pathways. This comparison will be performed using several different green chemistry indices and assessed one by one to give clear insight into the advantages and disadvantages of both production pathways.

2 Methodology

2.1 Block flow diagrams and mass data

The common denominator of the two assessed processes for aniline production is that both reaction unit processes are pyrolysis reactions. Pyrolysis is a thermochemical decomposition reaction of a material at high temperatures in the absence of oxygen. It is an irreversible, radical reaction that significantly changes the feedstock's chemical composition and physical state. In the pyrolysis reactor, the temperature gradually increases, yielding several different products at varying temperatures. Generally, pyrolysis yields three different phases of matter: (i) gaseous products including carbon monoxide, (ii) liquid products, industrially known as bio-oil and tars, (iii) solid residue, better known as char or bio-char [21]. Both assessed pathways have different characteristics which make them distinguishable. Firstly, the feedstock is significantly different. For the first pathway, semi-rigid polyurethane foam is used as feedstock, whereas wheat straw and lignin are assessed for the second pathway. Furthermore, the polyurethane pathway's pyrolysis reaction is non-catalysed and under an inert atmosphere. Meanwhile, the biomass/lignin pathway's reaction is catalysed in a reactive gaseous ammonia atmosphere. Both aniline separation procedures are equal, regardless of the composition at the reactor outlet. Although the feedstock, reaction environment and thus the composition of LPPs between the two assessed pathways is significantly different, the LPPs of the polyurethane pyrolysis are considered equal to the LPPs of the catalysed, reactive pyrolysis of lignin.

2.1.1 Polyurethane pyrolysis pathway

Pretreatment of the semi-rigid polyurethane only consists of a grinding step, which ensures sufficient small particle size for the pyrolysis. As no specific mass data is available for this procedure, a grinding efficiency of 100%, thus no mass loss has been assumed. The chemical mass composition of the reactor outlet has been adapted from the fluid bed pyrolysis of polyurethane (PUR) at 700°C, as presented in Table 2 [22]. The composition of products has been normalised for the unidentified/unknown products. In Table 3, the inlet and outlet stream can be observed where also the composition is indicated of what is considered desired LPPs in the polyurethane pathway. After the reaction, the pyrolysis outlet products enter a condenser to separate the gases from the liquid. Although the gas composition is known and contains useful combustible gases, it is treated entirely as waste in the green chemistry assessment as no data is available for the gas composition of the lignin pyrolysis. The solid fractions are considered to have already separated after the reaction. As no specific mass data is available of condenser efficiency, no mass loss and an efficiency of 100% is assumed. Although the LPPs, excluding water, can be considered a useful product, the separation

of aniline has been incorporated in the block flow diagrams. Firstly, a 50% NaOH solution, an equimolar amount to the amount of aniline and benzonitrile, is added to the LPPs, after which organic solvent methyl isobutyl ketone (MIBK) is added in a 1:1 (m/m) ratio to increase the affinity of aniline and benzonitrile for the organic phase. After extracting the organic phase, 30% HCl is added to the MIBK-aniline-benzonitrile mixture to reprotonate the deprotonated species. Three distillation steps are expected to be necessary based on the boiling points of the species present in the mixture to remove unwanted species and potentially recover MIBK. In the first distillation step, benzene and other aromatic compounds are removed. As the composition of 'other aromatics' Table 2 is not defined, complete removal of those species is assumed at the same distillation temperature of benzene. In the second distillation step, MIBK is removed from the mixture. As no mass data about MIBK's recovery efficiency and recyclability is available, it is assumed that all MIBK was wasted in this project. However, recovery and recycling of MIBK may be feasible in practice. In the third and last distillation step, naphthalene is removed. After the entire separation process, a mixture of aniline and benzonitrile (45/55 wt%) is obtained [23].

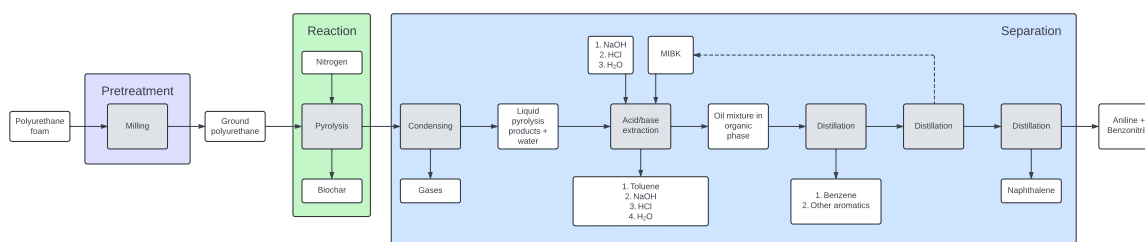


Figure 2: Block flow diagram of aniline production through polyurethane pyrolysis [22][23]

2.1.2 Catalytic lignin pyrolysis with ammonia pathway

In the biomass pathway, lignin extraction is necessary as lignin is the feedstock for the reaction step. For the extraction of lignin, a multi-step pretreatment of biomass is necessary. For the design of the block flow diagrams, the organosolv extraction methodology of Watkins et al. has been adapted [24]. Biomass, wheat straw in this project, first undergoes pulping, which consists of grinding and boiling it in a formic/acetic acid (FA/AA) solution to increase the lignin's solubility. The mixture is then washed with a formic acid solution and hot distilled water. After pulping, the pulp is further delignified by peroxyformic/peroxyacetic acid (PFA/PAA), where H_2O_2 gets added to the FA/AA mixture and left in a hot water bath. The delignified fibres are then bleached with H_2O_2 at pH 11-12, regulated with NaOH. The mixture is then washed with distilled water to remove residual lignin. This bleaching/washing process is repeated twice. The obtained solution in which all the lignin resides is then precipitated in distilled water before filtering and vacuum drying over P_2O_5 . Although the experimental procedure is described in the aforementioned paper, more mass data is needed to apply the green chemistry indices. Therefore, the organosolv extraction mass data from Karka et al. are used for the mass balances [25]. The lignin undergoes reactive pyrolysis under an

ammonia atmosphere, catalysed by ZnO/HZSM-5 at a temperature of 600°C. Composition at the reactor outlet is presented in Table 4 [26]. The inlet and outlet streams of the pyrolysis reactor can be observed in Table 5, where also the composition of the LPPs of the biomass pathway is indicated. The separation of the pyrolysis products is performed via the same pathway as the output of the polyurethane pyrolysis. Firstly, the liquid and gas products enter a condenser where total efficiency is assumed. As no data about gas composition is available, it is considered waste for the green chemistry assessment. After the condenser, acid-base extraction is performed. For this step, 50% NaOH solution is added in a 1:1 molar ratio to aniline-methylaniline and naphthylamine. This increases the affinity of those species for the organic phase, which is formed by adding a 1:1 ratio (m/m) MIBK to the aqueous layer. An equimolar quantity of 30% HCl to NaOH solution is added to reprotonate aniline, methylaniline and naphthylamine. Following the acid-base extraction, a series of distillation steps are expected to separate the aniline from the mixture of undesired compounds based on the difference among the boiling points of the products in the mixture. In the first distillation step, benzene is removed from the mixture. Then, the MIBK is removed as solvent. As previously indicated, the MIBK is considered waste as no data about the degree of recovery in this step is available. The third and fourth distillation steps are purposed to remove naphthalene and naphthylamine. Ultimately, a mixture of aniline and methylaniline (89/11 wt%) is obtained after separation [23].

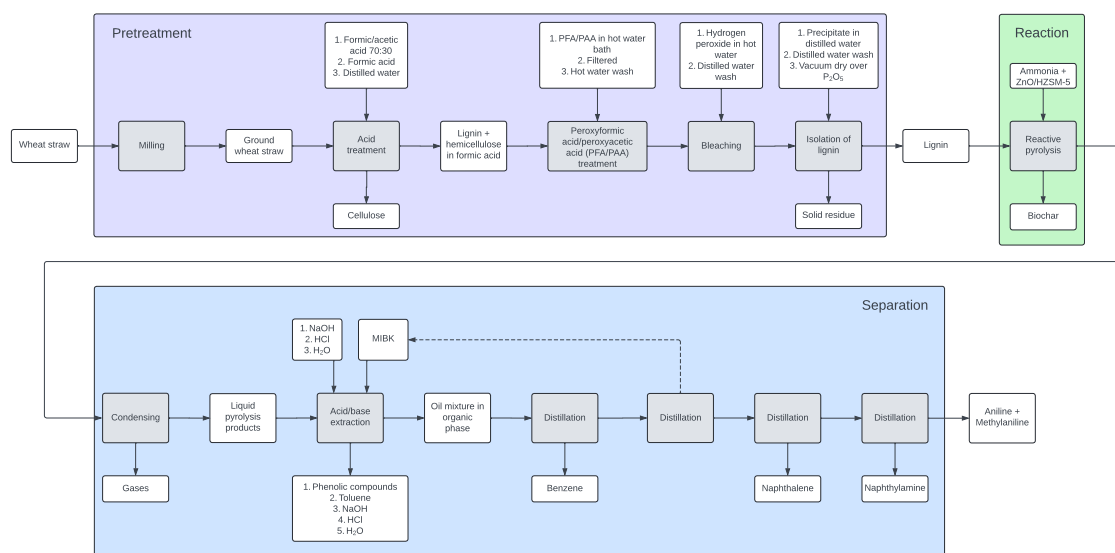


Figure 3: Block flow diagram of aniline production through lignin pyrolysis with extraction of lignin from biomass [23][24][26]

2.2 Green chemistry metrics assessment

2.2.1 Allocation factors

Allocation factors have been calculated and applied to assess both processes employing the green chemistry indices, which will be addressed subsequently. Allocation enables assessment based on one unit of the

product of interest[1]. As in this project, both aniline and LPPs are considered useful products separately, allocation factors for both products have been calculated and applied separately. The allocation factors of

both the polyurethane and biomass pyrolysis pathway Table 6Table 7 have been calculated based on Equation 1[1]. Appropriate allocation factors are applied as a multiplication factor to assign a specific amount of necessary substances to the desired product without penalizing the desired product for the entire amount of chemicals or water necessary for the whole process.

$$A_{fn} = \frac{x_{fn}}{\sum x_n} \quad (1)$$

where

A_{fn} = allocation factor of functional unit

y_{fn} = mass flow of functional unit

y_n = mass of nth product

As the biomass pathway requires lignin extraction, an allocation factor is calculated based on the mass data from [25]. The polyurethane pretreatment only consists of a grinding procedure which does not use any chemicals. Therefore, no allocation factor is applied during the pretreatment. For both pathways and regardless of considering aniline or LPPs as the product, the allocation factors are based on the mass ratio of the desired product at the reactor outlet [22][26]. The allocation factors of both processes, considering both aniline and LPPs as products separately, concerning separation have been considered as the mass ratio of the desired product to the total mass after the condenser.

2.2.2 Applied green chemistry indices

A selection of quantitative indices has been applied to the collected mass data to assess both aniline production pathways. As one of the most significant differences between both processes is the reaction step, metrics like the mass loss index (MLI), feedstock mass intensity (FMI), reaction mass efficiency (RME) and MCONC have been chosen. To gain more insight in the process as a whole regarding input mass and waste generation, process mass intensity (PMI) and E-factor have been employed. Indications about water and solvent use are obtained by calculating the solvent mass intensity (excluding water) (SMI(exc)) and process water mass intensity (PWI). All used indices, corresponding equations and other assumptions will be addressed separately below. Moreover, some of the applied indices can be substantiated based on the 12 Green Chemistry Principles Table 1, which will also be incorporated. Process water intensity (PWI)Equation 2

indicates the amount of water used in the production path per kilogram of the desired product [27]. In the polyurethane pathway, water is only used in the separation; therefore the PWI is obtained by multiplying the mass of water by its appropriate allocation factor depending on the desired product. Water is also used in the biomass pathway for lignin extraction pretreatment. The final value of the PWI index is obtained equally to the polyurethane pathway, except that the amount of water used in pretreatment times the allocation factor for lignin is added. A lower PWI is beneficial as wastewater treatment is undesirable, which is described by GC principles (i) waste prevention, not remediation. Moreover, as water is used as a solvent, decreasing the PWI also complies with GC principle (v) innocuous solvents and auxiliaries.

$$\text{Process water mass intensity (PWI)} = \frac{\text{Amount of water used in production path}}{\text{Amount of kilogram of product}} \quad (2)$$

Mass loss index (MLI)Equation 3 is the ratio of undesired compounds to the mass of desired products and co-products. It indicates the potential separation efforts and process efficiency [1][28]. A high MLI indicates high separation efforts and low process efficiency. The value of the MLI of the PU pathway with aniline as the product (MLI1) is obtained by dividing the total mass of the reactor outlet by the mass of aniline. The MLI for LPPs (MLI2) is calculated by dividing all solids, gases, and water by the sum of the mass of LPPs. MLI for aniline (MLI1) is calculated equally to the polyurethane pathway for the biomass pathway. The LPPs MLI (MLI2) is calculated by dividing the masses of solids plus gases by the mass of LPPs. Decreasing the MLI is essential to decrease separation needs and increase process efficiency, complying with GC principles (i) waste prevention, not remediation and (vi) energy efficient by design.

$$\text{Mass loss index (MLI)} = \frac{\text{Total mass at reactor outlet except products and co-products}}{\text{Mass of products and co-products}} \quad (3)$$

Process mass intensity (PMI) is defined as the total mass that enters the process boundary that is required to yield the desired product(s) [29]. For the PMI of the polyurethane pathway, the PMI is calculated by adding the mass of polyurethane and nitrogen, multiplying it by the appropriate allocation factor, and subsequently adding all chemicals and water necessary for separation, again multiplying by the appropriate allocation factor. The PMI values of the biomass pathway are calculated equally to those of the polyurethane pathway, except the amount of biomass plus the mass of substances for lignin extraction, multiplied by the allocation factor of lignin, is added. A low PMI indicates an efficient and selective process with minimum waste and unnecessary input masses. Improving PMI is therefore connected to GC principles (i) waste prevention, not remediation, (ii) atom economy and (vi) energy efficient by design. The feedstock mass intensity (FMI)

is the reaction unit's input mass that yields the desired product(s) [27]. For the polyurethane pathway, this means that the masses of polyurethane is stipulated per 1 kg of desired product, aniline or LPPs. The biomass pathway follows the same procedure, except now lignin is the reactor input. A low FMI indicates a high conversion efficiency of the feedstock to the desired product(s). Decreasing the FMI complies with the GC principle (i) of waste prevention, not remediation. Moreover, decreasing FMI will also increase atom economy as the total amount of mol necessary for a functional unit of the desired product is decreased. Therefore, it also complies with GC principle (ii). Reaction mass efficiency (RME) Equation 4 represents

the input streams participating in the primary reaction step [29]. The values for the RME are calculated in both pathways and desired by dividing the desired product's mass by the feedstock's mass plus the used gas. A low RME indicates low efficiency of the process and highly demanding reactions concerning resources. However, to simplify the analysis of the calculated data the trend has been inverted. Therefore a high normalized RME value is undesirable in this project. Increasing RME means that the atom economy increases, complying with GC principle (ii), but it also decreases the amount of waste produced, complying with GC principle (i).

$$\text{Reaction mass efficiency (RME)} = \frac{\text{Mass of desired product}}{\text{Mass of feedstock and other reactants}} \quad (4)$$

The solvent mass intensity (SMI) and solvent mass intensity excluding water (SMI_{exc}) indicates the ratio of solvent used per mass of desired products; in calculating the SMI, water used as a solvent is considered, whereas in SMI_{exc}, the water is neglected [27]. This distinction is made as water-intensive processes might have a high SMI, indicating much waste, but they have the potential to be less wasteful through effective wastewater treatment. The values for the SMI regarding the polyurethane process are calculated by adding all necessary liquid compounds for separation and multiplying by the appropriate allocation factor. The same procedure is used for the biomass pathway except for the solvents needed for lignin extraction times when the allocation factor of lignin is added. The same procedure is used for all SMI_{exc} values, except water is omitted from the solvents. Decreasing SMI and SMI_{exc} leads to waste prevention, complying with GC principle (i). Moreover, decreasing the number of solvents needed per functional unit of a desired product complies with GC principle (v), innocuous solvents and auxiliaries.

$$\text{Solvent mass intensity (SMI)} = \frac{\text{Amount of solvent used}}{\text{Mass of desired product(s)}} \quad (5)$$

$$\text{Solvent mass intensity excluding water (SMI}_{\text{exc}}) = \frac{\text{Amount of solvent used excluding water}}{\text{Mass of desired product(s)}} \quad (6)$$

The E-factor Equation 7 is defined by the mass of waste to the mass of the desired product [7]. All E-factors have been calculated based on 1 kg of the desired product. For both pathways and all products, all chemicals, solvents and water necessary for separation are considered waste. As MIBK recycling has not been taken into account for this project, MIBK is regarded as waste. For LPPs production through the biomass pathway, separation is not necessary. Therefore, separation was neglected when calculating that specific E-factor. In all reactions, the reaction gases (nitrogen/ammonia) are regarded as waste, as well as all solids, gases, and other products that are not the desired product. All necessary chemicals, water and delignified fiber residue from the lignin extraction have been considered waste for the lignin extraction step. Furthermore, as no specific data is available about the ZnO/HZSM-5 catalyst performance, no spent catalyst as waste is assumed for the biomass pathway. As the E-factor considers the process in its entirety, various GC principles can be applied to its use. Firstly, waste prevention leads to a lower, desirable E-factor. A higher atom economy leads to less waste and, therefore, a low E-factor. Decreasing the amount of solvent necessary for a functional unit of the desired product also leads to a decreased E-factor. Attempting to decrease the E-factor can arguably be done by reducing the amount of derivative and considering a shorter synthesis

pathway. Moreover, implementing a catalyst that increases selectivity and minimises waste, leading to a lower E-factor, is also possible. Therefore, GC principles (i), (ii), (v), (viii) and (ix) can be applicable. This shows the significant number of aspects comprised by calculating the E-factor.

$$\text{E-factor} = \frac{\text{Total mass of waste}}{\text{Mass of final product}} \quad (7)$$

The MCONC Equation 8 is the ratio of the desired product's mass to the total mass of all products at the reactor outlet [1][28]. For both processes, the MCONC was calculated by dividing the mass of the desired product(s) at the reactor outlet by the total mass of the reactor outlet. A high MCONC indicates low separation efforts for extracting the desired products and low waste. However, to simplify the analysis of the calculated data the trend has been inverted. Therefore a high normalized MCONC value is undesirable in this project. Decreasing the MCONC leads to the prevention of waste and possibly lowering the amount of energy needed, as separation has the potential to be energy-intensive. Therefore, it complies with GC principles (i) and (iv).

$$\text{MCONC} = \frac{\text{Mass of main product(s) at reactor outlet}}{\text{Total mass of all products at the reactor outlet}} \quad (8)$$

2.2.3 Extra index calculation for unbiased comparison

As mentioned before, the polyurethane pathway has a significantly shorter pretreatment, without any necessary chemicals or water, compared to the biomass pathway. Lignin extraction through organosolv methodology is very water-intensive, which inflicts a substantial detrimental impact on indices that consider pretreatment. A few metrics have been recalculated and assessed separately for the biomass pathway to prevent an unbiased assessment and conclusion of the process comparison and to show the importance of scope and process definition. The methodology, as mentioned earlier, is applied to these recalculated metrics. However, instead of considering the total mass involved with the organosolv extraction of lignin, lignin is considered raw feedstock that only needs grinding as pretreatment, like polyurethane in the polyurethane pathway. The indices which will be recalculated and assessed are (i) PWI, (ii) PMI, (iii) SMI, (iv) SMIexc and (v) E-factor. These indices will be calculated for both products, aniline and LPPs, and assessed compared to the original calculations of the polyurethane pathway.

2.2.4 Processing of the data

The raw values of the applied indices for both processes and products can be compared as they are. However, to simplify the comparison, all the values have been normalised to one (1) utilising Equation 9 and Equation 10 [1]. This means that the raw value of the calculated index is divided by the highest score of both processes considering the same desired product. By this method, the normalised value will always be equal to or higher than 0 and lower than or equal to 1. Radar charts are composed of these normalised values, which will be the basis for assessing the two processes.

$$N_b = \frac{B}{\text{Max}(B, P)} \quad (9)$$

$$N_p = \frac{P}{\text{Max}(B, P)} \quad (10)$$

where

B = raw value of polyurethane process of appropriate index

P = raw value of biomass process of appropriate index

N_b = normalized value for B

N_p = normalized value for P

3 Results and discussion

3.1 Estimated green chemistry indices

Following the methodology mentioned earlier, the calculated values are presented in Table 8 in the appendix. All calculated values are based upon 1 kg of desired product, where the indices calculated for 1 kg of aniline are denoted by one (1) and the indices calculated for 1 kg of LPPs are denoted by two (2). The normalised values calculated with Equation 9 and Equation 10 of both processes and both products are presented in Figure 4 and Figure 5. The radar charts are based on the normalised GC indices values presented in Table 9 and Table 10. Figure 4 depicts the assessment results if the desired product is 1 kg of aniline. Figure 5 shows the results of the assessed indices if the desired product is 1 kg of LPPs. These graphical representations visualise the data on which the assessment is based. As mentioned earlier, the LPPs of the polyurethane process are considered equal to the LPPs of the biomass process. All indices will be addressed separately, where the distinction between the two processes and the desired product is made. All differences and characteristics of both processes described below are based on the values in the tables mentioned earlier in the appendix. However, significant simplifications and assumptions have been made in the calculations and the design of the processes due to the incompleteness of the data. Therefore, the calculated values are regarded as rough estimations and will be assessed more theoretically than quantitatively.

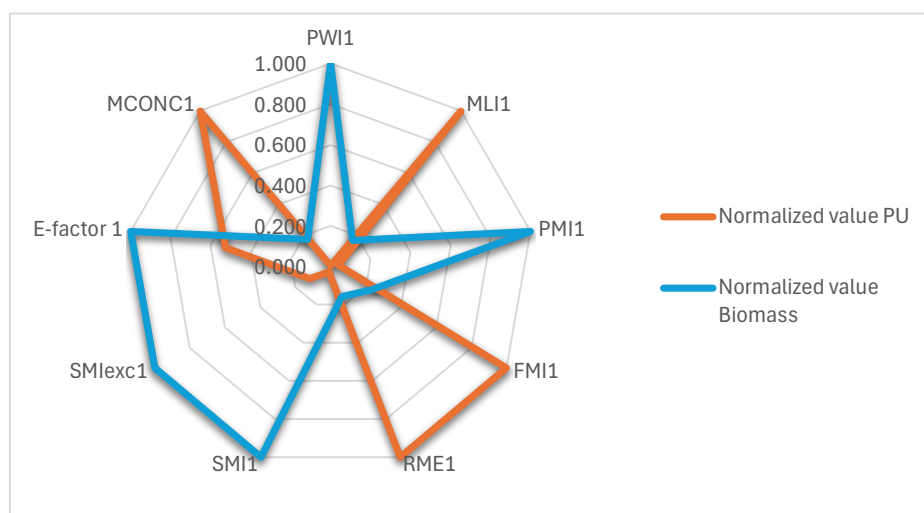


Figure 4: Radar chart of normalised values of the applied indices considering 1 kg of aniline as product

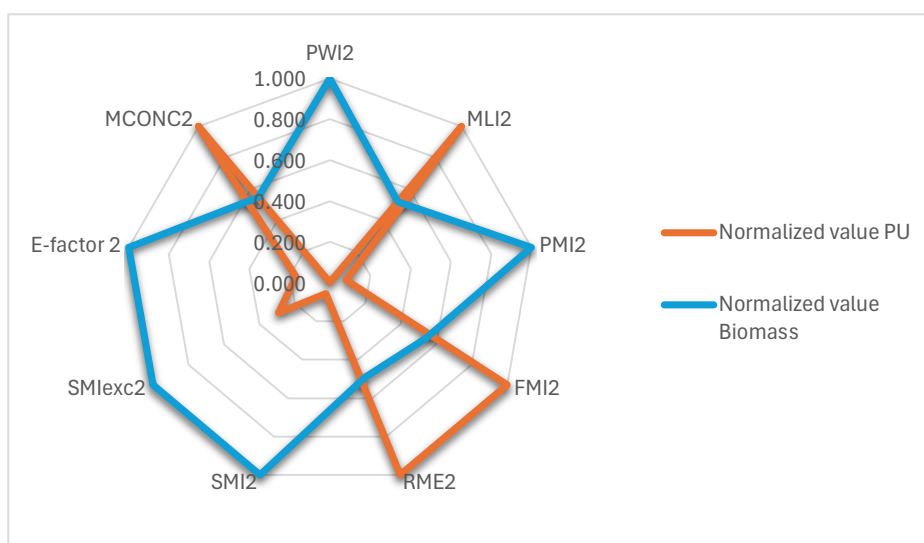


Figure 5: Radar chart of normalised values of the applied indices considering 1 kg of LPPs as product

Process water mass intensity (PWI)

A significant difference is observed when comparing the PWI values when aniline is the desired product. A higher value for the biomass pathway is expected as lignin extraction is highly water-intensive. The separation steps of both processes also need water to dilute the acids. However, the amount needed in the separation step for aniline is significantly less than needed for lignin extraction. The same trend is observed when LPPs are taken as the desired product. However, as the LPPs produced from the biomass process do not need separation as no water is reported at the reactor outlet, the PWI of the biomass process decreases somewhat. It can be concluded that the biomass pathway is significantly more water-intensive than the polyurethane process.

Mass loss index (MLI)

A high MLI indicates high separation efforts and low process efficiency. When taking aniline as the desired product, the polyurethane pathway has a significantly higher MLI than the biomass pathway. This has to do with the weight percentage of aniline in the reactor outlet composition being significantly lower for the polyurethane pathway than for the biomass pathway. The same trend is observed for the LPPs as the desired product. This has to do with the significant difference in solid and gas residue in the reactor outlet, which is considered an undesired product and, therefore, increasing the numerator of Equation 3 and increasing MLI. However, the difference in MLI is decreased, in favour of the polyurethane pathway, when changing the desired product to LPPs as the low selectivity to aniline is compensated. The increased separation efforts through a higher MLI for the polyurethane process are reflected in the mass of substances necessary for separation. Although the separation procedure is equal for both processes, the polyurethane process needs more than three times the total mass of necessary separation compounds than the biomass pathway.

Process mass intensity (PMI)

To calculate the PMI, all input mass that enters the process boundary has to be considered. A low PMI indicates an efficient and selective process. In the case of the biomass pathway for both products, the initial mass of biomass and the chemicals needed for the lignin extraction must also be considered. Therefore, the PMI of the biomass pathway is expected to be significantly higher than the polyurethane pathway, as the only pretreatment necessary for the polyurethane is grinding, which is not considered in calculating the PMI. This expectation is also reflected in the obtained values for the PMI. Regardless of the desired product, the PMI of the biomass process is significantly higher than the PMI of the polyurethane process. When LPPs are chosen as the desired product, the difference in PMI between the two processes does change due to the biomass pathway not requiring separation.

Feedstock mass intensity (FMI)

A high FMI indicates a low conversion efficiency from the feedstock to the desired product(s). The values of the FMI differ, regardless of the desired product, in favour of the biomass pathway. This means that the conversion of feedstock to the desired product is better through the catalysed lignin pyrolysis rather than the polyurethane pyrolysis. However, the difference shrinks when LPPs are regarded as the desired product. This has to do with the higher selectivity to aniline in the lignin pyrolysis compared to the polyurethane pyrolysis. A higher observed selectivity for aniline is also expected, as the lignin pyrolysis is catalysed and has a more extensive source of reactive nitrogen in the form of ammonia. Meanwhile, polyurethane already contains all of its nitrogen, which can be utilised to form aniline. The higher FMI calculated for the polyurethane pathway is also reflected in the higher amount of solids and gases at the reactor outlet.

Reaction mass efficiency (RME)

The RME is stipulated by dividing the desired product's mass by the feedstock's mass and other input streams for the reaction. In this project, a high RME indicates low efficiency and a highly demanding process regarding resources. When aniline is considered the desired product, the biomass pathway excels due to its superior selectivity towards aniline compared to the polyurethane pathway. The observed trend is equal when LPPs are regarded as the desired product. However, the diminishing difference between the two pathways when the desired product is changed is due to the higher selectivity towards aniline in the biomass pathway not having as much influence in calculating the RME for LPPs.

Solvent mass intensity (SMI)

The solvent mass intensity indicates the amount of solvent used per mass of the product of interest. As lignin extraction is highly water intensive, a high SMI is expected for the biomass pathway compared to the polyurethane pathway. This expectation is reflected in the calculated values where the SMI of the biomass pathway is significantly higher than that of the polyurethane pathway. Both pathways share the identical acid-base extraction step in the separation. However, polyurethane has a three times higher mass intensity of solvents in the acid-base extraction. Therefore, based on the separation, the SMI of the polyurethane pathway is expected to be higher than the SMI of the biomass pathway. This is not reflected in the calculated indices as the SMI of the lignin extraction alone is more than three times higher than the SMI of the total polyurethane process. The difference in the normalised SMI for the polyurethane pathway between the two desired products is caused by the separation not being necessary for the biomass pathway when LPPs are the desired product. Nonetheless, the SMI of polyurethane is significantly lower than that of the biomass pathway, regardless of the desired product.

Solvent mass intensity excluding water (SMI_{exc})

As mentioned before, the high SMI for the biomass pathway is caused by the high water-demanding lignin extraction. Therefore, a lower SMI_{exc} is expected as the water is omitted from the list of solvents considered. This expectation is reflected in the calculated values. However, the remaining chemicals necessary for lignin extraction are still fairly significant. Like the SMI, an improvement of the SMI_{exc} is observed for the biomass pathway when choosing LPPs as the desired product, as all solvents necessary for the separation of aniline can be omitted in the calculation. Nonetheless, also through the application of the allocation factors, the SMI_{exc} is higher for the biomass pathway compared to the polyurethane pathway regardless of the desired product.

E-factor

As everything other than the desired products is considered waste in both pathways, the E-factors are expected to be significant. This is reflected in the calculated values of the E-factors being 165 for the polyurethane pathway and 315 for the biomass pathway Table 8 when aniline is the desired product. For the polyurethane pathway, the high E-factor is caused by the low selectivity for aniline in the LPPs, combined with the high amounts of biochar and gases in the reactor outlet. Based on these observations, the biomass pathway is expected to yield a lower E-factor and less waste per kilogram of product. However, this is not reflected in the calculated E-factor. Although the biomass pathway yields more desirable FMI, RME and needs less mass solvent for separating, the calculated E-factor is nearly twice as high as the polyurethane pathway. Once again, this has to do with the extensive pretreatment necessary to obtain the needed lignin for the reaction and the waste formed in that part of the process. When LPPs are considered the desired product, the E-factor for both processes is expected to decrease as the mass of what is considered waste will decrease. This expected decrease is observed. However, the decrease of the E-factor of LPPs is not as significant as that of the polyurethane pathway. Where the E-factor for the polyurethane pathway decreases roughly by a factor of six, the E-factor for the biomass pathway only decreases by roughly half. The observed decrease of the E-factor of the polyurethane pathway is caused by the necessary feedstock for the production of 1 kg aniline, which is six times higher than for 1 kg of LPPs. For the biomass pathway, the same observation can be made for the decreasing E-factor. However, instead of six times the feedstock for 1 kg of aniline, two times the amount of biomass is necessary to produce 1 kg of aniline compared to 1 kg of LPPs. Moreover, as no separation is needed for the LPPs produced by the biomass pathway, the chemicals have been omitted. Therefore, the amount of waste produced by the process also decreases.

MCONC

The MCONC indicates separation efforts for extracting the desired products and the potential waste from a process. A low MCONC indicates low separation efforts and little waste production in this project. When aniline is considered the desired product, the normalised MCONC of the biomass pathway is significantly lower than that of the polyurethane pathway. This indicates less extraction efforts, reflected in the separation of aniline from the other LPPs, which is far less mass intensive in the biomass pathway than in the polyurethane pathway. When LPPs are considered a desired product, the same trend is observed. However, the difference decreases. This change can be elucidated by the low selectivity for aniline in the polyurethane pyrolysis, which no longer poses an issue. Nonetheless, the significant amount of biochar and gases produced through the polyurethane pathway impedes a better performance when considering the MCONC. Moreover, as the weight percentage of water in the reactor outlet of the polyurethane pyrolysis is relatively significant,

the total mass at the reactor outlet increases further, increasing the MCONC even more. As mentioned before, water is expected at the outlet of the lignin pyrolysis reactor, which is expected to increase the MCONC. So, although the biomass pathway excels regardless of the desired product, a lack of data could potentially contribute to the significant differences in the calculated MCONC values.

3.2 Estimated green chemistry indices neglecting lignin extraction

Considering the discussion of the indices mentioned earlier, the biomass pathway, including the organosolv lignin extraction and the polyurethane pathway, is observed to have a lot of rigorous differences. In many cases, this is caused by the organosolv lignin extraction requiring a significant amount of water. To look into the influence of the incorporation of lignin extraction on the comparison, the extraction is omitted, and lignin is considered a raw material like polyurethane foam. Following the methodology mentioned earlier, the calculated values are presented in Table 11 and Table 12. The visual representation of the green chemistry indices when 1 kg of aniline is considered as desired product is presented in Figure 6, whereas Figure 7 presents the indices when 1 kg of LPPs is desired. The graphs have been composed of the normalised values presented in Table 13 and Table 14, respectively.

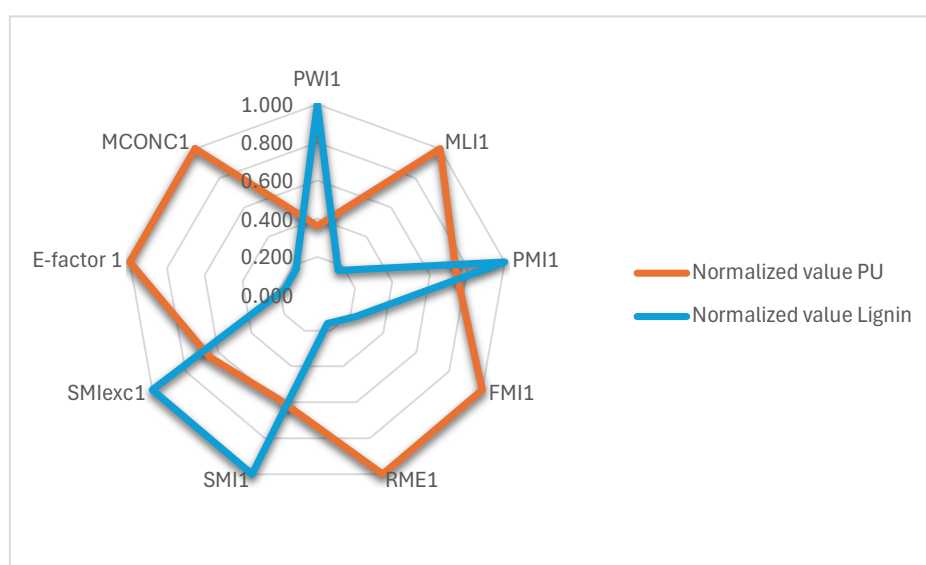


Figure 6: Radar chart of normalised values of the applied indices when lignin is considered raw feedstock with 1 kg aniline as the desired product

When aniline is regarded as the desired product, the biomass pathway's relative performance increases regarding PWI, PMI, SMI, SMIexc, and E-factor. Most of the generated waste from the biomass pathway is allocated to organosolv extraction. The amount of waste generated when the organosolv extraction is omitted is of such considerable magnitude that it even alters the trend, making the biomass pathway perform better than the polyurethane pathway regarding the E-factor. However, despite the increasing relative performance of the biomass pathway regarding the PWI, PMI, SMI and SMIexc the polyurethane pathway still excels on these metrics. This is due to the relatively low allocation factor for aniline with respect to separation Table 6 for the polyurethane pathway compared to the biomass pathway Table 7. This is caused by the high amount of water at the reactor outlet in the polyurethane pathway, which is considered in allocation factor calculations.

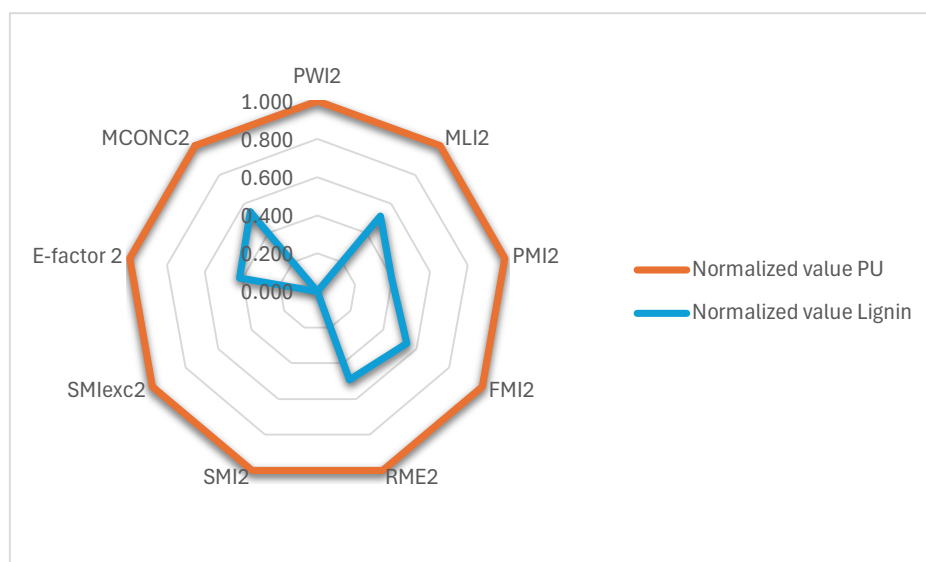


Figure 7: Radar chart of normalised values of the applied indices when lignin is considered raw feedstock with 1 kg LPPs as the desired product

If LPPs are the desired product, the biomass pathway will excel in all metrics. This is caused by the separation not being necessary, as no water is reported at the reactor outlet of the lignin pyrolysis reactor. Although water is expected at the reactor outlet and separation is necessary, the calculated values are likely incorrect in practice. This observed trend and substantiation merely signifies the need for completeness in data. However, the lignin pyrolysis of the biomass pathway still has higher selectivity to LPPs than biochar and gases compared to the polyurethane pathway. Therefore, the RME, MCONC, MLI and FMI perform better in the biomass pathway, regardless of whether the separation is necessary. The increasing performance regarding PMI is a combination of higher selectivity and unnecessary separation in the biomass pathway.

4 Conclusions and recommendations

4.1 Conclusions

This project aimed to perform a comparative study on the environmental impact of two renewable amines and LPP-producing pathways. The assessed green chemistry metrics have proven valuable tools for uncovering both processes' advantages and disadvantages. Analysing the calculations' results allows possible pitfalls to be recognised and prevented in developing further design stages. The estimated performance regarding sustainability at an early stage and the other aspects of the SSbD framework have proven significantly helpful, even before an experimental proof of concept has been performed. Both assessed processes

have clear advantages and disadvantages. The polyurethane pathway performs significantly better for both desired products regarding waste generation over the biomass pathway when organosolv extraction is taken into the process description. However, the waste generation of the biomass pathway significantly decreases when the organosolv extraction is omitted. Due to the biomass pathway's significantly higher selectivity to aniline, the overall mass intensity of the separation and reactor input masses are significantly lower than that of the polyurethane pathway. Besides the higher selectivity to aniline, the biomass pathway's reaction is more selective towards LPPs than biochar and gases. Moreover, due to the reported absence of water in the reactor outlet composition in the biomass pathway, no separation is necessary when LPPs are considered the desired product, which lowers the mass intensity of the overall pathway. When LPPs are chosen as the desired product and organosolv extraction of lignin is omitted, the biomass pathway excels in every index. However, this observation merely indicates the significance of data collection and system boundary definition.

4.2 Limitations and recommendations

The obtained data from the literature contains apparent gaps which had to be filled with very rough assumptions, like omitting the 10-15% unknown compounds at the reactor outlet, linear scaling from milligram to kilogram, 100% grinding and condenser efficiency and trusting no reported water at the lignin pyrolysis reactor outlet. As mentioned before, the processes as assessed have yet to be performed experimentally. A complete experimental proof of concept would be a rational subsequent step to verify these assumptions and gain a more detailed insight into these processes. Furthermore, weighting the indices based on an appropriate further research scope could be applied to appoint a more desirable process. In this manner, the study is not solely to indicate the advantages and disadvantages of both pathways but to objectively indicate the optimal pathway for the desired product.

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6 Appendices

Table 1: The 12 Green Chemistry Principles [4][6]

1	Waste prevention not remediation
2	Atom efficiency
3	Less hazardous/toxic materials
4	Safer products by design
5	Innocuous solvents and auxiliaries
6	Energy efficient by design
7	Renewable rather than depleting raw material
8	Shorter synthesis (avoid derivatization)
9	Catalytic rather than stoichiometric reagents
10	Design products for degradation
11	Analytical methods for pollution prevention
12	Inherently safer processes

Table 2: Chemical composition at the reactor outlet of fluid bed pyrolysis experiments[22]

Substance balances of the pyrolysis of PUR and EP, EP/F (referring to total organic input) (% wt.)

Material	PUR (700°C)	PUR (800°C)	EP (700°C)	EP (850°C)	EP/F (850°C)
Carbon dioxide	1.73	0.89	19.55	16.69	10.06
Carbon monoxide	33.98	35.72	11.29	26.01	24.68
Hydrogen cyanide	0.45	4.19	–	–	–
Methane	16.08	16.68	11.40	12.49	10.78
Ethene	7.17	4.89	4.84	3.22	1.49
Propene	1.32	0.20	0.90	0.10	0.06
Other gases	4.60	3.33	2.54	1.96	2.68
Aliphatics/naphthenes	<0.01	<0.01	0.02	0.07	0.01
Benzene	1.39	4.67	5.99	6.96	4.88
Toluene	0.14	0.60	4.14	1.15	1.15
Naphthalene	0.39	2.06	1.54	4.22	2.36
Other aromatics	1.67	3.41	3.11	4.85	2.82
Phenol	–	–	1.03	0.32	2.58
Other hetero- <i>O</i> -compounds	0.01	<0.01	1.68	0.49	1.03
Aniline	0.90	0.64	–	–	–
Benzonitrile	1.10	1.85	–	–	–
Other hetero- <i>N</i> -compounds	1.52	2.16	–	–	–
Not identified/detected	7.93	2.22	6.26	7.24	14.11
Tar fraction	13.49	8.22	23.42	11.44	7.53
Carbon black/coke	2.34	4.86	0.23	1.10	9.82
Water	3.80	4.14	2.05	1.68	3.97

Table 3: Input and output streams of the polyurethane pyrolysis reactor based on an aniline output of 1 kg, desired LPPs composition indicated in orange

Input streams	Mass (kg)	Phase
Polyurethane	100.600	s
Nitrogen	45.749	g
Outlet streams		
CO ₂	1.922	g
CO	37.747	g
HCN	0.500	g
Other gases	5.110	g
Benzene	1.544	l
Other aromatics	1.855	l
Semi-coke	2.599	s
Methane	17.863	g
Ethylene	7.965	g
Propylene	1.466	g
Naphthenes	0.011	l
Toluene	0.156	l
Naphthalene	0.433	l
Aniline	1.000	l
Benzonitrile	1.222	l
Resin	14.986	s
Water	4.221	l

Table 4: Chemical composition at the reactor outlet of catalysed reactive pyrolysis under ammonia atmosphere[26]

Entry	1	2	3	4	5	6	7
Catalyst	None	HZSM-5	HY	β -zeolite	MCM-41	ZnO/HZSM-5	ZnO/HY
Metal loading (wt %)						2.0	2.0
Identified carbon (C%)	78.1	85.2	87.8	86.4	87.1	86.0	85.7
Biochar	50.3	59.5	64.3	67.1	65.4	55.8	61.1
Gases	17.5	18.7	19.1	16.2	17.2	21.1	19.4
Carbon detected in the organic bio-oil	10.3	7.0	4.4	3.1	4.5	9.8	5.2
	Detected products in the organic bio-oil (C%)						
Phenolic compounds	10.3	1.0	0.3	0.1	0.1	2.3	0.4
Aromatic hydrocarbons	N.D.	1.7	0.2	0.8	1.1	1.9	0.3
Aromatic amines	N.D.	4.3	3.9	2.2	3.3	5.6	4.5
	Detected products Selectivity (%)						
Phenolic compounds ^b	100	14.3	6.8	3.2	2.2	25.3	7.7
Aromatic hydrocarbons ^c	N.D.	24.3	4.5	25.8	24.4	13.2	5.8
Aromatic amines ^d	N.D.	61.4	88.6	71.0	73.3	57.1	86.5
	Aromatic amines selectivity						
Aniline	N.D.	85.1	93.4	98.1	91.3	87.3	88.7
Methylanilines	N.D.	12.6	6.6	1.9	6.3	10.5	9.8
Naphthylamines	N.D.	2.3	0	0	2.4	2.2	1.5

^aReaction conditions: mass of lignin: 0.5 g, pyrolysis temperature: 600 °C catalyst usage: 1 g, ammonia flow rate: 60 mL/min, residence time: 0.57s.

^bPhenolic compounds: phenol, *m*-cresol, guaiacol, etc. ^cAromatic hydrocarbons: benzene, toluene, xylenes, ethylbenzene, naphthalene, etc.

^dAromatic amines: aniline, 2-methylaniline, 3-methylaniline, naphthylamine, etc.

Table 5: Input and output streams of the lignin pyrolysis reactor based on an aniline output of 1 kg, LPPs composition indicated in orange

Input streams	Mass (kg)	Phase
Lignin	17.624	s
Ammonia	5.634	g
Outlet streams		
Biochar	11.435	s
Gases	4.324	g
Phenolic compounds	0.476	l
Aromatic hydrocarbons	0.388	l
Aniline	1.000	l
Methylaniline	0.120	l
Naphthylamine	0.025	l

Table 6: Allocation factors calculated for the green chemistry indices of the polyurethane pathway

Allocated to	Allocation factor
LPPs as product with respect to reaction	0.063
Aniline as product with respect to reaction	0.010
LPPs as product with respect to separation	0.596
Aniline as product with respect to separation	0.096

Table 7: Allocation factors calculated for the green chemistry indices of the biomass pathway

Allocated to	Allocation factor
Chemicals etc. for lignin extraction from biomass	0.275
LPPs as product with respect to reaction	0.113
Aniline as product with respect to reaction	0.056
Aniline as product with respect to separation	0.498

Table 8: Values of the calculated indices, indices followed by one (1) are for 1 kg of aniline and indices followed by two (2) are of 1 kg of LPPs as product

Green Chemistry Indices	Polyurethane pathway	Biomass pathway
Water at reactor outlet (WRO)	0.044	0.000
Process water intensity, aniline (PWI1)	0.271	70.342
Process water intensity, LPPs (PWI2)	0.271	34.666
Mass loss index, aniline (MLI1)	99.622	16.767
Mass loss index, LPPs (MLI2)	15.171	7.844
Process mass intensity, aniline (PMI1)	3.311	86.655
Process mass intensity, LPPs (PMI2)	3.312	41.781
Feedstock mass intensity, aniline (FMI1)	100.600	23.258
Feedstock mass intensity, LPPs (FMI2)	16.170	8.779
Reaction mass efficiency, aniline (RME1)	0.007	0.043
Reaction mass efficiency, LPPs (RME2)	0.043	0.086
Solvent mass intensity, aniline (SMI1)	1.857	68.714
Solvent mass intensity, LPPs (SMI2)	1.857	32.676
Solvent mass intensity, aniline (SMIexc1)	1.586	13.380
Solvent mass intensity, LPPs (SMIexc2)	1.586	5.460
E-factor 1 (aniline)	164.743	313.616
E-factor 2 (LPPs)	25.641	152.537
MCONC 1 (aniline)	0.010	0.056
MCONC 2 (LPPs)	0.062	0.113

Table 9: Normalized values of the applied GC indices based on 1 kg aniline as desired product

Green Chemistry Indices	Normalized value PU	Normalized value Biomass
WRO	1.000	0.000
PWI1	0.004	1.000
MLI1	1.000	0.168
PMI1	0.038	1.000
FMI1	1.000	0.231
RME1	1.000	0.159
SMI1	0.027	1.000
SMIexc1	0.119	1.000
E-factor 1	0.525	1.000
MCONC1	1.000	0.177

Table 10: Normalized values of the applied GC indices based on 1 kg LPPs as desired product

Green Chemistry Indices	Normalized value PU	Normalized value Biomass
PWI2	0.004	1.000
MLI2	1.000	0.517
PMI2	0.079	1.000
FMI2	1.000	0.543
RME2	1.000	0.492
SMI2	0.057	1.000
SMIexc2	0.291	1.000
E-factor 2	0.168	1.000
MCONC2	1.000	0.547

Table 11: Values for the green chemistry indices where lignin in the biomass pathway is considered raw feedstock with 1 kg aniline as desired product

Extra green chemistry indices 1	Values polyurethane pathway	Values lignin pathway
PWI1	0.271	0.749
PMI1	3.311	4.487
SMI1	1.857	3.178
SMIexc1	1.586	2.429
E-factor 1	164.743	28.788

Table 12: Values for the green chemistry indices where lignin in the biomass pathway is considered raw feedstock with 1 kg LPPs as desired product

Extra green chemistry indices 2	Values polyurethane pathway	Values lignin pathway
PWI2	0.271	0.000
PMI2	3.312	1.310
SMI2	1.857	0.000
SMIexc2	1.586	0.000
E-factor 2	25.641	10.657

Table 13: Normalized values for the green chemistry indices where lignin in the biomass pathway is considered raw feedstock with 1 kg aniline as desired product

Green Chemistry Indices	Normalized value PU	Normalized value Lignin
PWI1	0.361	1.000
MLI1	1.000	0.168
PMI1	0.738	1.000
FMI1	1.000	0.231
RME1	1.000	0.159
SMI1	0.584	1.000
SMIexc1	0.653	1.000
E-factor 1	1.000	0.175
MCONC1	1.000	0.177

Table 14: Normalized values for the green chemistry indices where lignin in the biomass pathway is considered raw feedstock with 1 kg LPPs as desired product

Green Chemistry Indices	Normalized value PU	Normalized value Lignin
PWI2	1.000	0.000
MLI2	1.000	0.517
PMI2	1.000	0.396
FMI2	1.000	0.543
RME2	1.000	0.492
SMI2	1.000	0.000
SMIexc2	1.000	0.000
E-factor 2	1.000	0.416
MCONC2	1.000	0.547