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Review

Exploring industrial lignocellulosic waste: Sources, types, and potential as high-value molecules



Elisabeth A. Cazier^{a,b,c,*}, Thanh-Nhat Pham^{a,b}, Louis Cossus^{a,b}, Maher Abla^{a,b}, Tina Ilc^{a,b}, Philip Lawrence^{a,b}

^a UCLy (Lyon Catholic University), ESTBB, Lyon, France

^b UCLy (Lyon Catholic University), UR CONFLUENCE : Sciences et Humanités (EA 1598), Lyon, France

^c Nantes Université, Oniris, GEPEA, UMR 6144, F-44600 Saint-Nazaire, France¹

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ABSTRACT

Lignocellulosic biomass has a promising role in a circular bioeconomy and may be used to produce valuable molecules for green chemistry. Lignocellulosic biomass, such as food waste, agricultural waste, wood, paper or cardboard, corresponded to 15.7% of all waste produced in Europe in 2020, and has a high potential as a secondary raw material for industrial processes. This review first presents industrial lignocellulosic waste sources, in terms of their composition, quantities and types of lignocellulosic residues. Secondly, the possible high added-value chemicals obtained from transformation of lignocellulosic waste are detailed, as well as their potential for applications in the food industry, biomedical, energy or chemistry sectors, including as sources of polyphenols, enzymes, bioplastic precursors or biofuels. In a third part, various available transformation treatments, such as physical treatments with ultrasound or heat, chemical treatments with acids or bases, and biological treatments with enzymes or microorganisms, are presented. The last part discusses the perspectives of the use of lignocellulosic waste and the fact that decreasing the cost of transformation is one of the major issues for improving the use of lignocellulosic biomass in a circular economy and green chemistry approach, since it is currently often more expensive than petroleum-based counterparts.

1. Introduction

With the heavy environmental impact of petroleum and its everyday use, recycling waste is becoming increasingly necessary in an ever-expanding circular economic approach and is vital in terms of ecological impact. Indeed, 2 007 million tonnes of primary waste (*i.e.* waste generated during the extraction and processing of raw materials, during the consumption of final products and cleaning operations), were generated in Europe in 2020, corresponding to 94 % of total produced waste (Eurostat, 2023). Primary waste is composed mostly of mineral waste (66.5 %; Fig. 1), that is difficult to recycle (*i.e.* to transform into a new product) and tends to be reused without transformation for the same or a different use. Some categories of waste already have recycling pathways, such as for the production of the same material from waste (glass, wood, paper and cardboard), composting (household waste, food and animal waste), anaerobic digestion (household waste, sludges, food

and animal waste), or as an energy source (wood waste). However, not all waste is recycled or even treated. Biomass waste corresponded to 13.4 % of the total waste treated in Europe in 2020 (total waste corresponding to biomass, metal ore, non-metallic minerals and fossil energy material) (Table 1). Only 243 million tonnes of biomass waste were treated in 2020 in Europe, corresponding to 77 % of all biomass waste produced that year (Table 1). Of the biomass waste treated, 87.9 % of waste was recovered by recycling (59.7 %) or energy recovery (28.2 %) and the rest was discarded in landfill, for backfilling or incinerated, corresponding to a loss of potential secondary raw materials (Eurostat, 2021) (Table 1).

For industrial companies, recycling waste would be an advantage from an ecological and economical point of view. Research into using waste as a source of secondary raw materials is an increasing trend in many sectors, for example using minerals, metals (Spooren et al., 2020), incineration ash (Barbieri and Lancellotti, 2004; Quina et al., 2018),

* Corresponding author at: Nantes Université, Oniris, GEPEA, UMR 6144, F-44600 Saint-Nazaire, France.

E-mail addresses: Elisabeth.Cazier@univ-nantes.fr (E.A. Cazier), mabla@univ-catholyon.fr (M. Abla), tilc@univ-catholyon.fr (T. Ilc), plawrence@univ-catholyon.fr (P. Lawrence).

¹ Current address

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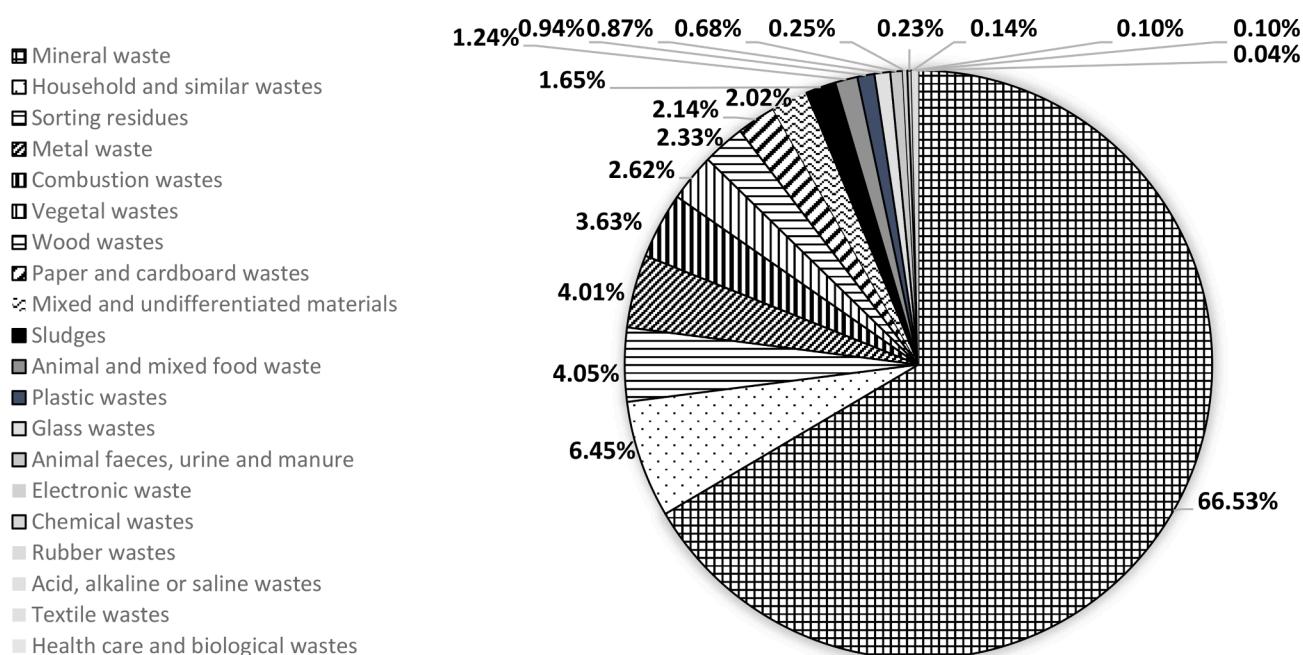


Fig. 1. Composition of different types of waste in Europe in 2020 (Eurostat, 2023), data code: ENV_WASGEN. Mineral waste = mineral waste from construction + other mineral waste + soils + dredging soils + mineral waste from waste treatment. Sludges = common sludges + industrial effluents sludges + sludges and liquid waste from waste treatment. Metal waste = ferrous + non-ferrous + mixed ferrous and non-ferrous. Electronic waste = discarded equipment + discarded vehicles + batteries and accumulator waste. Lignocellulosic waste: vegetable waste + wood waste + paper and cardboard waste + animal faeces, urine and manure + textile waste and part of household and similar waste.

Table 1

Type of waste treatment in Europe in 2020 according to Eurostat (2021), data code:ENV_WASSD, in tonnes.

In 2020	Biomass	Metal ores	Non-metallic minerals	Fossil energy material
Waste treated (tonnes)	243 721 000	101 916 000	1 409 715 000	65 553 000
Landfill	10,5%	4,1%	40,1%	19,5%
Incineration	1,1%	0,4%	0,1%	3,3%
Disposal (other)	0,3%	0,0%	5,1%	0,2%
Energy recovery	28,2%	5,4%	0,8%	29,0%
Recycling	59,7%	90,0%	37,1%	46,7%
Backfilling	0,2%	0,1%	16,8%	1,3%

rubber, plastics (Santos et al., 2022), or agricultural and food industry waste (Gagarina et al., 2020; Phadke et al., 2021; San Martin et al., 2021). However, to increase the use of secondary raw materials in industry, improvement in the definition (Hoernig, 2022), data collection (Dino et al., 2017) and even distribution of secondary raw materials in Europe is necessary. It is worthy to note that modern biorefineries, in the context of bioeconomics and ecological transition, could be defined as physico-chemical and/or biological processes applied to extract, purify and/or transform compounds from organic materials from natural sources, into bio-based chemicals. The latter might also then serve as platform molecules or raw materials for production of other bioproducts (Conteratto et al., 2021).

Several types of industrial waste are promising sources of secondary raw materials, including notably lignocellulosic waste (crop and vegetable residues, wood, food waste, paper and cardboard), chemical waste (i.e. wastewater (Bertin et al., 2004; Paździor et al., 2019)), inorganic waste (Radulescu et al., 2007), and organic solvent waste (Seyler et al., 2005). Of these, lignocellulosic waste has a high transformation potential due to its composition of lignin, cellulose and hemicellulose. In this review, only industrial organic waste that may be used as secondary raw materials will be presented. The first part of this review will present the composition of lignocellulosic biomass and its worldwide repartition. In

a second part, high-value chemicals which may be produced from lignocellulosic residues will be discussed. Physical, chemical and biological treatment strategies will be presented in a third part. The perspectives for the use of lignocellulosic residues in circular economies will conclude this review.

2. Industrial lignocellulosic waste

2.1. Composition of lignocellulosic waste

Lignocellulosic biowaste is a large part of the waste produced, not only in industry but also as agricultural or household waste (7 to 14% in Europe (Eurostat, 2023), Fig. 1). One of the biggest problems in valorising lignocellulosic biomass is their complex matrix structure. Lignocellulosic biomass, and more precisely the plant cell walls therein, is constituted of three main macromolecules polymers: cellulose, hemicellulose and lignin (Fig. 2). These macromolecules are connected in a three-dimensional structure which increases the difficulty for extraction or transformation. After removal of lignin, hemicellulose forms a matrix around cellulose fibrils and thus physically form a barrier between the cellulose and the external environment (Bledzki and Gassan, 1999; S. Brethauer et al., 2020a; Zhbakov, 1992). Within this structure, hemicellulose forms hydrogen bonds with cellulose, and covalent bonds with lignin via dimerization of hydroxycinnamic acids and internal covalent bonds (Sun, 2010).

2.1.1. Lignin

Lignin does not have a typical structure or repeatable units (Fig. 2), and is therefore chemically and physically heterogeneous due to variations in monomer composition and the frequency of inter-monomer linkages. Lignin is formed by the combination of proto-lignins: *p*-coumaryl, coniferyl and sinapyl alcohols by polycondensation and enzymatic dehydrogenation. The proportions of the different units in the lignin structure depend on the plant type. The chemical bonds present in lignin are: arylglycerol- β -ether linkages (β -O-4), phenylcoumaran (β -5),

Table 2
Combined post-production and pre-consumption food waste in European countries in 2009 according to OECD(OECD.Stat, 2023) data set code FOOD WASTE) in tonnes. In bold, the lignocellulosic waste.

Countries	Austria	Belgium	Czech industry	Denmark	Estonie	Finland	France	Germany	Greece	Hungary	Ireland	Italy	Netherland	Norway	Poland	Portugal	Slovak republic	Spain	Sweden
Alcoholic							50,000	4000	4000	4000	10,000				7000			50,000	
Beverages							636,000	21,000	1000	1000					1000				
Animal Fats	2000	1000	1000				9000	1,556,000	229,000	164,000	80,000	92,000	58,000			35,000	102,000	534,000	139,000
Cereals – Excluding	166,000	63,000	80,000	297,000	16,000														
Beer								6000	2000	2000	5000	2000	1000	1000	1000	3000	2000	17,000	2000
Eggs	170,000	5000	2000	1000		1000	511,000	346,000	303,000	18,000	14,000	1,114,000	93,000	17,000	222,000	132,000	19,000	849,000	37,000
Fruits – Excluding		65,000	48,000	18,000		10,000													
Wine								5000		13,000	3000				5000				
Meat				1000	4000		34,000	30,000	33,000	45,000	53,000	43,000		13,000	208,000	2000	3000		
Milk – Excluding	33,000		14,000																
Butter																			
Offal									2000	1000					6000				
Oilcrops	1000	495,000	10,000				61,000	162,000	30,000	6000		282,000	5000		2000	9000	16,000	67,000	1000
Pulses	2000		3000	1000			3000	6000	3000		1000	14,000		2000	9000	4000	3000	39,000	1000
Spices										2000									
Starchy Roots	51,000	293,000	21,000	243,000	6000		1,584,000	928,000	80,000	18,000	9000	50,000	171,000	11,000	740,000	23,000	4000	53,000	85,000
Sugarcrops		55,000										5000			11,000				6000
Stimulants																			
Treenuts	1000	1000	1000				1000	12,000	2000		4000		1000	1000	2000	2000		26,000	1000
Vegetable Oils	4000																	2000	
Vegetables	113,000	214,000	34,000	34,000	3000	26,000	898,000	798,000	445,000	59,000	35,000	1,217,000	207,000	31,000	557,000	280,000	34,000	1,433,000	70,000

agricultural sector, harvest residues from sugarcane, corn, rice, wheat or palm oil are the main agricultural crops per quantity in the world (Millati et al., 2019). The main types of waste produced are therefore sugarcane bagasse, corncobs, rice straw and husks, wheat straw, oil palm fibres, shells and empty oil palm fruit bunches (Millati et al., 2019). The quantity of waste produced and its relative composition are shown in Table 3. In Europe, the main countries producing agricultural waste are Spain with 6 254 000 tonnes and the Netherlands with 4 679 000 tonnes produced in 2018.

The type of lignocellulosic industrial waste from the manufacture of wood are mostly bark, sawdust and chips from hardwood and softwood, as described in Table 3 (Millati et al., 2019). Hardwood corresponds to deciduous trees such as oak, maple or birch and is mostly produced in East Asia and America (North and South). Softwood corresponds to coniferous trees such as pine, spruce or fir and is mostly produced in Europe and North America. Hardwood and softwood differ in density and in cell wall composition. Hardwood tends to be denser than softwood and is composed mostly of glucan and xylan compared to mostly glucan for softwood (Millati et al., 2019). In Europe, the main producers of wood waste are Germany with 2 736 000 tonnes, France with 2 104 000 tonnes and Finland with 1 756 000 tonnes produced in 2018 (Table 3).

The paper and pulp industry produces 17 % of global waste, which corresponds to wood waste (bark, sawdust, uncooked chips), alkali compounds used to remove lignin (mix of sodium hydroxide, sodium sulphite and water-alkali-soluble lignin fragments, called black liquor), chemical solvents for bleaching the pulp (chlorine, chlorine dioxide, hydrogen peroxide and ozone), and sludge from the water treatment (Haile et al., 2021; Millati et al., 2019). Paper consumption is estimated at 55 kg/person per year and is mostly produced from cellulosic fibres from both hard and softwood (Haile et al., 2021). The main waste product from the paper and pulp industry is black liquor (170 million tonnes per year) (Haile et al., 2021). The composition of black liquor depends on the type of wood and on the pulping conditions, with a higher rate of lignin recovery for softwood (Jardim et al., 2022). In Europe, the main producers of paper waste are Germany with 3 413 000 tonnes, Finland with 3 275 000 tonnes and France with 2 617 000 tonnes produced per year in 2018.

Another type of lignocellulosic waste is food waste, which has two origins: the food industry and households. Food waste composition and quantities vary markedly among European countries (Table 2). For example, in Belgium, in 2009, food industry waste was composed of 54 % meat food-waste and the rest corresponded to plant food-waste (OECD.Stat, 2023). Moreover, the percentage of food waste from industry was higher compared to households (with 1 073 240 tonnes and 34 948 tonnes respectively in 2018 in Belgium (OECD.Stat, 2023)). In France, however, the most abundant food waste sources were starchy roots with 1 584 000 tonnes, followed by vegetables (898 000 tonnes), animal fats (636 000 tonnes) and eggs (511 000 tonnes). However, in Germany, the composition was different, with cereal waste being the most abundant (1 556 000 tonnes), followed by starchy roots (928 000 tonnes), vegetables (798 000 tonnes) and fruit (346 000 tonnes). Among these types of food waste, many sources are primarily lignocellulosic in composition: cereal waste, vegetable and fruit waste, sugar crop, bagasse, starchy roots, nut waste, and pulses. However, food waste will very often correspond to a mix of various types of waste. Therefore, this waste would not be as easy to use as purer lignocellulosic waste, as shown in Table 2 with the global composition of food waste per country.

The manufacturing of textiles produces waste such as textile residues, pigments, peroxide, organic stabilizers, alkalis, chemical solvents, sludge, and heavy metals (Millati et al., 2019). In 2015, the textile industry produced 92 million tonnes of waste, with 0.14 tonnes of waste per tonne of production. The majority (41.7 %) of this waste corresponded to sludge, 3.2 % to chemicals and 13.7 % to textile residues (X. Li et al., 2021; Stanescu, 2021). Overall, 78 to 90 % of the solid waste can be recycled (Stanescu, 2021), however, only 15 to 20 % of textile

Table 3

Examples of industrial lignocellulosic waste in the world. Tonnes of wood is calculated from an average of the wood density of 300 to 800 kg/m³. Textiles and sludge waste are calculated from the percentage of each fraction in China (Li et al., 2021). The composition in cellulose, hemicellulose and lignin is in percentage of the waste on a dry weight basis. API: Active Pharmaceutical Ingredient (data obtained for 2017^a, 2013^b, 2016^c, 2002^d, 2009^e, 2003^f, 2008^g, 1990^h).

Industrial sector	Type of waste	Waste produced from industrial production (% weight basis)	Highest producing countries in the world (waste produced in tonnes)	Cellulose(%)	Hemicellulose (%)	Lignin(%)	References
Agricultural	Sugarcane bagasse	25–30 % of sugarcane	Brazil (94 million ^a), India (93 million ^a), Europe (55 million ^a)	46.4	23.9	28.1	(Millati et al., 2019)
	Corn cob	22 % of ear corn	USA (81 million ^a), China (49 million ^a), Brazil (20 million ^a)	69.2	22.8	8	(Millati et al., 2019)
	Rice straw	105 % of milled white rice	China (149 million ^a), India (114 million ^a), Indonesia (39 million ^a)	36	24	15.6	(Millati et al., 2019)
	Rice husk	28 % of milled white rice	China (39 million ^a), India (30 million ^a), Indonesia (10 million ^a)	43.3	28.6	22	(Millati et al., 2019)
	Oil palm empty fruit bunch	21.7 % of fresh fruit	Indonesia (8.8 million ^a)Malaysia (4.6 million ^a)	39.1–65	23–29.6	34.4–18	(Abdul Khalil et al., 2008; Millati et al., 2019)
	Oil palm fibres	12.3 % of fresh fruit	Indonesia (5 million ^a), Malaysia (2.6 million ^a)	56–60	27.5	11–20.5	(Abdul Khalil et al., 2008; Millati et al., 2019; Sreekala et al., 1997)
	Oil palm shells	7.1 % of fresh fruit	Indonesia (1.7 million ^a), Malaysia (0.86 million ^a)	7	26	50	(Millati et al., 2019; Okoroigwe and Saffron, 2012)
Wood	Wheat straw	85 % of the whole wheat	Europe (128 million ^a), China (110 million ^a), USA (40 million ^a)	37.8	26.5	17.5	(Millati et al., 2019)
	Hardwood (sawdust)	13 % of total wood	East Asia and Oceania (4.3 million ^b), North America (1.5 million ^b), Latin America (0.87 million ^b)	42–48	15–33	27–34	(Ahmad et al., 2016; Auxenfans et al., 2014; FAOSTAT, 2014; Millati et al., 2019)
	Hardwood (chippable waste)	35 % of total wood	East Asia and Oceania (11.4 million ^b), North America (4 million ^b), Latin America (2.3 million ^b)				(FAOSTAT, 2014; Millati et al., 2019)
	Hardwood (bark)	10 % of total wood	East Asia and Oceania (3.3 million ^b), North America (1.2 million ^b), Latin America (0.67 million ^b)	10–25	11–23	23–28	(FAOSTAT, 2014; Millati et al., 2019)
	Softwood (chippable waste)	35 % of total wood	Europe (28.6 million ^c), North America (20.9 million ^c), Asia (10.8 million ^c)	32	14	31	(Millati et al., 2019)
	Softwood (sawdust)	13 % of total wood	Europe (10.6 million ^c), North America (7.8 million ^c), Asia (4 million ^c)	55	4	29	(Auxenfans et al., 2014; Millati et al., 2019)
	Softwood (bark)	10 % of total wood	Europe (8.17 million ^c), North America (5.97 million ^c), Asia (3.1 million ^c)	19–25	11–18	23–28	(Millati et al., 2019)
Paper	Sawdust	1–3 % of dry pulp	Europe (0.3–0.95 million ^b)	42–55	4–33	29–34	(Auxenfans et al., 2014; Bloemhof-Ruwaard et al., 1996; Haile et al., 2021; Millati et al., 2019)
	Bark	10–30 % of dry pulp	Europe (3.2–9.5 million ^b)	10–25	11–23	23–28	(Bloemhof-Ruwaard et al., 1996; Haile et al., 2021; Millati et al., 2019)
	Wood fragments (chip, knot)	2.5–9 % of dry pulp	Europe (0.8–2.8 million ^b)	32–36	14–22.4	31–32	(Bloemhof-Ruwaard et al., 1996; FAOSTAT, 2014; Haile et al., 2021; Jirjis and Theander, 1990; Millati et al., 2019)
	Black liquor	170–180 % of dry pulp	Europe (53.8–57 million ^b)	33–42	7–23	1–29	(Bloemhof-Ruwaard et al., 1996; Haile et al., 2021; Jardim et al., 2022)
	Sludge (Primary and secondary)	4–5 % of virgin paper production	Europe (2.5–3 million ^b)	Primary: 24–61 Secondary: 2–28	Primary: 5–14 Secondary: 12–15	Primary: 2–21 Secondary: 17–58	(Bloemhof-Ruwaard et al., 1996; Haile et al., 2021; Kaur et al., 2020)

(continued on next page)

Table 3 (continued)

Industrial sector	Type of waste	Waste produced from industrial production (% weight basis)	Highest producing countries in the world (waste produced in tonnes)	Cellulose(%)	Hemicellulose (%)	Lignin(%)	References
Waste management	Organic (Municipal solid waste)	30–74 %	China (112 million ^d), USA (28.9 million ^d), Japan (22.6 million ^e)				(Millati et al., 2019)
	Paper (Municipal solid waste)	8–24 %	USA (70.7 million ^e), China (15 million ^d), Japan (11.8 million ^e)				(Millati et al., 2019)
	Textile (Municipal solid waste)	4–48 %	USA (70.7 million ^e), China (36 million ^d), India (19 million ^e)				(Millati et al., 2019)
Textile	Solid matter (textile)	1,9% per production	China (10.8 million ^a), Europe (6.7 million ^a)				(Juanga-Labayen et al., 2022; Li et al., 2021)
	Sludge, wastewater	6–15 % of textile produced	China (3.5 million ^a), Europe (2.2 million ^a)				(Juanga-Labayen et al., 2022; Li et al., 2021; R Ananthashankar, 2013)
Chemical	Solvents	2 500 to 10 000 % per kg of API					(Slater et al., 2010)

residues are currently recycled and the rest tends to be sent to landfill sites (70 %), or is incinerated (30 %) (Juanga-Labayen et al., 2022; Yalcin-Enis et al., 2019). Among different types of waste from the textile industry, only textile residues potentially contain lignocellulosic biomass (Stanescu, 2021), which is the topic of this review. However, only 37 % of textiles and fibres are currently sourced from natural fibers (mainly cotton and linen) and are thus composed of lignocellulosic biomass (Juanga-Labayen et al., 2022). The remaining 63 % of textiles and fibres are petrol-based (Yalcin-Enis et al., 2019). In Europe, textile waste is not among the highest waste types produced directly by industry and mainly corresponds to post-production waste, with recycling after use by the consumer. However, recycling of post-consumer textiles is increasing. For example, in France, a decree from November 2022 obliges textile producers to collect (from 35 % in 2022 to 60 % in 2028) and recycle textiles either by reuse (58 % in 2022) or by transformation (33 % in 2022), with a specific goal of recycling textiles containing 90 % of synthetic polymers (90 % in 2027) (Ministère de la Transition écologique et de la Cohésion des territoires, 2022).

In chemical product manufacturing, typical waste products are spent catalysts, chemical solvents, reactive waste, acids, alkalis, used oils, particulate waste, ash or sludge (Millati et al., 2019). Solvents are used in the industry for the extraction, dissolution or suspending of materials. The traditional way of recycling lignocellulosic biomass, such as composting or anaerobic digestion, cannot be used when solvent residues are still present in the biomass after extraction and therefore form solvent-containing waste. Most of the time, solvents are recovered by osmosis, distillation or nanofiltration, reaching 90 % solvent recovery for extraction solvents for example (Chen et al., 2017), but the rest of the waste will be incinerated after decanting the liquid and will not be recycled (Committee on Health Effects of Waste Incineration and Board on Environmental Studies and Toxicology, 2000). The main solvents used in 2006 in the pharmaceutical industry were methanol (44 800 tonnes), dichloromethane (22 300 tonnes), toluene (12 100 tonnes), acetonitrile (7 900 tonnes), hydrochloric acid (7 030 tonnes), nitrate solutions (5 210 tonnes), chloroform (3 710 tonnes), and *n*-hexane (2 990 tonnes) (Slater et al., 2010). The ratio of chemical production in European countries is very variable, with Germany as the highest producer with 30 807 thousand tonnes of chemicals produced in 2018 (Fig. 3). The next country is Poland with 5 997 thousand tonnes in 2018.

In conclusion, the main lignocellulosic residues which could be used for further transformation are wood, paper and agricultural waste, due to their lower variability in terms of composition and the fact that their production and recycling sectors are already organised. However, textile waste will have an increasing potential due to the various recycling demands in coming years, as seen in France. Industrial textiles may be more interesting for further use, compared to household textiles, due to the fact that they are still produced in Europe (such as Techtera, a competitiveness cluster for french textile for example), the fact that their composition is less mixed and that recycling pathways directly from the producers may be more easily created. For food waste use, concurrence with anaerobic digestion and/or compostage, as in France for example, may be hindering its development for further alternative transformation and use.

3. High value chemicals from industrial lignocellulosic waste

High value chemicals are defined as high added-value products such as platform chemicals, building blocks, fuels, and economically valuable products (Cho et al., 2020). Lignocellulosic biomass is a source of a large variety of chemical compounds, both in terms of their chemistry (acids, alcohols, aldehydes, carbon, ethers, lipids, phenolic compounds, polymers, proteins, saccharides and vitamins), and their applications (platform chemicals, materials, adhesives, solvents, food additives, flavours and fragrances, etc ...). Lignocellulosic biomass can be used directly as feedstock for the production of other compounds, for the direct extraction of valuable compounds such as polyphenolic extracts, cellulose,

hemicellulose, lignin, or for transformation of these extracted compounds into other molecules, using various processes such as catalysis, microbial fermentation, anaerobic digestion, enzymatic activity, acid hydrolysis, thermal hydrolysis, or chemical extraction (Ekman and Börjesson, 2011; Kastratović et al., 2022; Lorenci Woiciechowski et al., 2020; Merli et al., 2021; Takkellapati et al., 2018).

While cellulose is in itself a valuable polymer, a majority of cellulose-derived high-value chemicals (Fig. 4a) are issued from fermentation processes using glucose as feedstock (Takkellapati et al., 2018). For this purpose, cellulose is first depolymerised using a pretreatment (cf. Section 4), yielding glucose, which is then used as feedstock for microbial fermentations, most notably to produce ethanol (Cunha et al., 2020; Takkellapati et al., 2018).

Contrary to cellulose, hemicelluloses (Fig. 4b) are heteropolymers composed of different monosaccharide monomers, among which xylose is the most abundant. Like glucose, xylose can be used as a substrate in fermentation processes, yielding organic acids, alcohols and other chemicals (Takkellapati et al., 2018). It can also be chemically transformed to furfural, an important platform chemical or xylitol (L. Canilha et al., 2006; Kabbour and Luque, 2020).

Lignin is a complex polymer containing a large number of phenolic groups (Zevallos Torres et al., 2020). It can be used directly or as a source of phenolic compounds, such as vanillin or polyphenols (Fig. 4c). These products are mostly obtained via chemical extraction and modifications, whereas microbial or enzymatic transformation of lignin are less common (Zevallos Torres et al., 2020).

The various chemicals that may be produced from cellulose, hemicellulose and lignin will be presented in this part based on their chemistry (acids, alcohols, aldehydes, carbon, ethers, lipids, phenolic compounds, polymers, proteins, saccharides and vitamins), in alphabetical order.

3.1. Acids

Gluconic acid (Fig. 4a-b) is produced from cellulose (Buchholz and Seibel, 2008; Zhang et al., 2021). The production of gluconic acid usually requires catalysts, such as nitric acid, to improve biomass oxidation yield. However, low stability, low reusability and high toxicity of these catalysts raise environmental and economic concerns (Zhang et al., 2021). Gluconic acid is used in the cement industry as an additive (40 000 tonnes per year) and in the pharmaceutical industry (8 000 tonnes per year), for the production of biodegradable and/or amphiphilic polymers, such as poly-acetonide gluconic acid, and as a more environmentally-friendly chelating agent for metal extraction/coordination (Singh and Kumar, 2007; Zhang et al., 2021). Another use of gluconic acid is its conversion into glucaric acid, with a market forecast of 440 million US dollars (USD) in 2024 (Zhang et al., 2021). Glucaric acid is used in the production of corrosion inhibitors, as a precursor of adipic acid (Zhang et al., 2021), as well as an additive in the food industry (30 000 tonnes per year). The gluconic acid market has been forecast to reach 80 million USD in 2024 (Zhang et al., 2021). Replacing glucose with biolignocellulosic waste as feedstock in gluconic acid production by fermentation would decrease its production cost (Singh and Kumar, 2007).

Glycolic acid (Fig. 4a) is produced in high quantities from glucose or xylose (Lachaux et al., 2019). Glycolic acid is used in the pharmaceutical industry as a peeling agent and for treatment of acne, in the textile industry as a dyeing and tanning agent, in the food industry for preservation and flavour, and in the chemical industry as an adhesive, emulsion polymer, solvent or additive (Lachaux et al., 2019; Salusjärvi et al., 2019). The current market for glycolic acid is expected to increase with expanding industry demand (Salusjärvi et al., 2019). Glycolic acid may be purified by liquid–liquid extraction from aqueous by-products using amine solutions, like for example tri-*n*-octylamine alone or mixed with tri-*n*-butyl phosphate (Datta and Kumar, 2015, 2011).

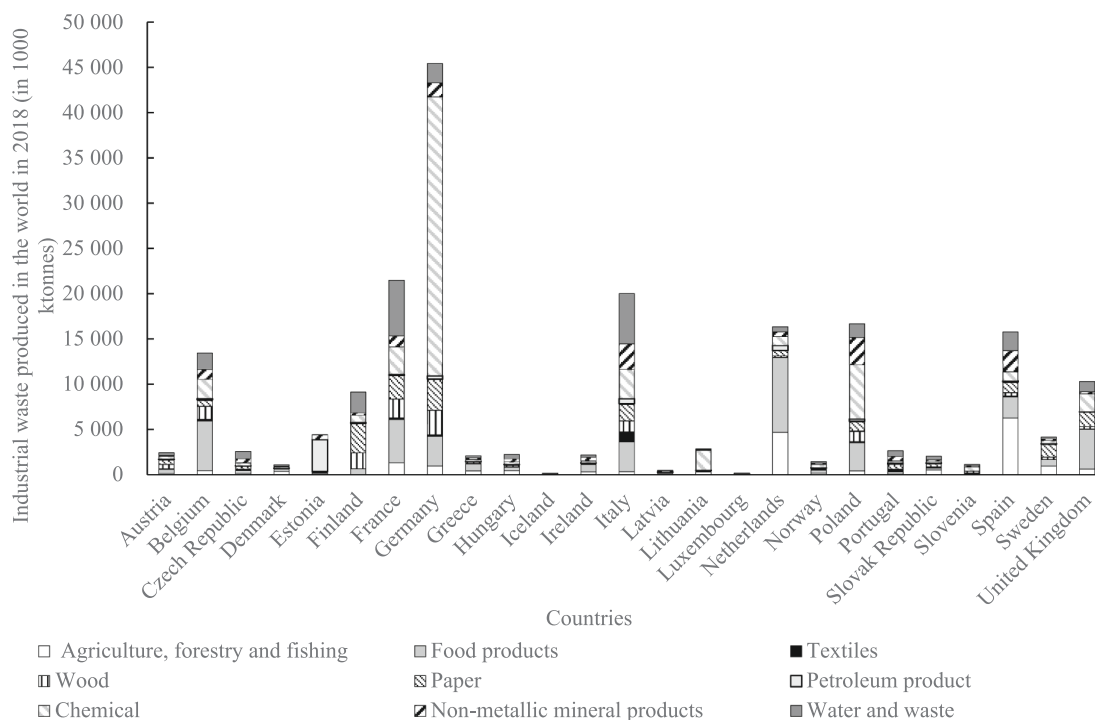


Fig. 3. Repartition of industrial waste in Europe based on OECD data (generation of waste by sector WSECTOR, (OECD.Stat, 2018)) in thousands of tonnes (or 1000 ktonnes) in 2018. The legends correspond to the sectors used in OECD with the corresponding code: S01-03: Agriculture, forestry and fishing, S10-12: Manufacture of food products; beverages and tobacco products, S13-15: Manufacture of textiles, wearing apparel, leather and related products, S16: Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials, S17-18: Manufacture of paper and paper products; printing and reproduction of recorded media, S19: Manufacture of coke and refined petroleum products, S20-22: Manufacture of chemical, pharmaceutical, rubber and plastic products, S23: Manufacture of other non-metallic mineral products, S36-39: Water supply, sewerage, waste management. The generation of waste due to the construction industry was not added to the graph.

Lactic acid (Fig. 4a-b) is a hydroxycarboxylic acid, used traditionally as a preservative in the food industry (corresponding to 85 % of the demand in the USA) and has new uses in the production of biodegradable plastics, fibres and solvents (Datta and Henry, 2006). Lactic acid is also used in the food industry as an acidulant or emulsifier, for flavouring or as a pH buffer, (Datta and Henry, 2006). Lactic acid is an organic acid produced from glucose, which can be sourced from lignocellulosic biomass (Shahab et al., 2018). The current worldwide production of lactic acid is 120 000 tonnes per year (Datta and Henry, 2006). The production of lactic acid by fermentation of carbohydrates is already used at an industrial level, for example by Musashino Chemical Laboratory (Datta and Henry, 2006) using for example *Lactobacillus pentosus*, *Lactobacillus rhamnosus*, *Lactobacillus brevis* or *Bacillus coagulans* (Shahab et al., 2018). Lactic acid is also a platform chemical and can be transformed into further useful molecules such as: ethyl lactate per esterification for use in bio-solvent blends; propylene glycol per hydrogenolysis, used in food processing; and further into propylene oxide per dehydration, used for polyurethanes, or even into acrylic acid and acrylate ester per catalytic dehydration, used in plastic films (Datta and Henry, 2006). Lactic acid can also be polymerised into another type of bioplastic, polylactic acid (PLA), often through a lactide intermediate (Brodin et al., 2017; Datta and Henry, 2006). This bioplastic is biodegradable, thermoplastic and may be used for thermoforming applications such as injection moulding, blow moulding, foaming, film extrusion and fibre extrusion. It is already commercialised by Nature-Works™, which uses corn starch as feedstock. This company converts starch into dextrose using enzymes and then uses microorganisms to convert the dextrose into lactic acid, which is then converted into lactide as the base for PLA. The industrial market for lactic acid corresponds to 714 000 tonnes in 2013 and 361 000 tonnes in 2013 for PLA (Brodin et al., 2017).

Propanoic acid or propionic acid (Fig. 4a-b) can be produced by fermentation from glycerol or from other biomass sources such as glucose, hemicellulose or from polysaccharide sources such as corn

starch hydrolysate using bacteria such as *Propionibacterium* (Ekman and Börjesson, 2011; Feng et al., 2011; Ranaei et al., 2020). The propanoic acid market worldwide was predicted to reach 470 000 tonnes produced after 2017, corresponding to 1.53 billion USD (Eş et al., 2017). It is used as a chemical intermediate in pharmaceutical industries to produce antimicrobial and/or anti-inflammatory molecules such as propionic anhydride or chloropropionic acid or to produce herbicides such as sodium 2,2-dichloropropionate (Ranaei et al., 2020). Propanoic acid is also used as a chemical intermediate in food industries to produce preservatives, such as sodium or calcium propionate, and flavours such as propionic ether or benzyl propionate (Ranaei et al., 2020). Indeed, propionic acid is transformed into sodium or calcium propionate by the reaction of propionic acid and sodium or calcium carbonate and is in used in salt form as a preservative against mold. Another use of propionic acid is its transformation into benzyl propionate by esterification, corresponding to a flavour of sweet, fruity, floral, banana, balsamic and jasmine (The Good Scents Company, 2021), or even into *n*-propyl propanoate by esterification with H₂SO₄ as a catalyst and used as floral fragrance in the food and perfume industry (Kastratović et al., 2022).

Acetic acid is a carboxylic acid, produced mostly from petroleum chemicals. A smaller proportion (10 % of world production) is produced biologically, from sugars by acetogenic anaerobic bacteria or from ethanol by acetic acid bacteria (Vidra and Németh, 2018). Bio-based acetic acid is used diluted in the food industry for vinegar production, for flavouring or as a preservative. The market for acetic acid increased from 13 million tonnes in 2015 to 16 million in 2020 (Vidra and Németh, 2018). Acetic acid is also an important platform chemical to produce vinyl acetate (44 % of use for acetic acid) (Fig. 4a), acetic anhydride (13 %), acetate esters, monochloroacetic acid and as solvent in the production of dimethyl terephthalate and terephthalic acid (18 %) (Kalck and Serp, 2015; Merli et al., 2021; Vidra and Németh, 2018). Vinyl acetate is produced by the reaction between ethylene and acetic acid using a noble-metal catalyst such as palladium at 175 °C–200 °C and 5–9 bars (American Chemical Society, 2023). It is present in vinyl plastic, adhesives,

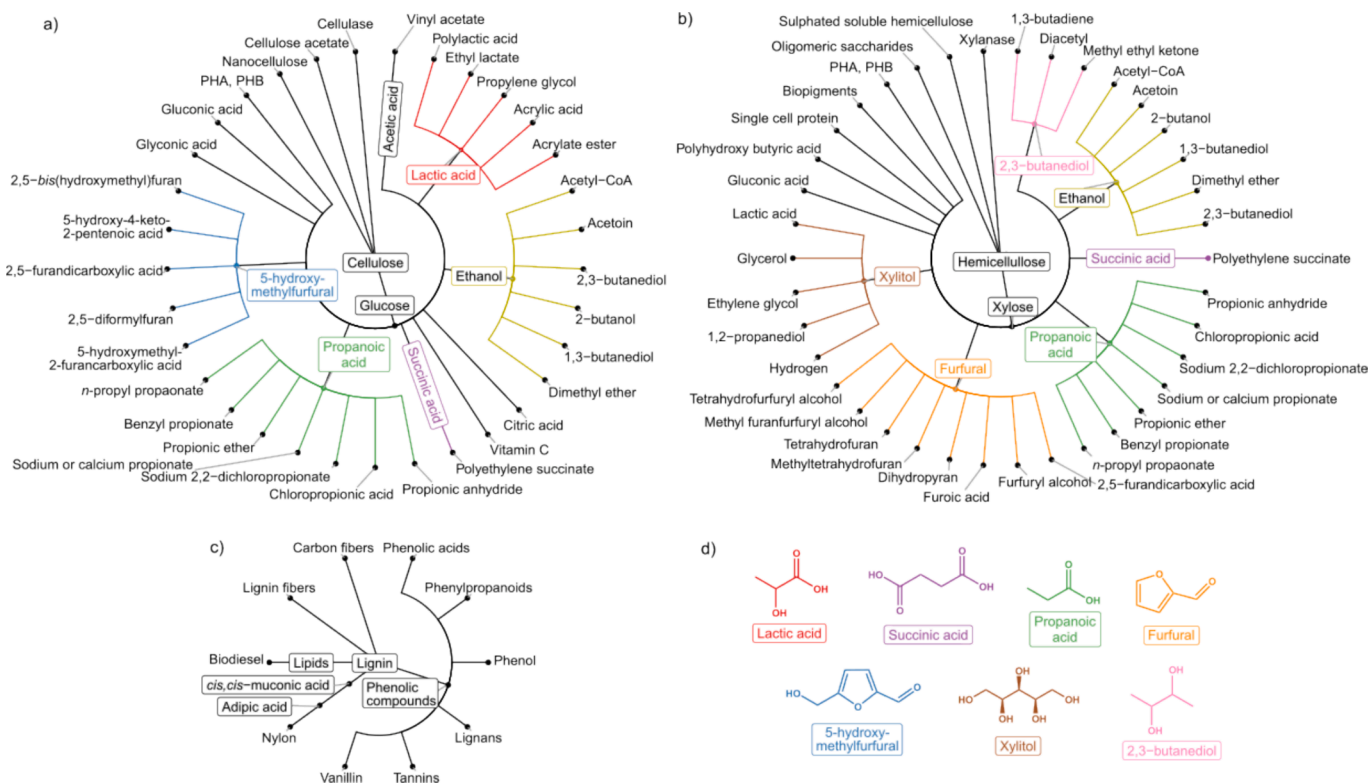


Fig. 4. Overview of the high-value chemicals from lignocellulosic biomass presented in this review: a) Compounds derived from the cellulose fraction, b) Compounds derived from hemicellulose fraction, c) compounds derived from lignin fraction, d) Color-coded structures of representative platform chemicals. (Fig. created with R).

textile finishes and latex paints and in synthetic fibres (Merli et al., 2021). Acetic anhydride is used in a high number of organic syntheses and is formed by deshydration. Acetate esters correspond to an esterification of acetic acid, such as for example butyl acetate, which is usually produced by catalytic distillation and is used as solvent in the production of paints, lacquers and varnishes, as a flavour (banana aroma) or fragrance (Mukhtarovna et al., 2021). It is also possible to produce short-chain fatty acids from lignocellulose using microorganisms, by combining aerobic fungi for the hydrolysis of the cellulose (*Trichoderma reesei*), and a facultative anaerobic bacteria (*Clostridium tyrobutyricum*) for the conversion of monosaccharides into lactic acid and subsequent conversion of the lactic acid into butyric acid (Shahab et al., 2018).

Citric acid is a weak organic acid used for its antioxidant properties, especially in food and pharmaceutical industries (Fig. 4a) (Amato et al., 2020). It may also be used as an acidifier in the food industry, as a flavour and aroma enhancer, as a foaming agent in the textile industry and as a phosphate substitute for detergents (Amato et al., 2020). Most citric acid is produced in China, corresponding to 2 million tonnes per year produced in 2020 (Ciriminna et al., 2017), and its worth was estimated to reach 3.2 billion USD by 2023, with an estimated increase in production of 5 % per year (Amato et al., 2020). Citric acid is a Krebs (TCA) cycle product, which results from the combination of acetyl-CoA with oxaloacetate. Industrially, citric acid is produced mostly by fungi such as *Aspergillus niger* and *Aspergillus wentii*, with fermentation using carbohydrates at 10–15 %, pH 1.5–4.5, stirring speed 120–400 rpm, temperature 27–35 °C (Amato et al., 2020). For example, the production of citric acid from glucose using *Aspergillus niger* has a yield of 200 g/L which corresponds to 95 % of the theoretical yield (Buchholz and Seibel, 2008). However, other microorganisms may be used to produce citric acid such as *Arthrobacter paraffinens*, *Bacillus licheniformis* and *Corynebacterium* sp. (Amato et al., 2020). Citric acid is also produced from agro-waste, such as molasses and syrups from the beet sugar industries, peels from oranges, kiwis, pineapples, coconuts and bananas, fruits and vegetable waste such as apples, grapes or carrots, bagasses from sugarcane and cassava, bran from rice and wheat, rice straw, coffee husks, corncobs, and food industry waste such as cheese whey and brewery waste (Amato et al., 2020; Dutta et al., 2014; Sawant et al., 2018). Extraction of citric acid from fermentation broth is performed with solvent extraction using insoluble or partially soluble solvents and recovered using water, followed by crystallisation and concentration (Amato et al., 2020).

Succinic acid (Fig. 4a-b) is another widely used organic acid with applications in food, chemical and pharmaceutical industries. It is used in the production of surfactants and biodegradable plastics as a precursor for polyethylene succinate (Lu et al., 2021). The market for succinic acid is expected to grow annually by 20 % and was estimated to represent 175.7 million USD in 2017 and to reach 900 million by 2026 (Li et al., 2021). Most succinic acid is produced using hydrogenation of fossil fuel-derived maleic anhydride (Li et al., 2021). However, it is also a Krebs cycle intermediate, suggesting potential for biotechnological production. Succinic acid can be produced from lignocellulosic biomass via enzymatic hydrolysis, followed by microbial transformation of polysaccharides into succinate, for example, from grass hydrolysate using *Basfia succiniproducens* BPP7, with a yield of 0.84 g/g (Ventorino et al., 2017), or from various sources of biomass, such as corn and cotton stalks, corn stovers, sugarcane bagasse hydrolysate, or oil palm empty fruit bunches using *Actinobacillus succinogenes* (Lu et al., 2021). Cotton-based textile waste was also used to produce succinic acid via hydrolysate rich in glucose (Stanescu, 2021). The industrial production of succinic acid was tested by the company BioAmber but failed due to high production costs and low production capacity (Li and Mupondwa, 2021), which shows that bio-succinic acid production still needs to be optimised. Currently, research is mostly oriented towards metabolically-engineered microorganisms to improve succinic acid yield, for example using yeast such as *Saccharomyces cerevisiae* (Baptista et al., 2021; Li et al., 2021; Lu et al., 2021).

Lignin (Fig. 4c) may also be used to produce acids such as *cis,cis*-muconic acid, a precursor of adipic acid used for fibres and plastic production (Zhaoxian Xu et al., 2019), which is currently mostly produced from petroleum but may also be produced from lignocellulosic biomass using engineered microorganisms (Becker et al., 2018; Kohlstedt et al., 2018; Sonoki et al., 2018; Vardon et al., 2015). Indeed, *cis,cis*-muconic acid is produced naturally by some bacterial strains by transforming lignin hydrolysate compounds such as benzene, benzoate, toluene, or phenol into catechol and then into *cis,cis*-muconic acid but does not accumulate in the cells due to further metabolic use. Engineered strains in which the degradation pathway of *cis,cis*-muconic acid is blocked could thus be used for *cis,cis*-muconic acid production. For example, the full transformation of lignin from soft wood hydrolysate to nylon was demonstrated using engineered *Pseudomonas putida* MA-9 and further transformation of *cis,cis*-muconic acid into adipic acid by catalytic hydrogenation and polymerization into nylon with a yield of nearly 100 % from lignin-based aromatic compounds (Kohlstedt et al., 2018).

3.2. Alcohols

Ethanol is an alcohol mainly produced from polysaccharides (Fig. 4a-b) via yeast and bacterial fermentation. Ethanol may be used directly as a solvent for the chemical industry, as a disinfecting agent or as a bio-fuel, often blended with gasoline. It is currently the most common liquid biofuel in the world, produced mostly in Brazil from sugarcane residues such as molasses for 27.6 billion liters and in US from corn for 57.7 billion liters produced in 2016 (Mohanty and Swain, 2019). First generation ethanol, produced directly from agricultural products, is in competition with food production and demands large areas of agricultural land. A more sustainable option is thus to produce second generation ethanol, using agricultural or industrial biomass waste, to avoid competition with food needs (Liu et al., 2019; López-Contreras et al., 2000). Use of agro-waste as a substrate for ethanol production has already been demonstrated at an industrial scale: corncob and wheat straw are used by Praj Industries in India to produce ethanol, with a capacity of 1 million L/year, rice straw is used by BetaRenewables in Italy and sugarcane straw and bagasse are used by GranBio and Raizen in Brazil for 82 and 42 million liters of ethanol per year, respectively (Millati et al., 2019). Empty palm oil fruit bunches can also be used for ethanol production, with a pilot plant for example having a yield of 144.4 kg anhydrous ethanol/1000 kg fruit bunch (Millati et al., 2019). Wood waste may also be used for ethanol production: in Sweden the company Sekab (in operation since 2004) uses softwood residues and has a processing capacity of 1 tonne of dry biomass/24 h (Millati et al., 2019), or a plant in the USA using Douglas-fir forest harvest residues with a capacity of 50 kg/batch using sulphite pre-treatment, followed by fermentation with the yeast *Saccharomyces cerevisiae* (Zhu et al., 2015). Other industrial biomass, such as cashew apple bagasse or black liquor, may be used to produce ethanol (de Araújo Padilha et al., 2020). Ethanol may be converted into acetyl-CoA using alcohol dehydrogenase and aldehyde dehydrogenase, with an NADH oxidase (Liu et al., 2022). Acetyl-CoA is then used for production of various chemicals or even as a source of energy by ATP production. Ethanol may also be converted into acetoin, 2,3-butanediol, and 2-butanol using enzymes such as ethanol dehydrogenase, formolase, 2,3-butanediol dehydrogenase, diol dehydratase and NADH oxidase (Zhang et al., 2018), or converted into 1,3 butanediol using formate dehydrogenase (Liu et al., 2022). It is also possible to produce bio-based plastics with the production of ethylene and polyethylene by deshydration and conversion of bio-dimethyl ether into olefins, using catalysts (Mohsenzadeh et al., 2017; Morschbacker, 2009). Currently, production is mostly done at the industrial scale using first generation ethanol (Mohsenzadeh et al., 2017).

2,3-butanediol (Fig. 4) is a reaction intermediate for numerous chemical reactions such as the production of liquid fuels, thermoplastic polymers or liquid fuel additives (Chandel et al., 2018). This molecule is also used in the production of hard rubbers when mixed with

naphthalene-1,5-diisocyanate, but also as a resin, a solvent for dyes or a blending agent (Dionisio et al., 2018). The global market for 2,3-butanediol is projected to reach a value of 220 million USD in 2027, with a predicted growth of 3 % between 2019 and 2027 (Maina et al., 2022). Production of 2,3-butanediol using microorganisms such as *Klebsiella*, *Enterobacter* or *Bacillus* is already being tested at an industrial scale with a demonstration plant in Korea built in 2019 to produce 300 tonnes per year (Song et al., 2019). The pathway for 2,3-butanediol production using microorganisms is complex and starts with a hydrolysis of polysaccharides into monosaccharides, followed by the production of pyruvate during glycolysis. Pyruvate is then transformed into α -acetolactate and then into acetoin and/or diacetyl, with a final transformation into 2,3-butanediol (Song et al., 2019). 2,3-butanediol may also be further transformed into 1,3-butanediene for the production of synthetic rubber and plastic, into diacetyl for food and flavouring agents or for the production of methyl ethyl ketone for fuel additives and solvents for resins and lacquers (Maina et al., 2022). 2,3-butanediol may also be used as a food additive, either directly or by conversion into diacetyl by dehydrogenation. Diacetyl and 2,3-butanediol may be used as flavouring agents for butter, cream and nut tastes (Dionisio et al., 2018). Diacetyl may also be used as a preservative in the food industry since it inhibits the growth of microorganisms (Celińska and Grajek, 2009).

Xylitol is a high value polyalcohol produced from xylose by microbial conversion and used in the pharmaceutical industry as a sweetener for diabetes patients and for its anticarcinogenic properties (Chandel et al., 2018). The metabolism degradation of xylitol is also independent of insulin, which makes it useful for diabetes patients (Chandel et al., 2018; Queiroz et al., 2022a). Currently, acid hydrolysates from steam exploded sugarcane and others lignocellulosic biomass are used as substrates for xylitol bioproduction with microorganisms such as *Candida utilis*, *C. intermedia*, and *C. guilliermondii* (L. Canilha et al., 2006; Chandel et al., 2010; Queiroz et al., 2022a; Umair et al., 2022). Scaling up this process presents some challenges, such as the presence of inhibitors in the hydrolysate and the slow xylose uptake rate by microorganisms (Chandel et al., 2018; Queiroz et al., 2022a; Umair et al., 2022). Other possible uses of xylitol are its utilisation as a platform molecule for hydrogen, 1,2-propanediol, ethylene glycol, glycerol and lactic acid using catalyst reactions (Xu et al., 2020). Overall, the global market for xylitol reached 921 million USD in 2020 due to its increasing demand (Queiroz et al., 2022a). Xylitol is also used in the food industry as an inhibitor of microorganism growth (Chandel et al., 2018). Lignocellulosic biowaste used as a substrate source for xylitol decreases its production cost, especially since the cost of carbon sources used for biotechnological production is one of its drawbacks (Chandel et al., 2018). Indeed, 30 % of the production cost corresponds to the cost of raw materials when using rye straw hemicellulose (Venkateswar Rao et al., 2016). The cost will depend of the lignocellulosic biomass with a variation of production cost from 0.46 US \$/kg using oil palm rachis, 1.48 US \$/kg with olive tree crops to 1.83 US \$/kg for various lignocellulosic biomass (Queiroz et al., 2022b).

3.3. Aldehydes

Furfural (Fig. 4) is a platform chemical and a precursor for furan-based chemicals such as furoic acid, furfuryl alcohol, 2,5-furandicarboxylic acid or dihydrofuran and is used to produce biofuel, plastics, drugs, bioplastic, flavour enhancers, lubricants or phenolic resins (Kabbour and Luque, 2020). Furfural may also be used directly as a selective solvent in numerous reactions and is used for the extraction of aromatics from fuels, unsaturated compounds from vegetable oils, butadiene and for wax recovery (Kabbour and Luque, 2020). Mostly, furfural is produced chemically by acid hydrolysis of pentose such as hemicellulose, followed by the dehydration of xylose into furfural, in a one or two step continuous process, using agricultural and wood residues (Kabbour and Luque, 2020; Steinbach et al., 2017). The furfural market consisted of 250 000 tonnes per year in the world in 2001, with 100 000 tonnes/year directly used as furfural (12 000 tonnes/year in Europe, and 8 000 in the

USA), with 129 750 tonnes/year of furfuryl alcohol produced worldwide in 2001 (37 000 tonnes/year in Europe and 20 000 tonnes/year in the USA) (Kabbour and Luque, 2020). The furfural market is estimated to grow 2 % per year (Kabbour and Luque, 2020). Furfural and its derivatives were mostly produced in China from corncobs (200 000 tonnes/year in 2001, corresponding to 70 % of world production), followed by the Dominican Republic using bagasse (32 000 tonnes/year in 2001, corresponding to 11 % of production) (Kabbour and Luque, 2020). In Europe, Spain produced 6 000 tonnes/year in 2001 (Kabbour and Luque, 2020). Furfural may also be a by-product of various pre-treatments of lignocellulosic biomass, such as steam explosion (Balan et al., 2020; Brethauer et al., 2020; Steinbach et al., 2017), hydrothermal pre-treatment (Chandra et al., 2012; Dimitriadis and Bezergianni, 2017; Fan et al., 2016; Nitsos et al., 2013a), acid hydrolysis (Steinbach et al., 2017; J. Yu and Stahl, 2008) or with alkaline solutions (Steinbach et al., 2017). It may also be further converted into other molecules such as furoic acid.

Another common furaldehyde is 5-hydroxymethylfurfural (5-HMF, Fig. 4), produced for example from cellulose by acid hydrolysis followed by acid isomeration of glucose to fructose, and finishing with acid dehydration (Menegazzo et al., 2018; Steinbach et al., 2017). Current production of 5-HMF uses syrup from energy crops as a biomass with a purity up to 99.9 % (Kläusli, 2014), which is necessary to limit its degradation during storage (Menegazzo et al., 2018). 5-HMF may also be further converted into 5-hydroxymethyl-2-furancarboxylic acid, 2,5-diformylfuran and 2,5-furandicarboxylic acid (FDCA, precursors of bioplastic) by oxidation of its formyl and/or hydroxyl group, of 5-hydroxy-4-keto-2-pentenoic acid by oxidation of the furan ring, 2,5-bis(hydroxymethyl)furan by reduction of the furan ring and/or the formyl group, used in polyurethane foams and further transformation into 2,5-dimethylfuran by hydrogenation, levulinic acid or dihydroxymethylfuran (Kabbour and Luque, 2020; Rosatella et al., 2011). Currently, only FDCA is commercialised (Galkin and Ananikov, 2019), even with the high potential of 5-HMF derived products, and a demonstration, by AVA Biochem with a commercial plant and a production of 40 tonnes/year in 2014 (Kläusli, 2014). Like furfural, 5-HMF is also produced as a by-product of pre-treatment of lignocellulosic biomass such as with steam explosion (Balan et al., 2020; Brethauer et al., 2020; Steinbach et al., 2017), hydrothermal pre-treatment (Chandra et al., 2012; Dimitriadis and Bezergianni, 2017; Fan et al., 2016; Nitsos et al., 2013a), acid hydrolysis (Rosatella et al., 2011; Steinbach et al., 2017; J. Yu and Stahl, 2008) or treatment with an alkaline solution (Steinbach et al., 2017). 5-HMF may be further converted using microorganisms as whole cell biocatalysts as a potential 'green' route, for example for furfural production (Cunha et al., 2022; Rosatella et al., 2011).

3.4. Carbon

Carbon may be directly used in the form of biochar, activated carbon or paper products. Biochar and activated carbon are produced from lignocellulosic biomass by pyrolysis transformation, gasification or hydrothermal treatment (Miliotti et al., 2020a; Wang and Wang, 2019). Biochar is used for soil, waste-water and water bioremediation, to improve anaerobic digestion and improve soil fertility (Cooney et al., 2014; Wang and Wang, 2019). Its recalcitrance to oxidation in soil also makes it an attractive climate change mitigation strategy through carbon sequestration (Chagas et al., 2022; Gross et al., 2021; Xu et al., 2021). It may also be used as a catalyser and activator or even for electrode material (Wang and Wang, 2019). Activated carbon corresponds to carbon that is retained on a 50-mesh sieve. Like biochar, activated carbon is used for bioremediation (Scott et al., 1995), or to improve anaerobic digestion by improving the consumption of volatile fatty acids such as propionate (Capson-Tojo et al., 2018). Activated carbon may also be reactivated after use by thermal oxidation and may therefore be used multiple times.

3.5. Ethers

Ethers such as dimethyl ether (DME, Fig. 4a-b) may be obtained from lignocellulosic biomass. DME is used as a second generation biofuel, produced from lignocellulosic biomass and could be used in diesel motors. DME is also used in the laboratory as a low temperature solvent and extraction agent (Harris et al., 2022). DME can be obtained from pyrolysis and/or gasification of lignocellulosic biomass (Li et al., 2009). The carbon monoxide of the syngas produced is then transformed into DME using catalysis after removal of the carbon dioxide by a pressure-swing adsorption unit (Li et al., 2009). An industrial pilot in China used 45 to 50 kg of corncob/h, producing up to 124–204 kg of DME/m³ of catalysers/h, with a final conversion ratio of 16.4 % of the carbon in dry corncob (Li et al., 2009). Methanol is also produced from syngas via pyrolysis, gasification or liquefaction (Mohanty et al., 2022), using lignocellulosic biomass, followed by low- and high-pressure catalysis. Methanol may also be further transformed into DME by dehydration (Mohanty et al., 2022). Pyrolysis should not be the first treatment applied to transform lignocellulosic biomass since the yield is low considering the high energy cost but may be used as a final transformation after all other possible transformation steps (Hoang et al., 2021b).

3.6. Lipids

Oleaginous microorganisms produce and accumulate lipids as an energy source, by transformation from a carbon source such as monosaccharides or lignin (Fig. 4). Depletion of nitrogen, sulphate, phosphate or magnesium is often required for microorganisms to accumulate lipids (Valdés et al., 2020). *Rhodococcus jostii* RHA1 and *Rhodococcus pyridinivorans* used lignin to accumulate up to 88 % lipids (Xu et al., 2019). Indeed, *Rhodococcus pyridinivorans* CCZU-B16 produced lipids from alkali lignin at 30 °C over 72 h (Chong et al., 2018). Another possible candidate for lipid production and accumulation is *Rhodosporidium* sp., which may accumulate up to 70 % lipids, using lignocellulosic biomass (Osorio-González et al., 2019). It is also possible to produce lipids from polysaccharides present in lignocellulosic biomass, with better yields when using both hexoses and pentoses (Valdés et al., 2020) by enzymatic hydrolysis. Polysaccharides are transformed into monosaccharides and further converted into lipids (Valdés et al., 2020). These bioprocesses can be inhibited by side-products of lignocellulosic biomass pre-treatment, including furfural, 5-HMF, acetic acid, formic acid or levulinic acid (Osorio-González et al., 2019; Valdés et al., 2020). Another possibility is to use pyrolysis as a pre-treatment for lignocellulosic biomass and use microorganisms to transform the products into lipids, with for example the use of *Trichosporon dermatitis* to produce lipids from a hydrolysate of pretreated rice straw using an autoclave (Palazzolo and Garcia-Perez, 2022; Yu et al., 2022). Lipids may also be further transformed into triglycerides for biofuel production as an alternative to petrol (Balcombe et al., 2019).

3.7. Phenolic compounds

Phenolic compounds are molecules containing at least one phenolic ring. Notably, lignin is a polyphenolic polymer composed of three main phenolic monomers (protolignans) proto-lignins: *p*-coumaryl, coniferyl and sinapyl alcohols, which makes it an abundant source of phenolic compounds (Fig. 2Erreur! Source du renvoi introuvable. and Fig. 4c). Currently, most phenolic compounds are produced using extraction from lignocellulosic biomass. However, phenolic compounds may also be biosynthesized using microorganisms such as *Bacillus subtilis*, *Rhizopus oryzae* or even *Pseudomonas aeruginosa* (Valanciene et al., 2020). For example, resveratrol, a natural stilbene with various potential applications, can be obtained by microbial biosynthesis from lignocellulosic materials (Costa et al., 2021).

Phenol is an important platform chemical (11.5 Mtonnes produced in 2019) used as a precursor for plastics and pharmaceuticals, amongst

other applications. It is currently synthesized from petrol-derived benzene. Recent advances, however, pave the way for biobased phenol from chemical transformation of lignin (Wang et al., 2018; Yan et al., 2020).

Vanillin is a phenolic compound used as a flavour and fragrance in food and cosmetic industries with a production of 12 000 tonnes/year. Most vanillin on the market is synthetic, with less than 1 % extracted from vanilla beans (Nayak et al., 2022). Vanillin is also produced by chemical or microbial transformation of lignin and lignin-containing biomass (e.g. wood) using various bacteria such as *Staphylococcus lentus* (Baghel and Anandkumar, 2019; Lora and Glasser, 2002; Millati et al., 2019). For example, vanillin and other lignin products are produced from wood at an industrial scale by the Norwegian company Borregaard (Millati et al., 2019), or can be produced from other biomass such as kraft lignin waste using oxidation followed by solvent extraction and distillation (Khwanjaisakun et al., 2020).

Polyphenols are abundant specialised plant metabolites consisting of at least one hydroxyl group on an aromatic ring and generally play important roles in plant defence systems against aggression by pathogens or ultraviolet radiation. They are categorised as either flavonoids or non-flavonoids such as phenolic acids, stilbenes and lignans (Abbas et al., 2017; Manach et al., 2004). It is worthy to note that the majority of plant-derived polyphenols are not only present within the cytosol, but can be also bound within cellular walls (Gligor et al., 2019). Polyphenols can be extracted from plant biomass using solvents such as 70 % ethanol. Ultrasound-assisted, microwave-assisted, pressured-liquid or enzyme-assisted extractions can further enhance extraction efficiency (Adebooye et al., 2018; Gligor et al., 2019; Nkhili et al., 2009; Pagano et al., 2021). Polyphenols can also be extracted from waste such as kraft and sulphite black liquors (Faustino et al., 2010). Another possibility is the production of polyphenol using natural or recombinant microorganisms (Dudnik et al., 2018; Milke et al., 2018). However, the difficulty in using recombinant microorganisms consists in the complex biosynthetic polyphenol pathways, which need the expression of multiple genes coding for the enzymes used in these pathways (Dudnik et al., 2018; Milke et al., 2018). The polyphenol market corresponded to 16 380 tonnes in 2015 equal to 757 million USD, with an annual growth of 8.4 % and is therefore expected to reach 33 880 tonnes in 2024 (Adebooye et al., 2018). The main applications of polyphenols are in the beverage (44 %) and food (33 %) industries (Adebooye et al., 2018).

Phenolic compounds and polyphenol derivatives are used as antioxidants and preservatives in the food industry (Amiri et al., 2021). Phenolic acids, phenolic diterpenes or flavonoids prevent the generation or release of free radicals and thus limit oxidation of lipids, which is a source of food spoilage (Amiri et al., 2021). In the food industry, antioxidants are used in processed foods containing meat, dairy or sauces (Baines, 2012). Polyphenols are also used in energy drinks (Adebooye et al., 2018). Polyphenols also have other health benefits linked to their activities as antioxidants, or as anti-inflammatory, anti-microbial, anti-cancer or anti-diabetic molecules (Abbas et al., 2017). Polyphenols have also been linked to prevention of cardiovascular diseases and neurodegenerative disorders (Potì et al., 2019). Recently, biomass polyphenols have been reported as potential tyrosinase inhibitors, which could have potentially valuable applications in cosmetics, food, feedstuffs and medicines (Pham et al., 2024).

3.8. Polymers

Bioplastic precursors such as polyhydroxyalkanoate (PHA) and specifically polyhydroxybutyrate (PHB) may also be produced from lignocellulosic biomass (Fig. 4). These polymers are compostable bio-biased polyesters and have comparable physical properties to petroleum polymers (Dietrich et al., 2019). PHA may be thermoformed and is used to produce multiple products from packaging materials to thermosensitive adhesives and smart latexes (Koller et al., 2015). Therefore, the market for these polymers is growing due to an increasing demand, with a current production of 2 million tonnes of bioplastic per year

(Rosenboom et al., 2022). One of the main problems is the production cost due to monomer production and equipment costs (Brodin et al., 2017; Jabeen et al., 2015; Koller et al., 2015). One possibility is to use lignocellulosic waste such as municipal solid waste (Ivanov et al., 2015), food waste or agricultural waste (Saratale et al., 2021), as a substrate for the fermentation process. PHA production in cells results from catabolic conversion of monosaccharides to pyruvate down to acetyl-CoA, followed by a three-step conversion to PHA (Dietrich et al., 2019). PHA may also be produced from hemicellulose acid hydrolysates, which may however be hindered by inhibitors present in the hydrolysates (*i.e.* steam explosion) (Dietrich et al., 2019). The maximum PHA yield from softwood hydrolysate stream was 60.5 g/L using *Cupriavidus necator* DSM 545 at 30 °C and pH 7 (Koller et al., 2015). After production by fermentation and accumulation in microorganisms, it is necessary to purify PHA by treatment with enzymes such as lysozymes, exonucleases or proteases or by solvent extraction using chloroform or methylene chloride (Brodin et al., 2017; Ivanov et al., 2015).

PHB corresponds to short-chain length PHA. Three pathways exist to produce PHB from polysaccharides: *i)* Embden-Meyerhof-Parnas for glucose conversion and the main pathway for microorganisms, *ii)* Entner-Doudoroff for glucose conversion, and *iii)* the Pentose-Phosphate Shunt for xylose conversion (Dietrich et al., 2019), using microorganisms such as *Azohydromonas australica* (McAdam et al., 2020), or *Pseudomonas cepacia* using steam exploded aspen with enzymatic hydrolysis (Dietrich et al., 2019). PHB is interesting as a bioplastic due to its low permeability. However, its thermal instability (glass transition temperature at 5–9 °C) and excessive brittleness due to its high degree of crystallinity, limit its actual use in industry (McAdam et al., 2020).

Lignin may also be directly used without modification, such as using lignin fibres for insulation, or using its chemical properties. For example, lignin was used as a component of sunscreen lotion, which increased the SFP index up to 88 % (at a 5 % concentration) (de Araújo Padilha et al., 2020). Lignin may also replace phenolic powder resin as a binder in polyurethane, polyisocyanurate foams or epoxy resins (Lora and Glasser, 2002). Lignin fibers can be further transformed *via* carbonization to carbon fibers, which can be used in batteries, as well as in composite materials (Wang et al., 2022).

Lignocellulosic biomass may also be used as an absorbent material for purification. For example, sugar cane bagasse was used for the purification of biodiesel, in three different forms: raw bagasse, steam pretreated bagasse and bagasse ash, to remove the glycerine present. Only 0.5 wt% of sugarcane bagasse was necessary to remove 40 % of the glycerine and obtain a purified biodiesel containing only 0.02 wt% glycerine (Alves et al., 2016).

3.9. Proteins and enzymes

Lignocellulosic biomass is also a source of substrates for enzyme production. Enzymes have a growing industrial demand and therefore a high market value, estimated in 2018 at \$7.1 billion (Ravindran and Jaiswal, 2016). Lignocellulolytic enzymes are biocatalysts breaking down lignin, cellulose and hemicellulose into further molecules by hydrolysis or oxidation (Chukwuma et al., 2020). They correspond to peroxidases, oxidases, cellulases, hemicellulases, pectinases, chitinases, amylases, proteases, esterases, and mannanases (Chukwuma et al., 2020). Lignocellulosic enzymes are used as pretreatment in industry or for producing other compounds, however their high price often limits their uses (Ravindran and Jaiswal, 2016). For example, bioethanol production price will mostly depend of the cost of saccharification enzymes, which limit the production of biofuels (Ravindran and Jaiswal, 2016). Decreasing the costs of enzyme by using lignocellulosic waste as a production source is a way of improving green chemistry and biofuel market potential (Ravindran and Jaiswal, 2016). For example, liquid hot pre-treated corncob (hydrolysate and solid fraction) was used to produce biomass degrading enzymes such as xylanase and cellulases by fungal fermentation using *Aspergillus niger* or *Trichoderma reesei*

(Michelin et al., 2018). Cellulose from textiles may also be used as a substrate for microorganisms to produce cellulase (Stanescu, 2021). Another example is the use of rice straw or coffee pulp to produce laccase by fermentation with *Streptomyces psammoticus* (Niladevi et al., 2007). Another possibility is the use of GMO-microorganisms to improve enzyme production (Ravindran and Jaiswal, 2016), such as for example an improvement of enzyme activity by 62.19 % compared to wild-type alkaline protease-producing strain *B. licheniform* (Zhou et al., 2020). Another interesting process is the use of lignocellulosic biomass as support for enzyme immobilization, with examples such as soybeans hulls, hazelnut shells, nutshells, sugarcane bagasse, green coconuts, corn stalks or even cashew apple bagasse (Neto et al., 2023). Enzyme immobilization improves the stability of the enzymatic reaction, and facilitates both the separation of the reaction medium from the enzyme and the reuse of the enzyme (Neto et al., 2023).

Protein consumption has been increasing by 9.3 % cumulative annual growth rate, with a need to decrease protein from meat production due to environmental concerns (Kumar et al., 2024). Proteins production from lignocellulosic wastes using microorganisms is also another increasing researched aspect (Kumar et al., 2024). Indeed, microorganisms such as fungi (31–43 % dry weight), algae (41–62 %), yeast (40–60 %) and bacteria (50–65 %), may contain higher protein content compared to usual meat sources such as chicken (27 % dry weight) (Kumar et al., 2024). For example, converting wood type lignocellulosic waste as a support for edible fungi is a new possible source of proteins (Scholtmeijer et al., 2023). Others microorganisms used for protein production are algae such as *Chlorella* and *Spirulina*, yeast such as *Candida*, *Saccharomyces*, *Rhodospiridium*, *Rhodotorula*, bacteria such as *Brevibacterium*, *Cellulomonas*, *Alcaligenes*, *Rhodopseudomonas*, *Lactobacillus* and *Clostridium butyricum*, which is accepted for food purposes in the EU (Kumar et al., 2024). Another possibility is the extraction of proteins from lignocellulosic waste in liquid form (directly for effluents or after pretreatment) using for example, membrane filtration, precipitation using organic solvent, pH-shift or salting-out or adsorption on silica (Piercy et al., 2023).

3.10. Saccharides

Extracting sugars from lignocellulosic biomass for use in further processing is also a possibility. For example, xylan may be extracted from biomass such as corncob using dilute acid, dilute alkali or sodium hypochlorite (Gowdhaman and Ponnusami, 2015). Xylan may then be used to produce xylooligosaccharides, probiotics and potential antioxidants, using bacteria such as *Bacillus aerophilus* (Gowdhaman and Ponnusami, 2015). Pilot production efforts using steam-explosion of corncob yielded 3.575 kg xylose per 22 kg of corncob (Zhang et al., 2014) and 10 L xylooligosaccharides per 40 kg of corncob (Yuan et al., 2004). In another example of saccharide production, raw rice husk biomass was used with a final yield of 95 % of nanocrystalline cellulose after alkaline delignification as pre-treatment, followed by bleaching with 15 % of sodium hydroxide and acid hydrolysis, to reinforce polymer nanocomposites (Dufresne, 2010; Islam et al., 2018). Wood was also used at a pilot scale for the production of nanocrystalline cellulose, with the production of ethanol at the same time, for a yield of 600 g of nanocrystalline cellulose per day (Mathew et al., 2014). Food grade glucose can also be produced from ligno-cellulosic biomass using acid-catalysed steam explosion followed by enzymatic hydrolysis of the cellulose (Wang et al., 2018), from rice straws, or from softwood residues (Balan et al., 2020; Brethauer et al., 2020a). At the industrial/pilot scale, the recovery of sugar from rice straw with 250 kg of biomass per day was tested, using dilute acid pre-treatment followed by enzymatic hydrolysis in a screw feeder horizontal reactor (Kapoor et al., 2017).

Extraction and conversion of saccharides can also be performed simultaneously in the same reactor. For example, hemicellulose was extracted from rice straw and husks with 4 % sodium hydroxide at 90 °C, purified using 5 % hydrogen peroxide and transformed into sulphated

soluble hemicellulose using two catalysts (N,N-dicyclohexylcarbodiimide and 4-dimethylaminopyridine) (Ragab et al., 2018). The sulphated soluble hemicellulose then was tested and showed anti-coagulation and fibrinolytic activities, with applications for the pharmaceutical industry (Ragab et al., 2018).

Cellulose acetate may also be produced from lignocellulosic biomass (Fig. 4a). Indeed, sugarcane bagasse can be pretreated using steam explosion to obtain a cellulose fraction. After acetylation to produce cellulose acetate, it is used to produce bioplastics (Shaikh et al., 2009). One of the applications of cellulose acetate is production of hollow fibre membranes for ultrafiltration (Kumar et al., 2019).

Another possibility is to use polysaccharides to produce biogas, using anaerobic digestion. Agricultural, organic waste or effluents are used as a lignocellulosic source for microorganisms (e.g. bacteria and archaea) (Sawatdeenarunat et al., 2014; Sayara and Sánchez, 2019).

3.11. Vitamins

The production of vitamin C (ascorbic acid, Fig. 4a) is over 100 000 tonnes/year (Buchholz and Seibel, 2008). It is mainly produced chemically from glucose by oxidation (Reichstein synthesis). Alternatively, microbial systems, using *Gluconobacter oxydans* and *Bacillus thuringiensis* are used, with an estimated production of 43 000 tonnes/year, with a decrease of one third of the cost compared to the usual production pathway, due to lower use of toxic solvents and reagents, and therefore involving less waste processing (Buchholz and Seibel, 2008). However, use of glucose as a substrate increases production cost of vitamin C, and therefore using polysaccharides from lignocellulosic biowaste could be a cheaper alternative.

4. Relevant treatments for transformation of lignocellulosic biomass

Lignocellulosic waste often needs pre-treatment to be transformed into high value products such as those as presented above. Ten essential pretreatment methods, together with their advantages and disadvantages are shown in Table 4. The detailed characteristics and examples of each treatment are presented in the following sub-sections.

4.1. Physical treatments

4.1.1. Ultrasound

Ultrasounds are acoustic waves that oscillate at frequencies above 16 kHz (Gallo, 2018). In liquid, ultrasounds rapidly form and subsequently collapse microbubbles. This phenomenon, called cavitation, disrupts cell wall structure and increases mass transfer during extraction and biomass conversion due to shear force from the shockwaves and microjets (Both et al., 2014; Flores et al., 2021; Ong and Wu, 2020). Cavitation increases the temperature at a rate of 10^{10} °C/s with local pressure of up to 2000 atm (Flores et al., 2021). Therefore, using ultrasound in a liquid medium will induce physical effects such as heating, acoustic streaming, acoustic cavitation, agitation, solubilisation and nebulization, and chemical reactions with formation of hydroxyl radicals from water molecules (Flores et al., 2021; Ong and Wu, 2020). Current use of ultrasound for biomass treatment involves direct application of frequencies below 50 kHz, with mainly physical effects due to shock waves, turbulence and increase of mass transfer, resulting in improved accessibility and/or solubility of the biomass (Flores et al., 2021). A decreased frequency (below 20 kHz) decreases the number of bubbles but increases their size. While this results in higher mechanical energy released during collapse, its effect is limited to the surface of the lignocellulosic material and is not enough to separate the lignocellulosic fraction (Flores et al., 2021). Ultrasound is often used to remove the lignin from lignocellulosic biomass and improve access to cellulose and hemicellulose, especially since lignin is more abundant at the surface of lignocellulosic fibers and is therefore directly in contact with the solvent

and with the energy released during cavitation (Flores et al., 2021). Indeed, using ultrasound for delignification is efficient and uses less time and lower temperatures compared to other processes such as solvent extraction. In addition, it decreases cellulose crystallinity due to the weakening of intermolecular hydrogen bonds (Flores et al., 2021). Ultrasound treatment may be used for extraction with the addition of a solvent. Indeed, the use of ultrasonic extraction in black tea increases polyphenolic content by + 15 % compared to maceration (Both et al., 2014). Ultrasound has been used at a pilot scale for biofuel production (Bussemaker et al., 2013; Bussemaker and Zhang, 2013; Chemat et al., 2017; Flores et al., 2021; Luo et al., 2014).

Ultrasound may also be combined with other pre-treatments such as acid hydrolysis, for example for furfural production from grass with 4 mol/L of HNO₃, at 30 °C, 50 % amplitude and 60 min of sonication (Bizzi et al., 2019). The combination of acid hydrolysis and ultrasound improved the diffusion of sugar molecules from the lignocellulosic biomass since lignin is disrupted by the ultrasound and the dilute acid disrupts hydrogen, covalent and van der Waals bonds, improving the hydrolysis step, as showed with grass for hydrogen production (Yang and Wang, 2019). Ultrasound may also be used with alkaline pre-treatment to reduce the time of the pre-treatment since ultrasound disrupts the hydrophobic wax layer on some types of lignocellulosic biomass (*Ipomoea carnea* and *Arundo donax*), which increases the contact surface between the biomass and the alkaline solution (Muthuvelu et al., 2019). The heat produced during cavitation also enhances the alkaline effect as shown with rice straw (Wu et al., 2017). The use of ultrasound with alkaline hydrogen peroxide in particular is highly effective due to the transformation of H₂O₂ into radicals (HO• and O₂•-), which disrupt intermolecular bonds between lignin and cellulose, and are therefore more effective, as shown with *Crotalaria juncea* biomass (Baksi et al., 2019). In another example, ultrasound was coupled with enzymatic hydrolysis for bioethanol production, improving the access of enzymes to cellulose and hemicellulose (Subhedhar and Gogate, 2013), by improving access of the hydrolytic enzyme and increasing the catalytic rate (Subhedhar and Gogate, 2013), thus doubling sugar production from sugarcane bagasse (Lunelli et al., 2014).

4.1.2. Microwaves

Microwave irradiation is an interaction of electromagnetic waves with polar molecules and ions. Microwaves cause thermal effects, such as hydrolysis reactions, and non-thermal effects, such as the rotation of polar groups. Microwave irradiation is particularly effective since it generates heat inside the target (due to dipole rotation and ionic conduction) and not through its surface (Ethaib et al., 2015; Yu et al., 2021b). Compared to other methods, heating and reaction time are reduced, biomass conversion increases and processing cost are lower (Yu et al., 2021b). Microwaves may be used in pyrolysis to produce 1) bio-oil, containing levoglucosenone, 5-HMF and phenolic compounds, 2) biochar and 3) syngas, composed of carbon monoxide and dioxide, hydrogen and methane (Yu et al., 2021b). Currently, microwave treatment is mostly used in drying processes in the food, ceramic and wood industries, whereas microwave-assisted biorefineries only exist at a laboratory or pilot scale (Yu et al., 2021b).

Microwave-assisted hydrolysis needs a polar medium, such as water, to absorb and convert the electromagnetic waves into thermal energy. Microwave pre-treatment accelerates the hydrolysis of cellulose and glucose by activation of specific groups, improving the hydrolysis of cellulose by 2.5 times compared to conventional heating (Sweyggers et al., 2018). Adding salt decreases the power needed to reach the target temperature during microwave heating, since it increases proton absorption on the substrate and disrupts hydrogen bonds (Jiang et al., 2018; Yu et al., 2021b).

Microwave-assisted extraction has been reported as an alternative to chemical extraction under heating conditions. Indeed, microwave irradiation creates highly localized environments of increased temperature and pressure, which accelerates migration of bioactive compounds from

Table 4

Overview of the advantages and disadvantages of each possible treatment to transform lignocellulosic biomass, further presented in the following sub-sections of this review.

Methods	Advantages	Disadvantages	References
Ultrasound	Cavitation, improve the access to cellulose and hemicellulose, decrease of the time and temperature, combination with other treatments	Need a liquid medium, not used at industrial scale	Both et al., 2014; Flores et al., 2021; Ong and Wu, 2020
Microwaves	Fast, hydrolysis reactions, combination with other treatments, alternative to chemical extraction	Need a liquid medium, actually used to dry substances in the food, ceramic and wood industry and not used for biorefineries at industrial scale	Ethaib et al., 2015; Jiang et al., 2018; Sweygers et al., 2018; Yu et al., 2021a
Steam explosion	Hydrolysis and cavitation, combination with other treatments, already used for lignocellulosic biomass in the energy sector	Inhibitors production, energy and water high cost	Balan et al., 2020; Brethauer et al., 2020; Duque et al., 2016; Fan et al., 2014; Ferreira et al., 2014a; Pang et al., 2013; Vivekanand et al., 2013; Wang et al., 2015; Wolbers et al., 2018
Pyrolysis	Do not use water or oxygen, use of all kinds of waste and may be used as a final transformation step	Inhibitors production, energy and economical high cost, 3 fractions to process	Akom, et al., 2020; Hoang et al., 2021b; Kurian et al., 2022; Yu et al., 2021b; Yogalakshmi et al., 2022
Gasification	Do not use water, may be controlled by the oxygen amount, use of all kinds of waste and may be used as a final transformation step	May need a catalyst (more expensive), energy and economical high cost, variation of the composition of syngas due to the composition of the feedstock, difficulty in the separation of the various gas produced	Akbarian et al., 2022; Ghodke et al., 2023; Rodionova et al., 2022; Watson et al., 2018
Hydrothermal	Hydrolysis, use of all kinds of waste and may be used as a final transformation step	Less effect than steam explosion (no cavitation), inhibitors production, energy and water high cost, 4 fractions to process	Fan et al., 2016; Gollakota et al., 2018a; Maddi et al., 2016; Miliotti et al., 2020b; Nitsos et al., 2013b; Panisko et al., 2015a; Pielhop et al., 2016; Torri et al., 2021; Watson et al., 2020
Acid treatment	Cleavage of glucosidic bonds, and solubilization of hemicellulose and lignin (partially), combination with other treatments, already used in industry	High cost of acid waste disposal, neutralization, inhibitors production	Amnuaycheewa et al., 2016; Bussemaker et al., 2013; Cao et al., 2018; de Araújo Padilha et al., 2020; Dziekońska-Kubczak et al., 2018a; Ghasimi et al., 2016a; Gowdhaman and Ponnusami, 2015; Hoang et al., 2021a; Kumagai et al., 2015; Mohammed et al., 2017; Pekařová et al., 2017; Santos et al., 2018; Um and Walsum, 2012; Woiciechowski et al., 2020; Yoon et al., 2015
Alkaline treatment	Lignin and hemicellulose solubilization, cellulose crystallinity reduction, combination with other treatments, already used in the pulp and paper industry, no inhibitor production, low investment cost, high sugar yield	High cost of alkaline chemicals	Alencar et al., 2017; Banerjee et al., 2011; Bussemaker et al., 2013; Dziekońska-Kubczak et al., 2018a; Fang et al., 1999; Gowdhaman and Ponnusami, 2015; Hoang et al., 2021a; Khan and Ahring, 2020; Mihiretu et al., 2019; Montané et al., 1998a; Sudiyan et al., 2010; Woiciechowski et al., 2020; Yao et al., 2013a
Enzymes	Can be adapted to lignocellulosic residues and to convert cellulose, hemicellulose and lignin, use for extraction, combination with other treatments	High cost of enzymes	Ahmad et al., 2011a; Atiweh et al., 2021; Brodeur et al., 2011; Bugg et al., 2011; Ellouze and Sayadi, 2016; Huang et al., 2013; Masai et al., 2007a; Modenbach and Nokes, 2013; Öhgren et al., 2007; Rahikainen et al., 2013
Lignin-degrading microorganisms	Fast (using bacteria), used for downstream and/or simultaneous transformation, combination with other treatments, versatile	Microorganisms are condition dependent, slow (using fungi), not pure products, production costs (less than enzymes)	Atiweh et al., 2021; Becker et al., 2018; Ghorbani et al., 2015a; Hashimah et al., 2013a; Jackson et al., 2017; Kohlstedt et al., 2018; Linger et al., 2014; Bingji Ma and Agblevor, 2014; Ravi et al., 2017; Si et al., 2018; Sonoki et al., 2018; Vardon et al., 2015; Xiong et al., 2014; Xu et al., 2022
Carbohydrate-degrading microorganisms	Fast (using bacteria), used for downstream and/or simultaneous transformation, combination with other treatments, versatile, already used in industry for ethanol production.	Microorganisms are condition dependent, slow (using fungi), not pure products, production costs (less than enzymes)	Brodeur et al., 2011; Buchholz and Seibel, 2008; Larissa Canilha et al., 2006; Cassuriaga et al., 2018; Chandel et al., 2010; Haji Esmaeili et al., 2020, 2020; Rueda et al., 2020; Singh and Kumar, 2007; Song et al., 2019; Vidra and Németh, 2018; J. Yu and Stahl, 2008
Anaerobic digestion	Well implanted in industry, can use a lot of various lignocellulosic waste sources	Not very efficient, takes a long time, especially with high lignin content	Cazier et al., 2015; Cu et al., 2015a; Khan and Ahring, 2019; Kobayashi et al., 2012; Motte et al., 2015; Pham et al., 2013a; Samoraj et al., 2022; Tian et al., 2021; Triolo et al., 2011

substrate to surrounding solvent and therefore could reduce both extraction time and solvent consumption (Nkhili et al., 2009; Yu et al., 2021b). This method is thus thought to be more effective than traditional maceration for extraction of bioactive compounds, with for example a 9 % increase in extracted polyphenols from green tea at 80–100 °C compared to maceration (Nkhili et al., 2009), or for the extraction of levulinic acid from hazelnut shells or giant reed (Yu et al., 2021b). Another example is extraction of hemicellulose using a microwave-assisted pressurized hot water system with a xylan extraction yield of 66 % for aspen wood and 50 % for sugarcane residues, and

an improvement of the digestibility of the leftover cellulose of up to 78 %, which facilitates further transformation (Mihiretu et al., 2017).

Microwaves may also be combined with other pre-treatments, such as steam-explosion, with an improvement of enzymatic digestibility of hemicellulose and cellulose of corn stover, and decreased cellulose crystallinity (Pang et al., 2013). Another example is the combination of microwave and oxidative depolymerization with $\text{Cu}(\text{OH})_2$ and Fe_2O_3 catalysts, and with addition of NaOH and H_2O_2 for the production of phenolic compounds from palm empty fruit bunches, with an improved yield by 2.6 times compared to autoclaving (Dai et al., 2018), or the

production of lactic acid from tomato plants with a $\text{Pb}(\text{NO}_3)_2$ catalyst at 3 MPa and 220 °C, with a reduced reaction time from 4 h to 2 min compared to conventional heating without the catalyst (Carnaroglio et al., 2015).

4.1.3. Steam explosion

Steam explosion is considered as one of the most powerful and versatile pre-treatment processes in lignocellulosic bio-refining, with low environmental impact and low capital investment (Duque et al., 2016; Wang et al., 2015). The mechanism of steam explosion corresponds to the autohydrolysis of biomass at high temperature and pressure, followed by sudden decompression. During steam explosion treatment, the cell wall matrix is significantly altered with various physicochemical modifications, such as an increase in porosity, redistribution of lignin, and defibrillation and depolymerisation of polysaccharides. Therefore, steam explosion can enhance the accessibility of solvents in lignocellulosic biomass and the mass transfer of bioactive components during the extraction process (Sui et al., 2019). Steam explosion is often characterised in terms of severity R_0 , shown in the following equation:

$$\log(R_0) = \log_{10} \left(t^* e^{\frac{T-100}{14.75}} \right) \quad (1)$$

Severity of the pre-treatment with R_0 the severity, t the time in seconds and T the temperature in °C

The higher the severity, the harsher the pre-treatment. During steam explosion, the optimum conditions (time and temperature) for hydrolysis of hemicellulose and cellulose are different, with an increase in hemicellulose hydrolysis with low severity pre-treatment and an increase in cellulose hydrolysis with high severity (Balan et al., 2020; Pielhop et al., 2016; Vivekanand et al., 2013). Indeed, for beech wood, the optimum severity for hemicellulose hydrolysis was around 4 and between 4.5–5 for cellulose (Balan et al., 2020). When severity exceeds optimal values, cellulose and hemicellulose are transformed into furans and 5-HMF, which may inhibit enzymes and microorganisms that may be used in further processing (Brethauer et al., 2020). Steam explosion may also be used in two steps to optimize the hydrolysis of each compound (Cotana et al., 2014; Zhang et al., 2012). It is also possible to recover heat during the process to limit the overall cost of steam production (Baral and Shah, 2017).

Steam explosion is often used as a pre-treatment for further transformation with enzymatic hydrolysis, anaerobic digestion or extraction. In one study, tea waste was pre-treated with steam explosion, which increased extraction yields of various components including polyphenols (+15.5 %), caffeine (+14.1 %), saponin (+28.8 %) and water-soluble sugars (+74.8 %) (Sui et al., 2019). Steam explosion also improved anaerobic digestion of pig manure (+30 to +100 %) (Ferreira et al., 2014b; Ortega-Martinez et al., 2016), corn stover (+22 %) (Lizasoain et al., 2017), and birch (+80 %) (Vivekanand et al., 2013). Steam explosion may also be combined with other pre-treatments such as acidification of the biomass (Fan et al., 2014), microwave irradiation (Pang et al., 2013), or potassium hydroxide treatment (Li et al., 2015).

Steam explosion is already used in the energy sector by companies such as Arbaflame in Norway, producing pellets since 2003 with a capacity of 6 tonnes/h from biomass sawdust, or Zilkha since 2015 in the US with batch type steam explosion for a production of 275 ktonne/year using sawdust, chips, shaving, tree-tops, limbs and thinnings (Wolbers et al., 2018).

4.1.4. Pyrolysis and gasification

Pyrolysis involves the partial thermal degradation process of material (here lignocellulosic material) without oxygen (as in combustion) or water (as in hydrothermal pretreatment). During pyrolysis, three products are obtained: *i*) char (solid fraction), *ii*) tars or liquid oil, (containing small carbonyl compounds (acids, ketones, aldehydes), sugar-based compound (furans and hydrosugars), and lignin-based compounds (phenols, aromatic oligomers) and *iii*) syngas (hydrogen, carbon

dioxide, carbon monoxide, hydrogen disulfur or gaseous hydrocarbon) (Hoang et al., 2021b). Important parameters of pyrolysis are the temperature, the decomposition time, heating rate, working pressure, and the composition of the substrate (Hoang et al., 2021b). Depending of the heating rate, the temperature and the residence time, the pyrolysis may be called: *i*) slow pyrolysis (temperature < 500 °C, long residence time, to make bio-char), *ii*) fast pyrolysis (heating rate (10–200 °C/s), reduced residence time (<2 s), for bio-oil), or *iii*) flash pyrolysis (high heating rate (10³–10⁴ °C/s), fast residence time (<0.5 s), bio-oil production) (Kan et al., 2016; Yogalakshmi et al., 2022). Usually, pyrolysis is between 200 and 400 °C for lignocellulosic biomass and is composed of three steps: the evaporation of available moisture, the primary biomass degradation and the secondary reactions (Yogalakshmi et al., 2022). Pyrolysis may be used for the whole biomass or for the various molecules such as the cellulose (325–400 °C), hemicellulose (250–350 °C) and lignin (300–550 °C). 1 kg of lignocellulosic biomass will produce around 0.36 to 0.45 kg of biochar (Akom, et al., 2020; Yogalakshmi et al., 2022). For lignocellulosic biomass, pyrolysis is interesting as a final treatment after all the others for recalcitrant components such as lignin residues, to produce bio-char, which can be used as a absorbent. Pyrolysis of lignocellulosic biomass is actually more used for the production of liquid fuel (from bio-oil) but the quality of the bio-oil is heavily dependent of the composition of the lignocellulosic biomass, and especially negatively by the quantity of lignin (Hoang et al., 2021b; Yogalakshmi et al., 2022). Another problem of pyrolysis is the high economical cost and the high energy needed (Hoang et al., 2021b; Yogalakshmi et al., 2022). To improve the pyrolysis yield, combination with others process such as thermo-catalytic reforming, catalytic fast pyrolysis, and microwave pyrolysis are tested (Kurian et al., 2022; Yu et al., 2021b).

Gasification corresponds to the conversion of lignocellulosic biomass at high temperatures with a controlled and limiting amount of oxygen, without or with catalysts (usually sulfur compound or calcium oxide), into syngas (containing hydrogen, methane and carbon monoxide) and biochar (Akbarian et al., 2022; Ghodke et al., 2023; Watson et al., 2018). Contrary to pyrolysis, the production of syngas will be higher with gasification (Akbarian et al., 2022). Gasification will have three steps: *i*) drying the biomass at 120 °C; *ii*) devolatilization at 350 °C i.e. the removal of volatile substances and *iii*) char gasification at 350–550 °C (Rodionova et al., 2022). The main parameters in gasification with an effect on syngas composition are feedstock composition, catalysts, reactor size, and residence time (Ghodke et al., 2023). Since the main product of gasification is syngas, it is mostly used in the energy sector to produce methane or hydrogen. Another problem is due to the variability of the feedstock, which will influence the composition of the syngas produced (Watson et al., 2018). Another problem is the separation of the various gases produced, especially since some of them are toxic and more pure gases are needed for industrial uses (Watson et al., 2018). New gasification process of lignocellulosic biomass, using new catalysts (calcium oxide, dolomite based catalysts,...), improved the yield of hydrogen and decreased the concentration of carbon dioxide and monoxide (Ghodke et al., 2023). One possibility to improve the yield of gasification is its combination with other treatment such as microwaves (Ghodke et al., 2023). Moreover, some biochar and bio-oil are also produced during the gasification process and will need to be used, similar to the bio-oil produced during pyrolysis (Rodionova et al., 2022).

4.1.5. Hydrothermal pre-treatment

Hydrothermal pre-treatment corresponds to the use of water under pressure at high temperature (>100 °C) (Nitsos et al., 2013a). Contrary to steam explosion, hydrothermal pre-treatment lacks pressure variation with the explosion phenomenon at the end of the pre-treatment. The severity of hydrothermal pre-treatment is calculated using the same equation as for steam explosion (cf. Equation (1)).

During hydrothermal pre-treatment, various transformations occur, including depolymerisation, dehydration/deoxygenation, hydrolysis of α - and β -aryl ether, fragmentation and condensation on phenolic

compounds, alkylation, decarboxylation, deamination, repolymerisation of lignin and production of organic acids from carbohydrates and decrease in pH to 6.5–2.5 (Gollakota et al., 2018b; Miliotti et al., 2020a).

Hydrothermal liquefaction occurs above 200 °C. During hydrothermal liquefaction, 4 fractions are obtained: the liquid fraction, called a biocrude oil, a gaseous fraction, an aqueous by-product and a solid fraction called the biochar. At the industrial scale, biocrude and solid products are separated from aqueous by-products through gravity, followed by centrifugation or filtration to separate the biocrude oil from the solid fraction. Biocrude oil is then transformed into hydrocarbon fuels, biochar into fertilizer and the gas can be used as syngas. The composition of aqueous by-product depends of the lignocellulosic biomass used for hydrothermal pre-treatment such as food waste, sludge or agricultural biomass (Maddi et al., 2016; Panisko et al., 2015b; Torri et al., 2021; Watson et al., 2020). For example, for food waste, the main compounds (>0,1% w/w) in aqueous by-products correspond to acetic acid, ethanol, glycerol, lactic acid, propanoic acid, pyroglutamic acid and sugars (Maddi et al., 2016; Panisko et al., 2015b; Torri et al., 2021; Watson et al., 2020). However, for agricultural biomass, acetic acid, ethylene glycol, glycolic acid and propanoic acid will be produced (Maddi et al., 2016; Panisko et al., 2015b; Torri et al., 2021; Watson et al., 2020).

Hydrothermal pre-treatment may be used for the transformation of residues such as lignin-rich stream from lignocellulosic ethanol biorefineries (Miliotti et al., 2020a), or other waste products such as sludge, manure or food waste (Torri et al., 2021; Watson et al., 2020). Cellulose in lignocellulosic residues will degrade into glucose and 5-HMF at temperatures over 250 °C, with complete transformation to water soluble fractions at 295–350 °C (Fan et al., 2016). Hemicellulose is completely hydrolysed at temperatures over 200 °C and yields acetic acid and furfural, which lowers the pH of the solution (Pielhop et al., 2016).

4.2. Chemical treatment

4.2.1. Acid treatment

Acid treatment improves digestibility of lignocellulosic biomass by cleaving glucosidic bonds and by solubilizing both hemicellulose and part of the lignin, and is mostly used as a pre-treatment for further transformations (Woiciechowski et al., 2020). Indeed, the benzyl oxygen group in lignin is protonated in an acid environment and will initiate the degradation of α and β -ether lignin units (Bussemaker and Zhang, 2013). Both organic and inorganic acids are used in the pre-treatment of lignocellulosic biomass. For example, inorganic acids, such as phosphoric acid, were used with pinewood sawdust, at 4 % w/w of acid and 106.7 °C for 4.57 h to obtain 60.95 % of xylose (Cao et al., 2018). Phosphoric acid had a higher effect on bark compared to wood, with a hydrolysis of 40 % for cellulose and 60 % for xylan in bark (Yoon et al., 2015). Sulfuric acid was used for example in pre-treating of *i*) corncob residues in a 0.1 % solution, for 12 h at 60 °C, with 14.7 % of xylan obtained (Gowdhaman and Ponnusami, 2015), *ii*) elephant grass at 5 to 20 % at 121 °C for 30 min for ethanol production (Santos et al., 2018), *iii*) Napier grass at 0.5–2.5 wt% at 70 °C for 1 h (Mohammed et al., 2017) or *iv*) woods chips at 0.5–2 % (w/v) at 121 °C for 1 h followed by enzymatic hydrolysis to obtain a yield of 41 % for aspen and 62 % for birch chips (Dziekońska-Kubczak et al., 2018b). In the pulping industry, sulphite delignification using HSO_3 and SO_3^{2-} degrades and solubilises lignin (Woiciechowski et al., 2020).

In scale up and industry, sulfuric acid is used more often than phosphoric acid and chloride acid, since it is less expensive and does not need further corrosion resistant materials (Woiciechowski et al., 2020). Sulfuric acid breaks carbon–oxygen bonds and alkyl-aryl ester bonds, both present in lignin (Kumagai et al., 2015). Organic acids such as acetic acid, citric acid and oxalic acid are also used for pre-treatment of lignocellulosic biomass. For example, acetic acid, in combination with sulfuric acid, was used in the pre-treatment of cashew apple bagasse to

obtain 37 g/L of reduced sugars and 16 g/L of ethanol with subsequent yeast fermentation (de Araújo Padilha et al., 2020). When oxalic acid was used to pre-treat rice straw (5.01 % of oxalic acid at 135.31 °C over 30.86 min) prior to enzymatic hydrolysis, the yield was 2.68 times higher compared to non-treated biomass (Annuyacheewa et al., 2016).

Variables for acid pre-treatment are: type of acid used, concentration, reaction time, temperature and the solid to liquid ratio. The severity of the acid pre-treatment is calculated as a combined severity factor (CSF) (Equation (2)):

$$\text{CSF} = \log \left(t - e^{\frac{T-T_R}{14.75}} \right) - \text{pH} \quad (2)$$

CSF=combined severity factor, where t : reaction time (h), T : reaction temperature (°C), T_R : reference temperature (100 °C) and pH the initial pH value of the solution. (Woiciechowski et al., 2020).

Cellulose is first hydrolysed into oligosaccharides and then to glucose, which are then present in the liquid fraction (Woiciechowski et al., 2020). Depending on the acid concentration, hemicellulose is either hydrolysed to monosaccharides such as xylose, mannose, arabinose and galactose or, if the pre-treatment is too strong, further down to acetic acid, furfural, formic acid, lactic acid and 5-HMF. These compounds may inhibit downstream transformations due to inhibition of hydrolytic enzyme and toxicity for microorganisms (Ghasimi et al., 2016b; Hoang et al., 2021a; Li et al., 2005; Pekařová et al., 2017; Um and Walsum, 2012). However, some microorganisms are able to transform such inhibitory molecules into other molecules. For example, furfural (at concentrations below 25 mM) can be transformed into furfuryl alcohol via anaerobic biotransformation with *Methanococcus* sp. (Boopathy, 2009). If the acid concentration is too high, humic-like molecules are produced via the condensation of furfural and saccharides (Hoang et al., 2021a).

Most often, dilute ($\leq 5\%$) acid pre-treatment is used in industry (Hoang et al., 2021a). Dilute acid pre-treatment limits the amounts of inhibitors produced, decreases the cost of chemicals, waste recycling, toxicity and corrosivity and improves sugar yields up to 75 % compared to no pretreatment (Hoang et al., 2021a; Woiciechowski et al., 2020). A problem in using acid treatment is the high investment cost due to the need for corrosive-resistant equipment and medium operation costs due to acid recycling, and the formation of inhibitory molecules, detrimental for further transformations (Hoang et al., 2021a). However, most of lignocellulosic biomass from industry is treated using acid pre-treatment (Hoang et al., 2021a; Woiciechowski et al., 2020). As an example, industrial scale production of bioethanol using dilute acid pre-treatment corresponds to 25 million USD for 56.1 million gallons per year of ethanol. Nonetheless, dilute acid pre-treatment has the highest economic efficiency compared to other pre-treatment methods for lignocellulosic biomass (Eggeman and Elander, 2005).

After acid pre-treatment, neutralization is often necessary, using alkalis such as KOH, CaCO_3 or Ca(OH)_2 , since the acid may have a negative effect on further transformation processes (Hoang et al., 2021a). Most of the time, enzymatic hydrolysis is used after acid pre-treatment to continue transformation of the cellulose into glucose and hemicellulose into xylose (cf. 4.3.1 Enzymes), especially after dilute acid pre-treatment, due to the partial removal of hemicellulose (Hoang et al., 2021a). Another possibility to limit the production of inhibitory molecules is two-step acid pre-treatment, such as with softwood, showing 10 % higher yields compared to single step pre-treatment and reducing the need of enzymes by 50 % (Nguyen et al., 2000), or combined with steam explosion to improve enzymatic conversion, with for example black spruce (Fang et al., 2011), corn stalk (Wang et al., 2019) or wheat straw with acetic acid for ethanol production (Zabihi et al., 2010). This combination is currently used in industry for energy production by Abengoa Bioenergy (Spain) using sugarcane bagasse, corn stover, wood, switch grass, miscanthus, sugarcane and wheat straw, BlueFire Renewables (USA) to pre-treat agricultural biomass, paper and

wood, Tembec and Georgia Pacific (USA) for wood transformation into cellulose pulp or woodchip pre-treatment at the Izumi Biorefinery (Japan) (Hoang et al., 2021a).

Moreover, the waste produced during these treatments needs to be processed to limit its environmental impact, which also increases the cost of the process. For example, bioethanol from bamboo using sulfuric acid pre-treatment needs a sugar-acid separation step, with a recovery yield of 77.6 % maximum for the sulfuric acid (Sun et al., 2013), and further treatment for the acidic effluent containing the left-over sulfuric acid.

4.2.2. Alkaline treatment

Alkaline treatment solubilizes lignin, partially solubilizes hemicellulose and reduces cellulose crystallinity. It is traditionally used in the pulp and paper industry to recover cellulose by removing hemicellulose and lignin (Woiciechowski et al., 2020; Singh et al., 2015). Lignin is degraded in alkaline and alkaline oxidative environments via cleavage of α and β -aryl ether linkages, and carbon-carbon links (Bussemaker and Zhang, 2013). Contrary to acid pre-treatment, no inhibitors are produced during the alkaline pre-treatment process, with low investment costs and high sugar yield (Hoang et al., 2021a). However, the alkaline chemicals used still need to be recycled (Hoang et al., 2021a). During pulping, lignocellulosic biomass is mixed with sodium sulphide and sodium hydroxide at 15–20 %, at 145–170 °C, and 6–7 bars for 2–3 h (Woiciechowski et al., 2020). Cellulose fibres are the only solid product left, with a yield of 45–50 %, as lignin and hemicellulose are solubilized into black liquor (Woiciechowski et al., 2020). Cleaving of β -O-4 and α -O-4 bonds during the process results in alkali or kraft lignin and production of phenolic hydroxyl groups (Woiciechowski et al., 2020). Other industrial alkaline processes exist, such as soda pulping process which uses sodium hydroxide and degrades and solubilise lignin by cleaving aryl-ether linkages, reducing primary aliphatic hydroxyl groups and producing phenolic acid (Woiciechowski et al., 2020).

Alkali pre-treatment may be used to solubilise hemicellulose, as was done with wheat straw with an optimum obtained yield of 92 % at 50 °C for 16 h and 2 % of hydrogen peroxide at pH 11.5 (Fang et al., 1999), and to extract xylan, for example in corncob with sodium hydroxide, with a maximum yield of 23 % of xylan on weight basis (Gowdhaman and Ponnusami, 2015). An estimated cost corresponds to US \$160 per tonne of corn stover biomass using low H₂O₂ concentration (0.125 g H₂O₂/g biomass) in alkaline medium (Banerjee et al., 2011).

Alkali pre-treatment is often combined with further transformation, such as: i) biodegradation of alkali lignin by microorganisms such as *Rhodococcus pyridinovorans*, with a degradation yield of 30.2 % at 30 °C after 72 h or *Novoshingobium* (Chen et al., 2012; Chong et al., 2018); ii) anaerobic digestion for methane production, which was done with poplar with an optimum yield at 5 % of sodium hydroxide and 35 g/L, a 113 % improvement in methane production compared to non-pre-treated poplar (Yao et al., 2013b), and for manure fibres with an improvement of 43.6 % in methane yield with 3 % w/w sodium hydroxide (Khan and Ahring, 2020); iii) with steam explosion to extract xylan from aspen wood (24 % yield) or sugarcane residues (51 % yield) (Mihiretu et al., 2019), or using steam explosion for wheat straw as the first step before delignification with alkali treatment (160 °C, 1 h and 20 % NaOH) for fibre residues (Montané et al., 1998b); and iv) enzymatic hydrolysis on various biomass such as aspen, birch and oak chips pre-treated at 0.5–2 % (w/v) NaOH at 121 °C for 1 h, with an optimum 80 % yield for the hydrolysis and 85 % for the fermentation, especially for aspen chip (Dziekońska-Kubczak et al., 2018b), on bagasse pre-treated with 10 % alkali at 90 °C for 1.5 h followed by 15 % peracetic acid at 75 °C for 3 h with an optimum of 80 % of glucan conversion after 24 h (Zhao et al., 2011), or on oil palm empty fruit bunch fibres at 12.5 % (w/v) NaOH at 30 °C for 90 min, with an optimum of 63 % saccharification after 45 h at pH 4.5 (Sudiyani et al., 2010).

Alkaline solution tends to be reused for treatment to limit its consumption and the waste produced. For example, corn stover pretreatment with 7.5 % v/v H₂O₂, with the solution recycled three times, was still efficient but with a decrease of cellulose conversion from 90 to 60 % and a decrease of H₂O₂ by 59.6 % (Alencar et al., 2017). Therefore, direct reuse is not a solution and waste management of the alkaline effluents need to be taken into account when using them as a pre-treatment.

4.3. Biological treatments

4.3.1. Enzymes

Various enzymes are involved in the degradation of molecules in lignocellulosic biomass and can be used in pre-treatment. Indeed, removing lignin improves access to cellulose and hemicellulose for further conversion (Brodeur et al., 2011) and reduces its inhibitory effect on cellulase (Rahikainen et al., 2013). Lignin reformed during pre-treatment such as during steam explosion or during dilute acid pre-treatment due to depolymerization also has an inhibitory effect on enzymatic hydrolysis (Hu et al., 2012; Rahikainen et al., 2013). Hemicellulose may also have an inhibitory effect on cellulase conversion. For example, the use of xylanase for acid-pre-treated, steam-exploded corn stover improved cellulose to glucose conversion yield with a maximum of 96 % (Öhgren et al., 2007).

Various enzymes may be used for lignin transformation such as laccase-like hydrogen peroxidase, lignin peroxidases, laccases and manganese-dependant peroxidases or dye-decolorizing peroxidases (Atiwesh et al., 2021). These enzymes are found in microorganisms. White-rot fungi synthesize lignin peroxidases, laccases and manganese-dependant peroxidases to degrade lignin. These enzymes are non-specific, secreted in the extracellular environment and also degrade similar structured molecules such as endocrine-disrupting drugs, pesticides, dyes and chlorinated phenols (Atiwesh et al., 2021; Ellouze and Sayadi, 2016; Rodríguez-Couto, 2017). Lignin peroxidases target non-phenolic units in lignin and are hydrogen peroxide-dependent (Atiwesh et al., 2021). Manganese-dependent peroxidase activity is dependent on Mn²⁺ ions, which are oxidized into Mn³⁺ ions and target both phenolic and non-phenolic units in lignin for lipid peroxidation (Atiwesh et al., 2021). Laccases catalyse oxygen-mediated oxidation of lignin and phenolic molecules followed by aryl-alkyl cleavage (Atiwesh et al., 2021). Most bacterial lignin-degrading enzymes are similar to those found in white rot fungi: lignin peroxidase in *Streptomyces viridosporus* and *Sphingomonas paucimobilis* (Atiwesh et al., 2021; Masai et al., 2007b), laccase in *Bacillus pumilus* and *atrophaeus* (Atiwesh et al., 2021; Huang et al., 2013), or manganese-dependant peroxidase in *Rhodococcus jostii* RHA1 (Ahmad et al., 2011b; Atiwesh et al., 2021). Other enzymes such as extracellular laccase-like peroxidase, which is hydrogen peroxide-dependent in *Pseudomonas putida*, do not have orthologs in fungi (Atiwesh et al., 2021; Bugg et al., 2011).

Enzymes are also used to transform polysaccharides into monosaccharides by enzymatic hydrolysis. Monosaccharides are further transformed by fermentation to ethanol, ether or other alcohols (Jørgensen et al., 2007). The main parameters for enzymatic hydrolysis are solid loading, i.e. the liquid to solid ratio, and enzyme loading (5 to 20 FPU/g (Modenbach and Nokes, 2013). High solid loading with a solid quantity of over 15 % is preferred economically due to higher final sugar concentration, with a lower production cost due to lower energy and water demands (Modenbach and Nokes, 2013). However, free water is necessary for hydrolysis and with over 20 % of solid loading, enzymatic hydrolysis yield decreases, whereas viscosity and inhibitor concentration increase (Modenbach and Nokes, 2013). Another parameter is the enzymatic bioreactor configuration, which may improve the enzymatic hydrolysis of lignocellulosic biomass, for example using an oscillatory flow bioreactor with a 97 % conversion yield of pretreated corn cob

(Zanuso et al., 2022). Most often, enzymes used for commercial enzymatic hydrolysis of lignocellulosic biomass are cellulase, β -glucosidase and xylanase (Modenbach and Nokes, 2013). The main bottleneck for enzyme use is their cost and immobilization has come out as a strategy to reduce this cost as discussed in Section 3.9 Proteins and enzymes.

Enzymes may also be used for extraction of high-value molecules such as polyphenol. Some polyphenolic compounds can be retained in the lignocellulose matrix of vegetable cell walls, not only via hydrogen and/or hydrophilic interactions, but also by ether and/or ester linkages between phenols and polysaccharides. Cell wall degrading enzymes such as cellulases, hemicellulases, pectinases and tannases decompose the lignocellulosic network, hydrolyse polyphenol-polysaccharide bonds and enhance the release of polyphenols during extraction (Hong et al., 2013). Therefore, multi-enzyme complexes are often more efficient than one enzyme. For example, Viscozyme (containing arabinase, cellulase, β -glucanase, hemicellulose and xylanase) from *Aspergillus* sp. was the most effective enzyme among those studied for green tea polyphenol extraction, with a 15 % higher yield compared to extraction without enzymatic treatment (Hong et al., 2013).

4.3.2. Lignin-degrading microorganisms

High cost is the main disadvantage of purified lignin-degrading enzymes (lignin peroxidases, laccases and manganese-dependant peroxidases (not lignin specific)) (Atiwesh et al., 2021). To avoid this cost, lignin-degrading micro-organisms can be used directly. White rot fungi are the most studied species for lignin degradation, including *Irpex lacteus* for corn stover, with a degradation of 43.8 % after 42 days at 28 °C (Song et al., 2013), or *Trametes* sp. degrading poplar wood at 28 °C over 8 weeks with a yield of 85 % (Wang et al., 2013), tobacco stalk at 28 °C for 15 days with a yield of 51.57 % (Su et al., 2016) or rice straw at 30 °C, pH 4 for 30 days with a yield of 56 % (Ghorbani et al., 2015b). However, lignin degradation by fungi is too slow (several weeks) for industrial applications.

Therefore, lignin-degrading bacteria, which are faster, are now more often used (Atiwesh et al., 2021). Most of these bacteria are mesophiles and neutrophiles, making them easier and cheaper to use at an industrial scale. For example, *Pseudomonas putida* can be used at 30 °C and pH 7 over 48 h to degrade various lignocellulosic biomasses such as kraft lignin, wheat straw, wood lignin or pre-treated corn stover (Hashimah et al., 2013b; Linger et al., 2014; Ravi et al., 2017; Xu et al., 2022), producing various enzymes such as laccase-like hydrogen peroxide, lignin peroxidases, laccases and manganese-dependant peroxidases (Hashimah et al., 2013b; Ravi et al., 2017; Xu et al., 2018). Other microorganisms have been used for the degradation of lignin such as *Cupriavidus basilensis* using rice straw at 30 °C with a degradation yield of 88.5 % using NaOH pre-treatment (Si et al., 2018), or *Pantoea* sp. at 30 °C for 6 days using rice straw or kraft lignin, with an degradation yield between 37.9 and 69.7 % (Ma et al., 2016; Xiong et al., 2014). Other enzymes may also be used by microorganisms to degrade lignin such as hydroquinone peroxidase by *Azotobacter* sp. for most types of lignin except soft wood kraft lignin (Morii et al., 1995).

Microorganisms are also able to transform the lignin into other molecules of interest, such as lipids or PHA (Xu et al., 2019). For example, *Rhodococcus jostii* RHA1 and *Rhodococcus pyridinivorans* are able to produce lipids from lignin and accumulate up to 88 % of lipids (Xu et al., 2019). PHA was produced using *Pandora* sp. from kraft lignin, a waste from the biopulping industry (Xu et al., 2019), or using other microorganisms such as *Cupriavidus basilensis* from rice straw with a yield of 482.7 mg.L⁻¹ (Si et al., 2018). Another possibility is to use engineered microorganisms to produce valuable molecules such as vanillin, pyruvate, lactate or even *cis,cis*-muconic acid, as a precursor of adipic acid used for fibres and plastics production such as nylon (Becker et al., 2018; Kohlstedt et al., 2018; Sonoki et al., 2018; Vardon et al., 2015; Xu et al., 2019).

Some microorganisms, such as *Pantoea* sp. Sd-1, *Pantoea ananatis* and *Rhizobium* sp. YS-1, can simultaneously transform lignin, cellulose and

hemicellulose (Jackson et al., 2017; B. Ma and Agblevor, 2014; Xiong et al., 2014). Removing lignin may also improve the conversion of carbohydrates by enzymatic hydrolysis such as with *Cupriavidus basilensis* using rice straw (Si et al., 2018).

4.3.3. Carbohydrate-degrading microorganisms

The transformation of carbohydrates using microorganisms has been used since antiquity for the production of ethanol (Fig. 4a-b), obtained by fermentation using fungi with *Saccharomyces cerevisiae*, *Trichoderma reesei* or *Pichia* sp. or bacteria such as *Zymomonas mobilis*, *Bacillus subtilis* or *Thermoanaerobacter ethanolicus*. Second generation bioethanol is seeing an increasing demand, since it is used as a replacement of petroleum-based fuels (Buchholz and Seibel, 2008), while limiting competition with food production needs and decreasing production costs (Esmaili et al., 2020). For example, ethanol was produced from sodium hydroxide-pre-treated corn stover and rice straw using *Trichoderma reesei*, *Aspergillus niger* or *Pichia stipitidis* at 30 °C for 48 h (Zhao et al., 2018). Other alcohols may also be produced. Indeed, xylitol (Fig. 4b) can be produced from *Candida guilliermondii* at 30 °C over 54 h using pre-treated wheat straw followed by enzyme hydrolysis (L. Canilha et al., 2006). 2,3-butanediol (Fig. 4b) was also produced using *Klebsiella oxytoca* and/or *pneumoniae*, *Aerobacter aerogenes*, *Bacillus subtilis*, *licheniformis* or *amyloliquefaciens* using various biomasses such as corn step liquor, corncob molasses, Jerusalem artichoke, glucose or apple pomace, and obtaining yields between 34 and 98 % (Białkowska et al., 2015; Celińska and Grajek, 2009; Chandel et al., 2010; Li et al., 2013; Ma et al., 2009; Song et al., 2019; Sun et al., 2009; Yang et al., 2013, 2011). Another system produced both 2,3-butanediol and ethanol from starch using *Bacillus polymyxa* (Chandel et al., 2010). 2,3-butanediol is produced with a transformation of carbohydrate into pyruvate, then into α -acetylactate, into acetoin and/or diacetyl and finally into 2,3-butanediol (Song et al., 2019).

Other carbohydrate transformations are possible, for example for acetic acid production (Fig. 4a) using anaerobic bacteria such as *Clostridium* sp., *Moorella thermoacetica* or *Acetobacterium* (Vidra and Németh 2018), corresponding mostly to acetogenic bacteria. Acetic acid is produced from conversion of carbohydrates through glycolysis to form pyruvate, oxidized to acetyl-CoA, converted to acetyl phosphate by phosphotransacetylase and then acetate using an acetate kinase (Vidra and Németh 2018). Another possibility is the production of gluconic acid (Fig. 4a-b) from glucose, corn starch or food waste using fungi such as *Aspergillus niger*, *Penicillium*, *Gliocadium*, *Scopulariopsis* and *Gonobotrys*. Gluconic acid is produced from fungi by the dehydrogenation of glucose and catalysed by glucose oxidase, forming a gluconolactone, followed by a spontaneous transformation into gluconic acid or with an lactone hydrolysing enzyme, which decompose H₂O₂ into water and oxygen (Singh and Kumar, 2007). Some bacteria may also produce gluconic acid, such as *Gluconobacter oxydans*, *Zymomonas mobilis*, *Acetobacter methanolicus* or *Pseudomonas fluorescens* (Ramachandran et al., 2006; Singh and Kumar, 2007). Gluconic acid is then produced using another pathway with glucose oxidized by glucose deshydrogenase into gluconic acid (Ramachandran et al. 2006; Singh and Kumar, 2007).

Precursors of bioplastics such as PHB (Fig. 4 a-b) may also be produced from lignocellulosic residues using microorganisms. Indeed, PHB has been produced from steam exploded wood with *Pseudomonas cepacia* at 30 °C for 60 h (Ramsay et al., 1995), from the hydrolysate of dilute acid-pre-treated sugar maple wood chip with *Burkholderia capacia* at 30 °C, pH 7 over 96 h (Pan et al., 2012), or from the hydrolysate of pre-treated sugarcane bagasse using *Ralstonia eutropha* and *Cupriavidus necator* at 30 °C, pH 7,5 for 48 h (Yu and Stahl, 2008). Cyanobacteria and microalgae are also known to be able to produce biopolymers from carbohydrates (such as xylose or arabinose). This has been demonstrated with *Chlorella fusca* or with a consortium of cyanobacteria originating from wastewater. These strains produce PHB under nitrogen or phosphorus limitation (Cassuriaga et al., 2018; Rueda et al., 2020).

4.3.4. Anaerobic digestion

Anaerobic digestion can transform lignocellulosic residues such as food waste and agricultural waste into bioenergy and digestates using microorganisms at temperatures between 35 °C and 55 °C in anaerobic conditions. Anaerobic digestion is well established in the world with 20 000 biogas and biomethane plants in 2021 in Europe, corresponding to 5 % of natural biogas production (Sainz Arnau and Lelievre, 2021), and its use has increased due to its potential of 78 billion m³ for biomethane for Europe, compared to 20 billion m³ used in 2020, and to the high demand for renewable energy (Sainz Arnau and Lelievre, 2021; Scarlat et al., 2018).

Anaerobic digestion is composed of four steps: *i*) hydrolysis, where organic matter is hydrolysed into soluble monomers and oligomers by extracellular enzymes; *ii*) acidogenesis, where amino acids, sugars and fatty acids obtained during hydrolysis are converted into volatile fatty acids such as acetate; *iii*) acetogenesis where they are converted to acetate, carbon dioxide and hydrogen; and *iv*) methanisation where acetate, hydrogen and carbon dioxide are converted to methane (40–70 %) and carbon dioxide (30–60 %) (Cazier et al., 2015). The biogas needs to be purified to remove the carbon dioxide and have a purity up to 96 % of methane, in order to be injected in the gas grid by membrane filtration or pressure absorption into water. Another option is to transform the whole biogas into energy and heat using a combined heat and power engine, with an efficiency of up to 15–45 % maximum (Tian et al., 2021). The biogas can also be used directly locally. The digestate, corresponding to the solid and/or liquid residues at the end of the anaerobic digestion, can also be used as a source of nitrogen and phosphate to replace chemical fertilizers (Samoraj et al., 2022).

As an example, the estimated methane production for pig manure is 172–208 ml/g of volatile solid, 155 to 199 ml/g for cow manure and around 200 ml/g for grass (Cu et al., 2015b; Pham et al., 2013b). In anaerobic digestion of lignocellulosic biomass, the carbohydrates are the molecules transformed into biogas and the lignin content tends to be negatively correlated to methane potential (Cu et al., 2015b; Triolo et al., 2011). It is also possible for lignin to be transformed into biogas, however the time needed for the transformation is longer than 60 days and/or requires pre-treatment (Khan and Ahring, 2019; Motte et al., 2015). Food waste methane potential is difficult to evaluate due to the high variability of its composition depending on the country considered (Kobayashi et al., 2012).

5. Perspectives

Circular economy is an economic system that encourages efficiency in the use of resources. It is based on the 3R principles: Reduction, Reuse and Recycling of materials and energy; and is necessary to avoid depletion of finite resources (Sanguino et al., 2020). Since 2015, the idea of circular economy is used by policymakers in Europe, with the implementation of “Closing the Loop” and illustrated by its presence in research calls such as in “Horizon 2020” and “Horizon Europe” (Sanguino et al., 2020). Since 2018, the European Commission has also considered waste management and secondary raw materials in its initiatives, with a new waste legislative framework aimed at improving recycling and reuse of waste (Sanguino et al., 2020). The use of lignocellulosic waste as secondary raw material for production is a part of these schemes and its use is set to increase in the future, especially since it can also bring higher revenues to existing processes. However, the collection, transport and handling of industrial waste needs to be implemented at a greater level to improve the re-use of lignocellulosic residues (Sarsaiya et al., 2019).

One perspective for lignocellulosic biomass in a circular economy is the production of renewable energy. Indeed, renewable energy is in high demand due to the energy crisis and climate change. Agricultural and food waste are already used in anaerobic digestion to produce biogas, electricity and digestate as a fertilizer. Use of anaerobic digestion has increased, with 40 % more biomethane plants in 2021 compared to 2020

and its potential production is estimated at 1 000 TWh (30–40 % of the European Union gas consumption) by 2050 (Sainz Arnau and Lelievre, 2021). In France, only secondary raw materials (*i.e.* waste) are used for anaerobic digestion, with a maximum of 15 % weight per year of input, which may come from food or energy crops (Ministère de la transition énergétique, 2022), and France has the highest increase of biogas plants in 2021 compared to 2020 in the European Union (+91) (Sainz Arnau and Lelievre, 2021). Other renewable ways of producing energy are the production of ethanol and lipids, which are converted to bioethanol and biodiesel. Ethanol for fuel was the largest liquid biofuel per volume in 2019, produced from agricultural feedstock with easy access to sugars such as sugar cane or corn, and blended with gasoline (Liu et al., 2019). However, this production corresponds to first generation bioethanol and is in competition with food production. Pre-treatments are needed to improve the use of lignocellulosic waste for ethanol production, mostly in the use of corn stover, rice and wheat straw in second generation bioethanol. Indeed, the use of lignocellulosic residues for ethanol is still not economically competitive compared to production using sugar feedstocks or petroleum alternatives, with 45 USD per liter for second generation ethanol versus 0.6 USD per liter for conventional ethanol production (Liu et al., 2019; Mujtaba et al., 2023). One possibility to decrease bioethanol cost is to combine its production with other high value molecules such as lactic acid or xylitol, using genetically modified microorganisms such as *Saccharomyces cerevisiae* as proposed by Baptista et al (2021). However, this approach does not take into account the difficulty and the higher expense involved in separating the various compounds produced and the possible competition for substrates to produce the various molecules, which may decrease the global yield of the process.

Another possibility is the production of lipids from lignocellulosic waste. Lipids may also be further transformed into triglycerides for biodiesel production for ships, planes, trucks, buses or cars (Balcombe et al., 2019). Moreover, even if it is possible to have alternatives for electric or hybrid cars, it is more difficult to use electricity for buses, trucks and small ships, but not at all possible for large ships and planes due to current battery capacities, their cost and the required energy (Balcombe et al., 2019). Most of the ships using electricity are hybrid ferry ships with small capacity and regular routes and do not need a high number of batteries (Balcombe et al., 2019). Decarbonisation of marine fuels is necessary and biofuels such as biodiesel offer a good compromise in terms of cost, availability and technology readiness. Biodiesel is the most energy efficient alternative for marine fuel but still produces non-CO₂ greenhouse gases such as methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride (Law et al., 2021). Another problem is the cost, with a 90 % increase in overall cost using biodiesel compared to current fuels (Law et al., 2021). Biodiesel has the advantage of already having regulations for its use (ISO 8217: 2017 fuel standards), however it is only produced at a small scale and needs more research to be economically produced at an industrial scale (Law et al., 2021). Plane biofuel does not currently use lignocellulosic biomass and is mostly produced using hydrotreated vegetable oils and hydro-processed esters and fatty acids with an actual capacity of 2,4 Mtonnes/year, which is well below what is necessary (Prus et al., 2019). Lignocellulosic biomass needs to be transformed into synthetic paraffinic kerosene using the Fischer-Tropsch process, by gasification, catalytic polymerization and hydrogenation of CO into crude oil and then into biofuel (Ng, et al 2021). Like other biofuels, problems with possible use of lignocellulosic biomass for jet-fuel production are mostly due to the higher cost compared to traditional kerosene jet-fuel and is currently up to 8 times more expensive to produce (Ng et al., 2021).

Green chemistry is also part of a circular economy, with the bonus of limiting the use of chemicals, especially those that are derived from petroleum (Anastas and Warner, 2000). Lignocellulosic biomass may be used to produce high added-value molecules that can serve in green chemistry. For example, plastic pollution is a priority area for Europe (Sanguino et al., 2020), and the production of bioplastics is therefore a

necessity. Lignocellulosic biomass may be used to produce bioplastic precursors for PHA, PHB, PLA, bio-nylon or bioplastic film from cellulose acetate. However, not all plastics are replaceable by bio-based alternatives, due to differences in physical and chemical properties (high-water vapor and oxygen permeability, fragility, low thermal resistance, low mechanical properties, vulnerability to degradation, low processability), and production costs tend to be higher than for petroleum-based plastics, mainly due to bioprocessing and purification costs (Abe et al., 2021; Brodin et al., 2017; Jabeen et al., 2015; Mujtaba et al., 2023; Rosenboom et al., 2022). Moreover, not all bioplastics are biodegradable and may still be responsible for plastic pollution. One possibility is to concentrate research into biodegradable bioplastics such as PLA (Mujtaba et al., 2023) to limit future pollution.

Another example of high added-value molecules from lignocellulosic biomass is the production of molecules for biomedical use, such as polyphenols for cosmetics or the use of cellulose-based suspensions for 3D printing (Mujtaba et al., 2023). Indeed, one of the ways to limit cost production problems is to produce high added-value molecules, which is the case in the pharmaceutical domain and not so much in the biofuel or the bioplastic industries (Liguori and Faraco, 2016). In the case of lignin, potential high added-value products are chemicals such as vanillin, syringic acid, anti-oxidants or hydrogels and not biofuels, which are not currently economically viable (Garlapati et al., 2020).

One of the principles of green chemistry is replacing oil-based chemicals, including solvents, with biosourced products (Anastas and Warner, 2000). Many solvents in use today are partially or completely biobased: ethanol, dimethylether, acetate esters, 1,3-butanediol, propylene glycol or furfural. With improvements in biorefinery processes, solvents produced from lignocellulosic waste could replace solvents from first-generation feedstocks (e.g. grain alcohol). In addition to biobased solvents, green chemistry encourages use of safer and biodegradable solvents. Recently, natural deep eutectic solvents (NaDES) emerged as a new class of green solvents (El Achkar et al., 2021). In NaDES, natural metabolites (sugars, organic acids, polyols, choline) form complexes through hydrogen bonding, which makes them liquid at room temperature (El Achkar et al., 2021). Different combinations of hydrogen bond donors and acceptors give rise to NaDES with different chemical properties. In recent years, numerous applications have been described, including extraction of polyphenols (Ali Redha, 2021) or use of NaDES in lignocellulosic biomass pretreatment (Satlewal et al., 2018). Many potential NaDES precursors, such as organic acids, sugars, and polyols could be sourced from lignocellulosic waste, to provide truly sustainable green solvents.

6. Conclusions

In conclusion, a large quantity of lignocellulosic residues is produced in Europe and may be further used for valorisation and production of high-value compounds. However, their variable compositions, often mixed with other molecules, increases the difficulty for further use. Wood, paper and agricultural waste are the easiest to use, due to their high quantity and considering that they tend to be less mixed with other molecules. Another possibility is to use biological treatments such as microorganisms, which may be more able to adapt to changing/non-standardized or complex compositions. All of the possible molecules produced from lignocellulosic biomass bring multiple possibilities for the future use of lignocellulosic biomass in circular economy models. The future of lignocellulosic biomass use would be mostly in the energy and green chemistry sectors. However, larger-scale commercial use will only happen if the processes are cost effective and comparable to existing or competitive products. This is not currently the case for example for biofuels, bioplastics or bioethanol production. Industrial lignocellulosic residues represent interesting option from the point of view of a circular bioeconomy, for an integral biorefinery concept and will become increasingly necessary due to new challenges such as climate change and decreases in natural resources. Therefore, an

economic shift is necessary to make the various currently available transformation processes economically viable, notably requiring a decrease in production costs compared to current petroleum transformation processes.

CRedit authorship contribution statement

Elisabeth A. Cazier: Writing – review & editing, Writing – original draft, Investigation. **Thanh-Nhat Pham:** Writing – original draft, Writing – review & editing. **Louis Cossus:** Writing – review & editing. **Maher Abla:** Writing – review & editing. **Tina Ilc:** Writing – review & editing. **Philip Lawrence:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Cazier Elisabeth A. reports financial support was provided by MANE compagny. Pham Thanh-Nhat reports financial support was provided by MANE Compagny. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper].

Data availability

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