

3 Environmental impact and industrial development of the biorenewable resources for
4 the polyurethanes

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9 ABSTRACT: Polyurethanes are one of the most developing branches of the polymers.
10 They consist of the two primary sources, such as the polyols and the diisocyanates.
11 So far, both of the main substrates have been obtained through the petrochemical
12 processes. The reduction of the petroleum based resources and ecological trend in
13 the chemistry, chemical technology, and materials engineering have generated the
14 increasing interest in the utilization of biorenewables in polymer syntheses. This paper
15 aims at giving comments of the environmental impact of the petrochemical-based
16 component replacement by the bio-based chemicals in the polyurethane synthesis.

17 KEYWORDS: Biopolymers; Bio-based Polyurethane; Bioresources; Environmental
18 impact;

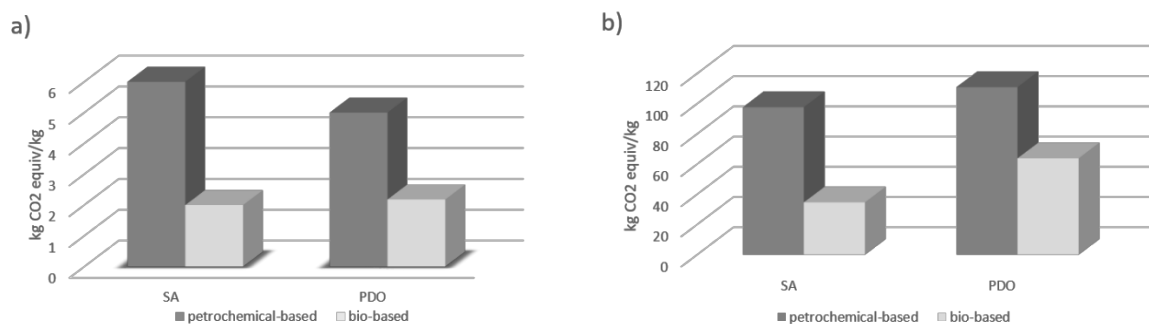
19 1. INTRODUCTION

20 Polyurethane industry is one of the most intensively developing fields in the plastic
21 industry. Nowadays, polyurethane materials play an important role in various primary
22 areas of life, beginning from furniture, clothes and food packaging, through
23 motorization to health care [1]. Since 2000 the world consumption of polyurethanes
24 has been constantly growing. In 2004 polyurethanes represented 5 % of the worldwide

23 polymer consumption [2]. Currently, they constitute 7,5 % (in 2015), what puts them
24 at the forefront of the most consumed polymers [3].

25 Due to the growing ecological trend in chemistry, in the last decades, great effort
26 has been devoted to the study of the possibility to utilize biorenewable resources in
27 the polymer industry [4–7]. It is also seen in the field of polyurethanes (PUR) which
28 today make it possible to substitute, partly or entirely, petrochemical resources by the
29 materials of natural origin, mainly in the field of the polyol synthesis. Besides the
30 ecological advantages, the substitution of the component allows for the economic
31 volatility reduction by the decrease in the fossil fuel stocks utilization and consequently
32 the economic stability improving for the countries without access to the fossil fuels [8].
33 Moreover, the bio-based component synthesis enables the decrease in the production
34 costs with increasing production scale.

35 The environmental advantages of the bioresources utilization represent the
36 reduction of energy consumption during production, the greenhouse gases emission
37 reduction, CO₂ emission reduction [9] and, in the term of polyesters, the
38 biodegradability improvement [4, 7]. Figure 1 presents the comparison between bio-
39 based and petrochemical-based components impact on the energy consumption
40 (Figure 1a) and greenhouse gas emission (Figure 1b) in the example of the two
41 primary components in the polyurethane polyester polyols synthesis – succinic acid
42 and 1,3-propanediol. The degree of all of the presented advantages depends on the
43 bioresources type and production method. In the certain cases, the biotechnological
44 method of the chemical synthesis for polyurethanes allows for component obtainment
45 with higher purity level than the petrochemical counterpart.



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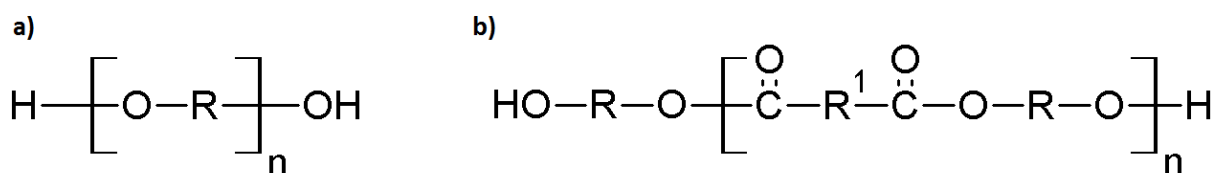
47 Figure 1 Impact of the bio-based components on the a) energy consumption and b)
 48 greenhouse gas emission in the example of petrochemical- and bio-based succinic
 49 acid (SA) and 1,3-propanediol (PDO).

50 The main objective of this paper is to review the literature on the components for
 51 the polyurethane production from the renewable resources. The impact of the
 52 biorenewables industrial usage on the environment was compared with the commonly
 53 used petrochemical sources. The advantages of the bio-resources usage in the
 54 polyols synthesis are also presented. The resulting benefits were confirmed by
 55 comparing properties of the polyols from the renewable resources and the
 56 petrochemicals. Moreover, the text includes the comparison between polyurethane
 57 materials based on petrochemical and bio-based components. The article also
 58 introduces perspectives for the polyurethane industry in the field of sustainability.

59 2. COMPARISON BETWEEN PETROCHEMICAL-BASED AND BIO-BASED 60 COMPONENTS FOR POLYURETHANES

61 Polyols constitute one of the two main components for polyurethane synthesis [2].
 62 They can be grouped by a functional group which occurs in the macromolecular chain
 63 as polyether [10, 11], polyester [12] and polyether-ester polyols [13]. Polyols are
 64 usually liquid, reactive substances mostly terminated by the hydroxyl or partially amine
 65 groups [14]. These groups are responsible for the reaction with isocyanates [15]. The

66 polyether polyols are characterized by the following general repeating unit and the
 67 molecular weight in the range from 2000 to 6500 g/mol (for elastic polyurethanes)
 68 (Figure 2a). They constitute ca. 80 % of the polyols globally used in the polyurethane
 69 synthesis [2]. The polyester polyols are characterized by lower molecular weight, in
 70 the range from 1000 to 4000 g/mol (for elastic polyurethanes) (Figure 2b) [2, 15]. They
 71 represent the second most important group with around 18 % of the polyols global
 72 usage. Both general formulae of the polyols mentioned above is given in Figure 2 a
 73 and b.

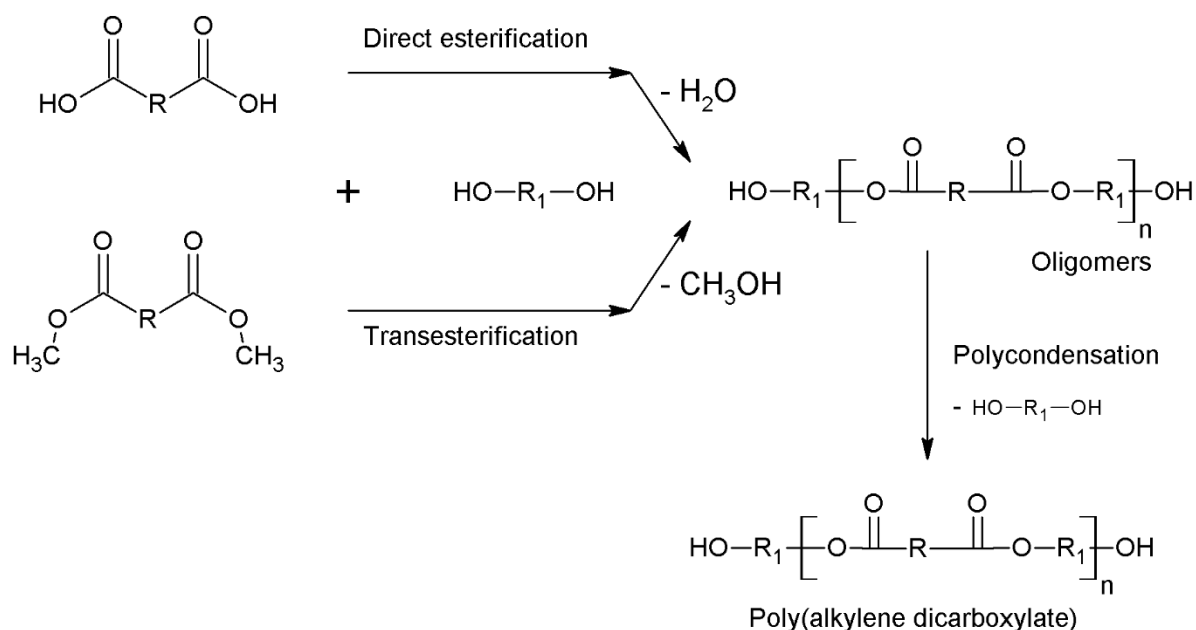


74
 75 Figure 2 General formula of the a) polyether polyols and b) polyester polyols.

76 The polyester polyols constitute the main group of polyols, which gives the
 77 greatest possibilities for obtaining the biorenewable PUR materials due to the ester
 78 bonding which undergoes hydrolysis. Currently, the bio-components are readily
 79 accessible, which allow producing polyester polyols in 100 % consisting from bio-
 80 resources [6].

81 The primary reaction of the polyester polyols obtaining is the polycondensation
 82 reaction between the carboxylic acid or carboxylic acid ester and the excess of the
 83 dihydroxyl alcohol [2, 14, 16] (Figure 3). This reaction can be divided into esterification
 84 reaction, namely, the direct esterification and the transesterification reaction, when the
 85 carboxylic acids or the carboxylic acid esters are used, respectively [17]. During
 86 reactions, beyond the polyester polyols, the by-products are produced. These by-
 87 products constitute water or alcohols, which hinders the polycondensation process

88 towards the polyester polyols. To shift the reaction towards the main product, water
 89 and alcohols must be eliminated from the reaction system [2, 17–19].



90

91 Figure 3 Scheme of the polycondensation reaction.

92 Polyols with another functional group in the macromolecular chain can be
 93 synthesized via different kinds of chemical modification. The most developed reaction
 94 which leads to the polyether polyols is the ring-opening polymerization [20–22]. This
 95 method makes possible of using milder polymerization conditions, furthermore, the
 96 side-products are not generated in the ring-opening polymerization reaction [23].
 97 Copolymerization is the reaction with the use of which the polyether-ester polyols can
 98 be obtained [24, 25].

99 The polyurethanes obtained with the use of polyester polyols are less resistant
 100 to hydrolysis compared to the polyether polyols. However, it makes them more
 101 favorable due to the biodegradability [18, 26, 27]. Due to this, polyurethane materials
 102 produced based on polyester polyols can be submitted for different kinds of recycling
 103 processes. Through the secondary forces between polyester chains, they have more

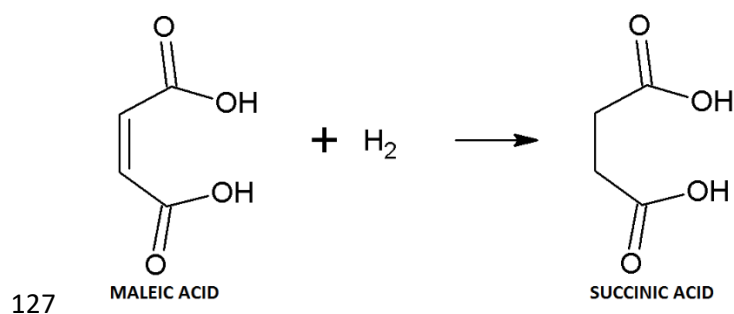
104 crystalline structure [2, 15]. Polyurethanes based on the polyester polyols have better
105 thermal and fire resistance than the polyether-based PUR and superior solvent
106 resistance [2, 15]. The polyether-ester polyols characterized by the hybrid of the
107 polyester and polyether polyols properties [13, 28]. Due by the ester bonding in the
108 molecular chain, the polyurethanes based on this kind of polyols undergoes
109 biodegradation, when the ether bonding increased the mechanical resilience of the
110 polyurethane materials.

111 Although the polyether polyols constitute the greatest part of the polyols total
112 worldwide production, the polyester polyols have a stable position in the polyurethane
113 market [2, 29]. Due to the properties resulting from the process of obtaining
114 polyurethanes based on the polyester polyols, they have many practical applications.
115 The greatest value in this product global consumption is generated by the
116 polyurethane elastomers (ca. 43 %), flexible foams (ca. 15-18 %), coating, adhesives,
117 etc. [2].

118 2.1. Succinic acid (SA) as one of the most prospective components for bio-based
119 polyols.

120 One of the most important bio-components in the bio-based polyol synthesis is the
121 succinic acid (SA) [5–9, 12, 30–33], which so far has been obtained by the catalytic
122 hydrogenation of the petrochemical compound as a maleic anhydride [34] or maleic
123 acid [34, 35]. This production method was allowed to utilize 15 000 tons C4-fraction of
124 the naphtha per year at the price from 5.90 \$/kg to 8.80 \$/kg [36, 37]. Figure 4
125 illustrates the reaction between maleic acid and hydrogen leading to the SA creation
126 [35].



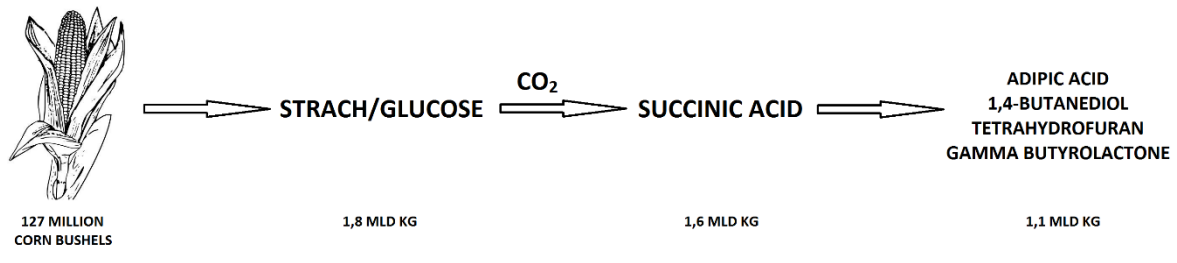


128 Figure 4 Scheme of the reaction between maleic acid and hydrogen leading to the
129 succinic acid.

130 Succinic acid is a C₄ building-block chemical compound which recently has also
131 been obtained by the corn fermentation [38, 39]. This biotechnological process makes
132 it possible to produce bio-succinic acid production in the range from 5 000 tons per
133 year at the price of 2.20 \$/kg, to 75 000 tons per year at 0.55 \$/kg [37]. The
134 fermentation method proves economic advantages of the bio-succinic acid utilization
135 due to the reduction of production costs coupled with the increasing production scale.

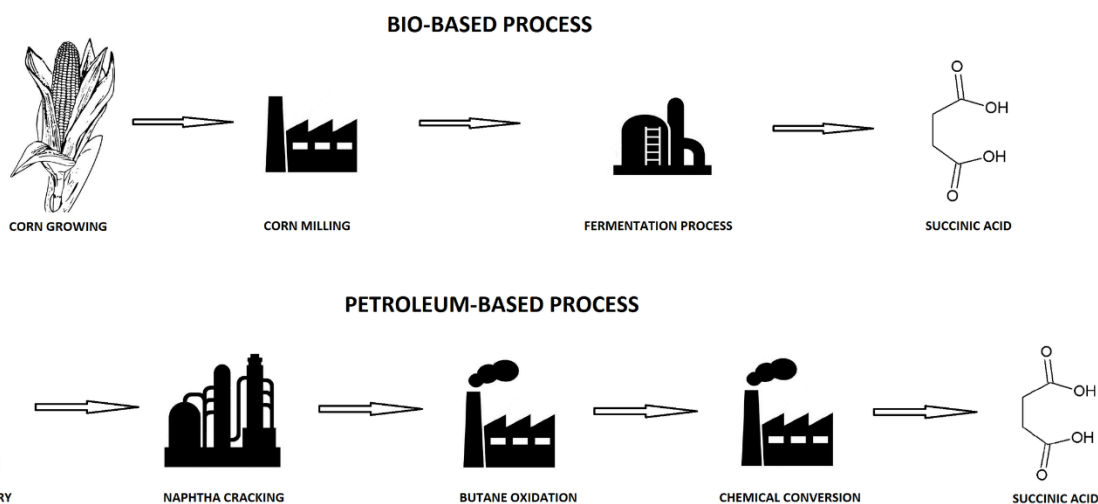
136 Figure 5 shows how to obtain the succinic acid with the use of fermentation
137 method. This method consists of the corn fermentation of a large group of
138 microorganisms such as fungi, yeasts [40] or Gram-positive bacteria [36]. The first
139 identified and the most studied succinic acid over-producers were the
140 *Anaerobiospirillum succiniciproducens* [41–45] and the *Actinobacillus succinogenes*
141 [46–51]. They allowed to the succinic acid obtaining in the large scale [36]. Then, more
142 attention was paid to the bacterium called *Mannheimia succiniciproducens* MBEL55E
143 [52–55], due to its natural isolation from the bovine rumen [56]. Currently, the most
144 important and applicable are the *Escherichia coli* bacteria [57–64]. Nevertheless, due
145 to the economic disadvantages such as the high costs of this method, scientists in the
146 field of bio-industries work upon other microorganisms applications [34]. The
147 Mitsubishi Chemicals use the *Coryne*-type bacteria for the succinic acid production

148 [65, 66]. The tests proved that using Coryne-type bacteria leads to significantly higher
 149 succinic acid productivity compared to Escherichia coli bacteria [34].



151 Figure 5 Steps of the corn fermentation process and opportunities to the resulting
 152 products utilization.

153 The succinic acid, based on the biomass fermentation using various types of
 154 bacteria or yeasts, is commercially available on a large-scale from such companies as
 155 BioAmber [67], BASF/Purac [68], Myriant [69] and Reverdia [70]. The BioAmber
 156 company produces the bio-based succinic acid accordingly to the bio-based process
 157 illustrated in Figure 6. In order to obtain the homogenous consistency of corn, it is
 158 milled before fermentation. Then the bacteria or yeasts are added in order to initiate
 159 the fermentation process. When the process has finished the product is purified. This
 160 method allows obtaining the bio-based succinic acid with the purification level of even
 161 99,5 % [34].



162

163 Figure 6 Scheme of the bio-based process and the petroleum-based process of the
 164 succinic acid obtaining.

165 Figure 6 shows differences between the bio-based and petrochemical-based
 166 succinic acid preparations [37, 67]. It is clear that the biotechnological process of the
 167 SA production reduces the manufacturing stages in comparison to the petrochemical
 168 process. Moreover, each step in the petroleum-based SA production requires more
 169 energy than steps of the fermentation process. The reduction of the SA utilization from
 170 the petrochemicals can result in even 60 % energy consumption reduction [67]. The
 171 examples corroborate the economic advantages. Each of the petrochemical process
 172 stages produces the greenhouse gases in large amounts. The reduction of the
 173 petrochemical SA utilization and the increase of the bio-based SA usage can lead to
 174 even a 100 % greenhouse gases reduction in terms of ecologically friendly
 175 requirements [67].

176 The reduction of the petrochemical sources utilization and growing interest in the
 177 bio-component usage leads to the economic volatility reduction [8]. The bio-based
 178 component usage generates alternative sources for polymer syntheses. The
 179 decreasing trend in the petroleum-based sources consumption was determined by the

180 fossil fuel stocks depletion. Moreover, the increasing possibilities of the plant product
181 usage or non-food residue utilization from the food industry allow improving the
182 economic stability of the countries without access to the fossil fuels [71].

183 2.2. Bio-based 1,3-propanediol (Bio-based PDO) – bio-based glycol precursor.

184 At the end of the 20th century, the three independent methods to the 1,3-
185 propanediol production were developed. Two of them refer to the petrochemical-based
186 PDO and the last one pertains the bio-based PDO [72]. The first of the above-
187 mentioned method represents the two steps process connected with the acrolein
188 conversion. The second 1,3-propanediol production mode is connected with the two
189 step reaction where the propylene oxide constitutes the main substrate. The bio-based
190 PDO obtaining process consists of the glucose fermentation. All of the methods are
191 currently used commercially in the industry. Table 1 summarizes the 1,3-propanediol
192 production methods.

193

194

195 Table 1 Differences between the 1,3-propanediol industrial production methods.

1,3-PDO PRODUCTION METHOD	REACTION SCHEME
Petrochemical based PDO	
Acrolein based process	$\text{H}_2\text{C}=\text{CH}-\text{CHO} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{HO}-\text{CH}_2-\text{CH}_2-\text{CHO} \xrightarrow{\text{H}_2} \text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
Hydrocarbonylation of ethylene oxide	$\text{C}_2\text{H}_4\text{O} \xrightarrow{\text{H}_2, \text{CO}} \text{HO}-\text{CH}_2-\text{CH}_2-\text{CHO} \xrightarrow{\text{H}_2} \text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
Bio-based PDO	
Glucose fermentation	$\text{GLUCOSE} \longrightarrow \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH} \longrightarrow \text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$

196

197 The acrolein based 1,3-propanediol production process constitutes the two step
 198 reaction. The first step of this method is formed by the acrolein hydration reaction
 199 which leads to 3-hydroxypropanal obtaining. The temperature at 100 °C and active
 200 catalyst are necessary for this reaction. Under optimal conditions, the reaction allows
 201 obtaining the semi-product even in 85-90 % of the overall yield [73, 74]. The ion
 202 exchange hydration catalyst which is polyamine/polycarboxylic acid resins formed the
 203 usually used catalyst for this step [75]. After the removal of unreacted acrolein from
 204 the first step reaction mixture, the main semi-product - 3-hydroxypropanal, is
 205 hydrogenated [73, 76]. For this reaction, the catalyst is also necessary. The active
 206 group metals catalysts constitute the primarily used catalysts in the second step. This
 207 group represents such catalysts as Raney nickel, platinum, ruthenium catalysts or
 208 metal oxides such as titanium oxide or aluminum oxide [77, 78]. In the laboratory
 209 conditions, these steps allow obtaining 1,3-propanediol with almost 100 % yield [72].

210 The ethylene oxide based PDO production method depends on a two-step
211 process. The first step is the hydrocarbonylation reaction which leads to the 3-
212 hydroxypropanal as a semi-product. The selective and very active catalyst is
213 necessary for this reaction. The various rhodium system catalysts modified
214 phosphines or a number of acids constitute the most used catalysts in the industry.
215 The second step is similar to the second step of the above-mentioned method based
216 on the acrolein. The Eastman Chemical Company [79] developed the 1,3-propanediol
217 production process in one step reaction. To obtain the PDO through the ethylene
218 oxide, the mixed phosphine-modified rhodium/ruthenium catalyst was used [80].
219 Although the process yields up to 90 %, the poor activity of the catalyst makes it
220 prolonged [72].

221 The bio-based 1,3-propanediol production process is related to the glucose
222 fermentation process. In 1990 the DuPont Company developed the two step
223 production method. Glucose, obtained from industrial starch, undergoes in the next
224 step the fermentation process using patented biocatalyst. Sugar is converted to
225 glycerol by yeast (*Saccharomyces cerevisiae*). Subsequently, the obtained glycerol
226 are submitted to bacterium activity. *Klebsiella* (*pneumonia* and *oxytoca*) [81], *Clostridia*
227 (*butyricum* [82] and *pasteurianum*), *Enterobacter agglomerans*, *Citrobacter freundii*
228 [83] and *Lactobacilli* (*brevis* or *buchneri*) [81] are bacteria the most common used to
229 produce 1,3-PDO. These microorganisms allow for the industrial production of PDO
230 with the 99,97 % purity [84–86].

231 The bio-based PDO Life Cycle analysis allows confirming the greenhouse gases
232 emission reduction by more than 50 % in comparison to the petroleum-based 1,3-
233 propanediol. Moreover, the bio-based process leads to the reduction of energy
234 consumption by more than 40 % compared to the petrochemical process [84].

235 Miller, Janssen, and Theunissen [6] investigated the properties of the bio-polyol,
 236 for the thermoplastic polyurethanes application, with 100 % bio-carbon content. The
 237 researchers used bio-based 1,3-propanediol (Susterra, DuPont) [86] and bio-based
 238 succinic acid (Biosuccinium, Reverdia) [87]. The thermoplastic polyurethanes were
 239 prepared by the prepolymer method with hard segment concentration ca. 20-30 %.
 240 For comparison, the polyurethanes based on petrochemical 1,4-butanediol (Alfa
 241 Aestar) were prepared. The received bio-based thermoplastic polyurethanes
 242 accomplished nearly 70 % renewable carbon content. Table 2 shows selective
 243 properties of the obtained bio-polyols.

244 Table 2 Selective properties of the bio-polyols obtained with the use of bio-based
 245 succinic acid, bio-based 1,3-propanediol, and petrochemical 1,4-butanediol.

PROPERTIES	BIO-POLYOLS	
	PDO-SA	BDO-SA
RENEWABLE CARBON CONTENT [%]	100	~50
Acid value [mg KOH/g]	1.16	1.92
Hydroxyl value [mg KOH/g]	57	59.7
Viscosity [cPs]:		
- 50.0 °C	4601	Solid
- 70.0 °C	1360	Solid
Average Mw [g/mol]	1968	1879

246
 247 Comparison between the two polyols mentioned above shows that there were no
 248 significant differences between the hydroxyl value, but, on the other hand, PDO-SA

249 polyol revealed less acid value. Moreover, BDO-SA polyol discloses higher viscosity
 250 than PDO-SA, which leads to the difficulties in the industrial processes due to the
 251 requirement of higher temperature [6].

252 Based on the obtained polyols the thermoplastic polyurethanes were prepared.
 253 The bio-based 1,3-propanediol and petrochemical 1,4-butanediol, which were used in
 254 the polyols preparation, were also used as extenders. Table 3 shows selective
 255 properties of the obtained bio-based thermoplastic polyurethanes.

256 Table 3 Selective properties of the bio-based thermoplastic polyurethanes.

PROPERTIES	BIO-BASED THERMOPLASTIC POLYURETHANES		
	PDO-SA-PDO	PDO-SA-BDO	BDO-SA-BDO
Renewable carbon content [%]	~ (63 – 70)	~ 60	~ 30
Hard segment [%]	22	23	24
Density [g/cm ³]	1.29	-	1.20
Hardness [°Sh A]	64	67.1	
[°Sh D]			55
Tensile strength [MPa]	18.55	4.25	37.38
Elongation at break [%]	831	655.94	671
Resilience [%]	10	25.56	15

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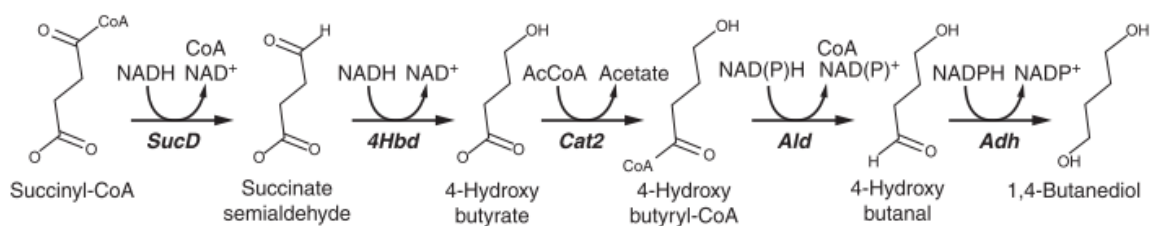
258 As can be seen from Table 3, with the similar hard segment content in all of the
259 bio-thermoplastic polyurethanes, hardness increases with the growth of the chain
260 length. The thermoplastic polyurethane with the 1,4-butanediol based polyol and 1,4-
261 butanediol as the extender reveal the highest value of the tensile strength. In the case
262 of elongation at the break the highest value discloses the material with the highest bio-
263 based carbon content (PDO-SA-PDO). Furthermore, the same material discloses the
264 lowest resilience, where the 1,4-butanediol usage as the extender, makes it the
265 material with the highest resilience value.

266 The tests results mentioned above show that depending on the material desired
267 application, the 1,3-propanediol based thermoplastic polyurethanes can be
268 successfully used.

269 2.3. Bio-based 1,4-butanediol (Bio-based BDO).

270 Other important bio-based component for the polyester polyols obtainment
271 constitutes the 1,4-butanediol (BDO). Nowadays, such huge chemical companies as
272 BASF [88] and DuPont [85], produce the bio-based 1,4-butanediol (bio-BDO) using
273 the fermentation process developed by Genomatica [89, 90]. The process technology
274 for the renewable BDO production includes the single-step fermentation based on the
275 dextrose, glucose, sucrose and biomass sugars as renewables. This production
276 process allows to produce the bio-BDO with 100 % bio-based carbon content, using
277 specialty micro-organisms - the genetically-modified Escherichia Coli bacteria [89, 91–
278 95]. Figure 7 illustrates the biosynthesis pathway for the BDO [94].





279

280 Figure 7 Biosynthesis of the 1,4-butanediol.

281 Some smaller companies like BioAmber [67] or Myriant [69] produced their bio-

282 based BDO by means of the bio-based succinic acid converting through the single

283 catalytic step [96–98]. Minh at al. [96] investigated the catalytic converting of the

284 succinic acid in 1,4-butanediol using the modified Pd and Ru catalysts with the variable

285 amounts of Re. The researcher investigated that the yield and selectivity were in the

286 range from 62 to 66 %. The converting reaction was carried out at the temperature of

287 160 °C and the pressure of 150 bars. Kang et al. [97, 98] also studied the bimetallic

288 catalysts as catalysts for the succinic acid conversion to BDO. They investigated the

289 Re–Ru bimetallic catalysts supported on the mesoporous carbon and the mesoporous

290 rhenium–copper–carbon composite catalysts. All the reactions needed high

291 temperature and pressure, which indicates that the specific conditions are needed for

292 the succinic acid conversion. Table 4 illustrates two methods of the bio-based 1,4-

293 butanediol production.

294

295

296 Table 4 Differences between two methods of the bio-based BDO production.

METHOD	PROFILE
Single step method	Obtaining of the bio-BDO from corn milling product with the use of specialty micro-organisms - the genetically-modified Escherichia Coli bacteria
Double step method	First step: obtaining of the bio-based succinic acid from corn milling product with the use of specialty micro-organisms; Second step: bio-based succinic acid converting in single catalytic step to bio-BDO

297

298 Currently used petrochemical-based BDO was obtained from the fossil fuel stocks.

299 There are many methods which leads to the petro-based 1,4-butanediol. The most
 300 important method for the BDO production since the last 20th century has been the
 301 hydrogenation process [72]. This method is based on the liquid phase hydrogenation
 302 of maleic anhydride [99] and leads to 1,4-butanediol [100].

303 The opportunity to obtain BDO is also given by the butynediol hydrogenation.
304 Nevertheless, this method needs the palladium or nickel catalyst to finalize the
305 reaction. Butynediol was obtained using the formaldehyde ethynylation process
306 (Reppe process) [101–103].

307 Mitsubishi Chemicals developed the petrochemical route to the BDO obtaining
308 based on the butadiene acetoxylation process [72, 104]. The acetic acid and the 1,3-
309 butadiene connection, obtained with the use of palladium/tellurium catalyst, leads to
310 the 1,4-diacetoxy-2-butene. This reaction product, in the next step, was hydrogenated
311 and hydrolyzed to the 1,4-butanediol [72].

312 The BDO production is also possible with the use of butane. The butane oxidation
313 reaction leads to the maleic anhydride with the use of vanadyl pyrophosphate
314 ($(VO)_2P_2O_7$), as the catalyst. When the maleic anhydride is obtained, the
315 hydrogenation process leads to the 1,4-butanediol forming [72].

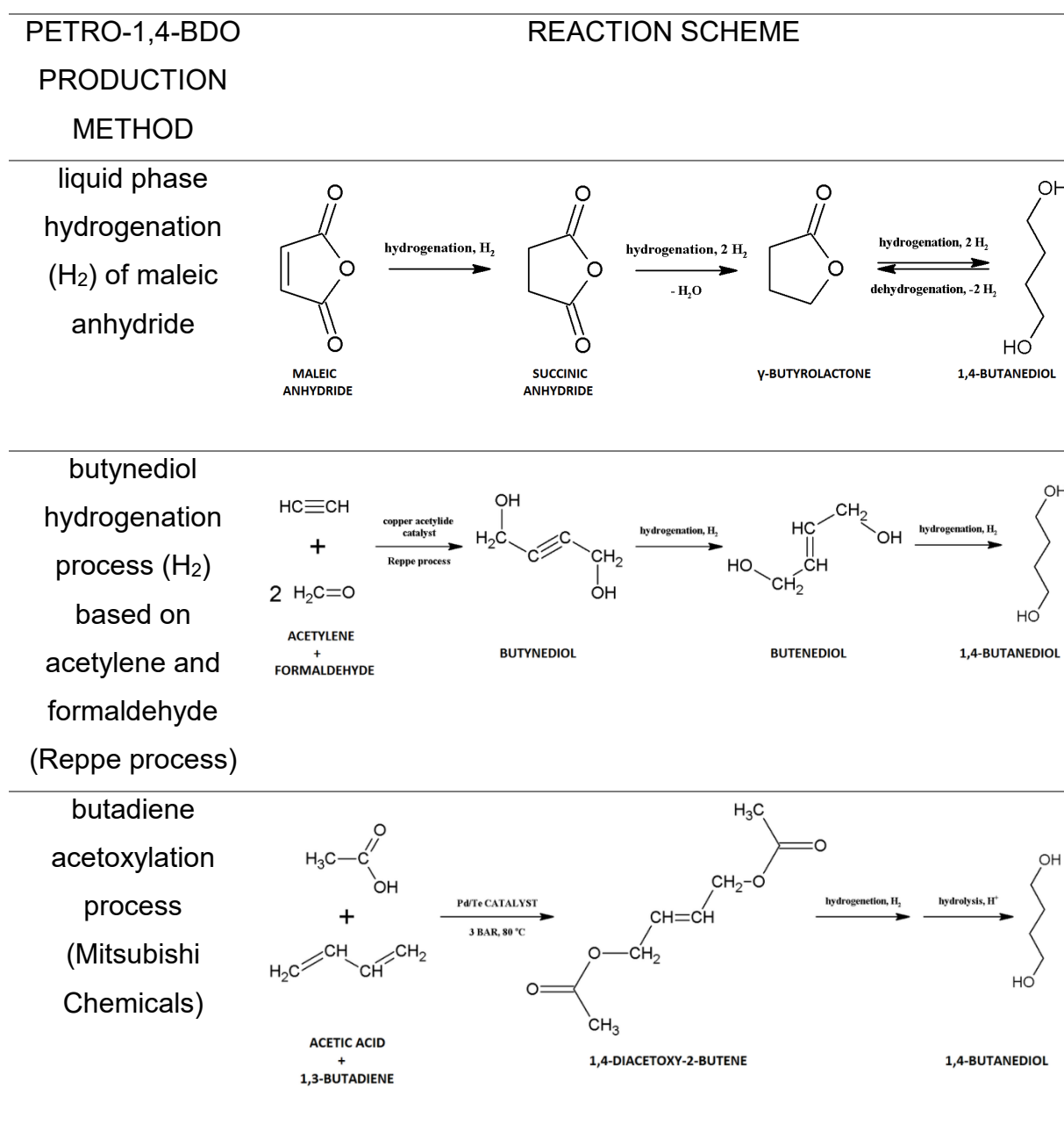
316 Eastman Chemical Company developed the commercial method for BDO
317 production based on the butadiene epoxidation process. The butadiene epoxidation
318 reaction leads to the 3,4-epoxy-1-butene using silver as a catalyst. In the next step,
319 the product is hydrated and hydrogenated with the use of special catalysts, the mixture
320 of a hydriodic acid and organic soluble iodine salts and a precious metal catalyst,
321 respectively [72, 105, 106].

322 The LyondellBassell Company developed another, commercially used, a method
323 for the BDO production [107]. This method is based on the hydroformylation process
324 of the allyl alcohol via the hydroformylation technology licensed by the Kuraray
325 Company [108]. In the first step, the propylene oxide is isomerized to the allyl alcohol
326 by the lithium phosphate (Li_3PO_4) as the catalyst. The received product is

327 subsequently hydroformylated by the rhodium catalyst in the triphenylphosphine and
 328 1,4- diphenylphosphinobutane presence [72].

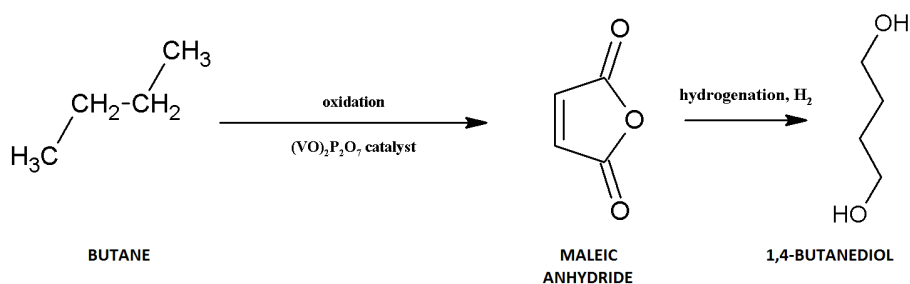
329 Table 5 illustrates the differences between the BDO production methods
 330 mentioned above.

331 Table 5 Differences between the petrochemical-based BDO production methods.



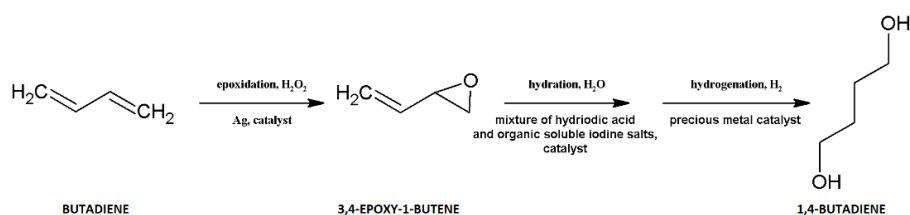
butane oxidation

(O₂) process



butadiene
epoxidation

process
(Eastman
Chemical
Company)



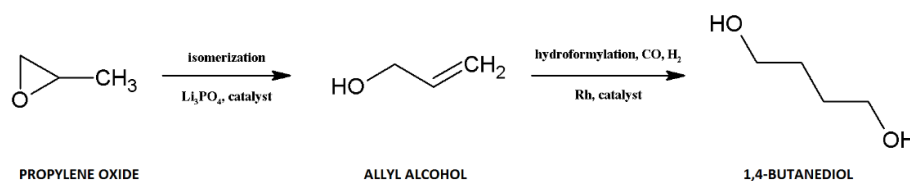
allyl alcohol

hydroformylation

(CO + H₂)

process

(LyondellBassell
Company)



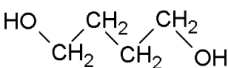
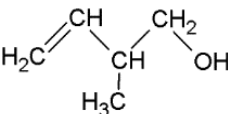
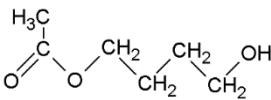
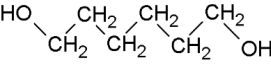
332

333 The comparison between the bio-based and petrochemical-based 1,4-butanediol
334 production methods allowed to verify a number of advantages for the biotechnological
335 method. First of all, the usage of the dextrose in the bio-based production method led
336 to the 67% lower fossil energy usage and with up to 83% lower total CO₂-equivalent
337 emissions/kg BDO [92, 94]. Relative to the petrochemical BDO production methods,
338 where there exist many steps of the synthesis, the bio-based process decreases the
339 amount of the steps. Moreover, biotechnological processes allow to reduce the
340 catalyst demand and consequently decrease the difficulties in the catalyst recycling
341 and reusing. Petrochemical processes generate the big amounts of chemical waste,
342 which in the next step, must be submitted to reprocessing. The bio-based process

343 allows to reduce the amount of hazardous waste and makes it possible to submit them
 344 for the another application.

345 One of the most important companies which used bio-BDO on the huge scale is
 346 the DSM company [109]. The DSM developed the high-performance thermoplastic
 347 copolyester elastomer (Arnitel) production with the high bio-based carbon content. The
 348 differences between the bio-based and the petrochemical-based 1,4-butanediol were
 349 analyzed by DSM scientists [110]. Table 6 illustrates the results of the tests.

350 Table 6 Purity differences between bio-based BDO and petrochemical-based BDO
 351 [110].

COMPOUND	STRUCTURE	QUANTITY [%]	
		Bio-based 1,4-BDO	Petrochemical- based 1,4-BDO
1,4-butanediol		99.95	99.85
2-methyl-3-buten-1-ol		-	0.10
1,4-butanediol, monoacetate		< 0.01	-
1,6-hexanediol		-	0.04
others		< 0.05	< 0.02

352
 353 The test results proved the occurrence of differences between the bio-based and
 354 petrochemical 1,4-BDO. The biotechnological process of the 1,4-BDO production
 355 allows for more pure product obtainment. This fact leads to the reduction of the

356 purification process. The smaller number of process steps leads to the costs cutting
 357 due to the reduction of the energy utilization. Moreover, it makes it possible to
 358 decrease the waste formation.

359 The scientists from the DSM company analyzed the properties of one of the
 360 products obtained with the use of two kinds of BDO. The results of the comparison
 361 between the poly(butadiene terephthalate) PBT with the bio-based carbon content and
 362 its lack of the product, are shown in Table 7.

363 Table 7 Comparison between the poly(butadiene terephthalate) obtained with the use
 364 of two kinds of the 1,4-butanediol.

Properties	PBT based on:	
	Bio-based BDO	Petro-based BDO
Polycondensation time [min]	129	128
COOH end group content [meq/kg]	12.9	13.1
Relative viscosity in m-cresol	1.87	1.87
DSC analysis		
Glass transition temperature T_g [°C]	45	44
Crystallization temperature during cooling T_c [°C]	180	180
Crystalline melting point T_m [°C]	224	224

365 As follows from the table, the comparison between PBT obtained with the use of
366 two kinds of BDO reveals no significant differences. Each of the investigated
367 properties discloses similarity in the results. The polycondensation time, relative
368 viscosity in m-cresol, such DSC results as crystallization temperature during cooling
369 and crystalline melting point, appear to have the same value. Only with respect to
370 COOH end group content and glass transition temperature, both materials reveal the
371 minor differences.

372 2.4. Vegetable oil-based polyols.

373 The food industry also offers the huge amount of waste which can be utilized in the
374 polymer synthesis. Due to the growing interest in the utilization of excess quantity and
375 wastes from vegetable oils processing from food industry its usage in the polymer
376 industry became the subject matter of a large amount of researchers. The vegetable
377 oils turned out the excellent and very heterogeneous renewable raw materials for
378 polyurethanes. A variety of new structures in polyols depending on the method of
379 synthesis, resulting in polyurethanes with new properties, suitable for a range of
380 applications such as lubricants, soap - now largely replaced by synthetic detergents,
381 paints, and plasticizers. Attractive properties related to the specific structure of oils
382 e.g. conjugated double bonds, which tend to easily polymerize when exposed to air,
383 high purity, relatively high molecular weight, possibility to genetically engineering
384 enforced their prospective utilization in the chemical industry. Moreover, they are freely
385 available, cheap, non-hazardous and biodegradable [111]. Year by year, the increase
386 in the use of vegetable oil-based polyols can be expected in the polyurethane field.

387 A lot of scientists investigate the possibility to utilize the vegetable oil in the field of
388 polymers [112–115]. Polyols based on the oils are characterized by a wide range of

389 the molecular weight of the oligomers and usually substantial branching degree [116]
390 what makes them suitable for the polyurethane foams industry. Non-food oil
391 derivatives such as soybean oil [117–124], rapeseed oil [125, 126], palm kernel oil
392 [127, 128], cottonseed oil [111, 129], castor oil [130–132] and many others are
393 investigated on a large scale by scientists in the field of polymers. Wise prices and
394 freely availability of soybean oil, palm oil, and rapeseed oil are the most attractive for
395 large-scale industrial products. The results of the many types of research
396 demonstrated that the vegetable oil polyols must be used in conjunction with
397 petrochemical polyols in flexible foams, but they could be used as sole polyols in other
398 applications. For the higher utilization in the polyurethane materials, natural oils have
399 to be chemically modified due to the incompatibility in the polyurethane system [133].
400 This incompatibility results in a heterogeneous structure, physical instability, phase
401 separation and in the sequel – poor properties [134].

402 One of the most popular vegetable oil in the plastics industry is soybean oil. It is
403 produced commercially in large quantities from soy seeds during pressure stamping
404 operation. The production process is based on the next step of chemical extraction
405 with the solvent. Nowadays it is ample available for human consumption and the food
406 industry and only 4% of soybean oil is used in industrial products [135]. This low-cost
407 vegetable oil is liquid at room temperature, hydrophobic and relatively stable to
408 hydrolysis. Its double bonds can be converted to epoxy groups. To use soybean oil as
409 a polyol in polyurethane synthesis there is need to carry out its modification, e.g.
410 oxidation with hydrogen peroxide and acetic or formic acid and then conversion into
411 polyols by ring opening reactions of the epoxy groups [118].

412 The most commercially available polyols based on this type of vegetable oil
413 constitute Honey Bee Biobased Soy Polyol [136] and Agrol [135]. Soyol bio-based

414 polyols with a high bio-content ranging from 80.8% to 99%, revealed such properties
415 as functionality ca. 2-3 and molecular weight between 1000-2000 Da. Their wide range
416 of densities and reaction times make possible to their potential application as seating
417 foam furniture, foam insulation, carpet backing, shoe soles or roof coatings. The
418 soybean oil usage as polyol discloses cost less than the petroleum polyols which they
419 replaced and their use benefits the agricultural business. Soybean polyols have very
420 low volatile organic compounds content and produce less air pollution, acidification,
421 smog formation and ecotoxicity versus petroleum. The researchers from Agrol team
422 investigated that approximately 5.5 pounds of carbon dioxide equivalents are removed
423 or prevented from entering the atmosphere for every pound of Agrol bio-based polyol
424 [135]. They also claimed that 5% of petroleum-based polyether polyols replacement
425 via soybean bio-based polyols will make it possible to 3.15 billion pounds of carbon
426 dioxide removal from the atmosphere.

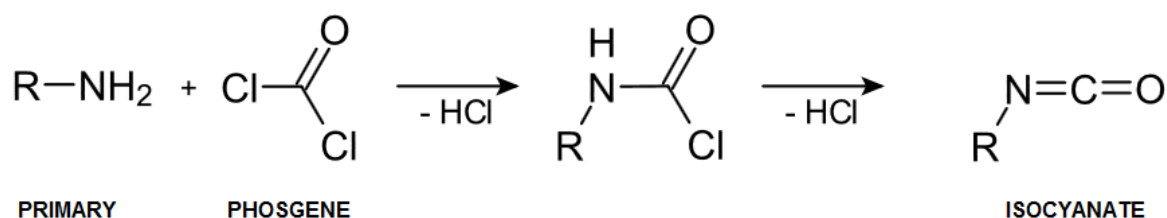
427 One of the cheapest from vegetable oil is the palm oil. It is extracted from both
428 palm fruit and seed. Their crop requires less land and absorbs more carbon dioxide
429 than other vegetable oil. Palm fruit and seed produces up to 10 times more oil per unit
430 area than soybean, rape seed or sunflower. Moreover, uses less water and energy for
431 the same output. To obtain polyol the modifications are necessary. Palm oil-based
432 polyols are usually used for flexible polyurethanes foam due to their hydroxyl number,
433 which is lower than 200 mg KOH/g. Commercially available palm oil-based polyol
434 represents the PolyGreen [137].

435 Castor oil is obtained from the seeds of *Ricinus communis*. This is a fatty acid and
436 glycerin ester which ca. 90% of its fatty acids composed of ricinoleic acid. The seeds
437 are highly toxic but the compounds responsible are not soluble in the oil. The oil was
438 used in medicine and as a lamp oil but also as a precursor for plastics. The average

439 functionality of castor oil is 2.7, so it is widely used as rigid polyol and coating. Because
440 of low reactivity of castor oil, the focus has been directed to its derivatives. In the
441 example, castor oil derivative with propylene oxide can be used in the polyurethane
442 foam synthesis for adhesives, mattresses and automotive seats. Commercially
443 available castor oil-based polyols represent Polycin polyols (Vertellus), Lupranol
444 Balance 50 (BASF) or Ulfcar Polem A (Nivapol). The advantages of the castor oil-
445 based polyol employment in the polyurethane production constitute e.g. up to 25% of
446 bio-mass in resulting polyurethane foam, less: energy and resource consumption,
447 global warming potential and less SO₂ emission, so more ecologically friendly
448 production processes [138]. The castor oil utilization characterized in the limited
449 competition with food chain in comparison with other vegetable oils.

450 2.5. Bio-based diisocyanates for polyurethanes.

451 Isocyanates are usually industrially produced from petroleum. Nevertheless, the
452 industrial route of the isocyanates production is phosgenated of primary amines or
453 their salts. The high toxicity of phosgene, the rather high temperature necessary to
454 decompose the intermediate carbamoyl chloride, and the poor selectivity toward
455 different nucleophiles are some disadvantages that limit the synthetic use of
456 phosgene.

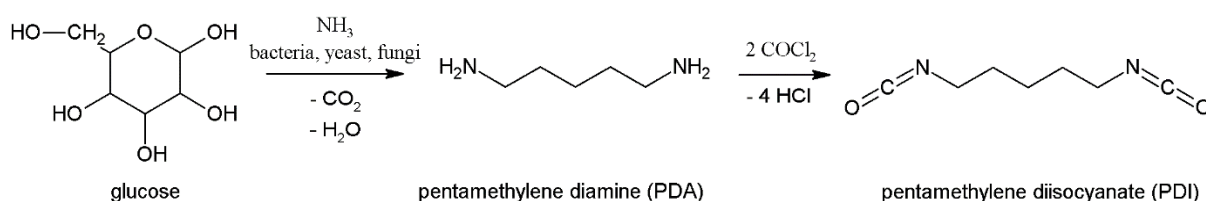


457

458 Figure 8 Scheme of the petrochemical-based isocyanate production process.

459

460 The Covestro company creates the first bio-based diisocyanate – pentamethylene
461 diisocyanate (PDI) - with significant biocontent of 71% renewable carbon. The
462 corresponding derivatives are similar to hexamethylene diisocyanate (HDI) based
463 ones. This bio-based diisocyanate is produced very efficiently from biomass combining
464 biotechnological and chemical processes. The production of the pentamethylene
465 diisocyanate (PDI) involved the two step method: biomass fermentation, and in the
466 next step phosgenation and derivatization. Bio-based and significantly improved
467 carbon footprint cradle-to-gate in comparison to HDI represents one of its advantages.
468 The biotechnological production process characterized significant improvement on
469 energy efficiency. It is associated with a reduction of the manufacturing stages in
470 comparison to the petrochemical process (4 step petro-based synthesis vs. 2 step bio-
471 based synthesis) [139].



473 Figure 9 Scheme of the biotechnological production process of the pentamethylene
474 diisocyanate (PDI).

475 Hojabri at al. [140] as first synthesized a new linear saturated terminal diisocyanate
476 from oleic acid via Curtius rearrangement. The researchers established a synthesis of
477 linear saturated terminal diisocyanate derived from fatty acids and prepared
478 polyurethanes based mostly on lipid feedstock. The feasibility of utilizing this new
479 diisocyanate for the production of polyurethanes was demonstrated by reacting it with
480 commercial petroleum-based polyols and canola oil-based polyols, respectively. It was

481 found that the fatty acid-based diisocyanate was capable of producing polyurethanes
482 with comparable properties within acceptable tolerances [141–144].

483 More and co-workers [145] investigated the preparation of new vegetable oil
484 based diisocyanates using simple organic modifications for polyurethanes synthesis.
485 They have efficiently used castor oil derivatives to synthesize two new diisocyanates
486 via diacyl hydrazide intermediate with high yield and purity. The diisocyanates thus
487 synthesized have been used as efficient comonomers in polyurethanes synthesis.

488 2.6. Future perspective

489 Biorenewable resources for the chemical industry are represented by non-food
490 sources from biomass. They are often called the second generation biorenewables.
491 This group of biorenewables includes such biorenewable feedstocks as wood, both
492 from natural forests and plantation, agricultural residues (straw, corn), algae, municipal
493 solid wastes and wastes from the industrial processes [146]. The first generation of
494 biorenewables is totally destined for the food industry.

495 There is a number of resources which can be successively used for the semi-
496 product production for the polyurethanes syntheses. Extracted components from plant
497 and wood biomass such as cellulose, hemicellulose or lignin, can be used as
498 renewable carbon resources [1]. The difficulties in the catalyst selection for the
499 biomass production and their conversion to the chemicals [146] pose one of the most
500 important problems. Furthermore, a number of researchers investigated the problem
501 associated with the catalysts deactivation and reuse possibility [147]. The catalysts
502 usage in the biomass production and in the polymers synthesis provokes the several
503 primary difficulties of good choice. The typical criteria of the good catalyst choice
504 include the catalyst fouling, poisoning, and destruction [147]. The most important one



505 can be caused by heavy oil components (asphaltenes) due to the bad process
506 conditions [148]. Fouling is also caused by the destruction in overhigh temperature.
507 Thermal decomposition of sugars leads to chemical substances which include the
508 catalysts fouling [149]. These examples and others, make researchers work on the
509 selective catalyst for the biorenewable chemicals [150].

510 A number of companies produce bio-based materials for polymers syntheses.
511 Such biorenewable resources for polyurethanes as succinic acid, ethylene glycol, 1,3-
512 propanediol and 1,4-propanediol [32, 38, 50, 72] are freely available. Based on this
513 bio-components the polyester and polyether polyols were produced and collated with
514 analog petrochemical-based polyols [12, 151, 152]. The obtained results indicate that
515 bio-based polyols revealed approximate industrial properties to petrochemical-based
516 equivalent. Due to the development in the area of biorenewables, it can be expected
517 that other bio-based components for the polyols production such as the adipic acid
518 [67, 153] and 1,6-hexanediol [154] will be accessible.

519 The chemicals mentioned above constitute substrates for aliphatic polyester
520 polyols production. In recent years the increasing interest is also visible in the term of
521 aromatic monomers for polyurethane synthesis. The major sources for aromatic
522 components derived from bioresources constitute carbohydrates and lignin. The most
523 important examples, which revealed huge potential to polyester polyols and
524 polyurethanes production processes employment, are 2,5-furandicarboxylic acid and
525 vanillic acid [155]. The researchers investigated the polyesters based on aromatic bio-
526 based monomer as furandicarboxylic acid as the bio-based alternatives of
527 terephthalates. Such polymers as poly(ethylene terephthalate) (PET),
528 poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) are
529 thermoplastic polymers with excellent performance properties, but they all are

530 petroleum-derived. Papageorgiou and co-workers [156–158] synthesized
531 poly(butylene 2,5-furan dicarboxylate) (PBF) with the use of 2,5-furan dicarboxylic acid
532 and 1,4-butanediol and studied its thermal properties with comparison with
533 petrochemical poly(butylene terephthalate) and poly(ethylene terephthalate). Other
534 compounds from aromatic bio-based monomers can be represented by 2,5-bis-
535 (hydroxymethyl)furan [159], and 2,5-diformylfuran which are important monomers for
536 polyesters, polyamides or polyurethanes. They are produced from 5-
537 hydroxymethylfurfural, derived from dehydration of C6 sugars. Mou at al. [160, 161]
538 investigated the synthesis of the three valuable monomers for polyurethane materials,
539 5,5'-dihydroxymethyl furoin (DHMF), 5,5'-bihydroxymethyl furil (BHMF), and 5,5'-
540 bihydroxymethyl hydrofuroin (BHHM). Based on the obtained polyols the polyurethane
541 materials were prepared and tested. The extensive literature on the bio-based
542 polyester polyols, both types - aliphatic and aromatic, and constantly increasing a
543 number of novel investigations proclaim the opportunity of fully bio-based polyols
544 industrial employment in the future.

545 With triglycerides or fatty acid as starting materials, different chemical approaches
546 have been explored to synthesize novel polyols and multi-isocyanate for
547 polyurethanes. Cayli and Kusefoglul [162] synthesized soybean oil iodo isocyanate by
548 reacting iodine isocyanate with double bonds in soybean oil triglycerides. Hojabri and
549 co-workers [140] used oleic acid to produce 1,7-heptamethylene diisocyanate and
550 1,16-diisocyanatohexadec-8-ene. Oleic acid was first converted to diacids and then to
551 diisocyanates. The researchers also prepared the polyurethanes for the comparative
552 study of the materials properties. Polyurethanes based on 1,7-heptamethylene
553 diisocyanate have similar physical properties as those made from petroleum-derived
554 1,6-hexamethylene diisocyanate when the 1,16-diisocyanatohexadec-8-ene-based

555 polyurethanes exhibited an even higher tensile strength than those commonly derived
556 from a petroleum-based 1,7-heptamethylene diisocyanate. They confirmed also other
557 good properties for bio-based polyurethanes.

558 All examples, mentioned above, prove that biorenewables are one of the most
559 developing resources in the field of chemical industry. The investigation of the bio-
560 based components for the polyurethane synthesis confirmed its good properties as an
561 alternative for a petrochemical equivalent. It is expected that in the future the bio-
562 based products will be freely available on the market and a whole range of the
563 biorenewable feedstocks will be successively utilized.

564 3. CONCLUSION

565 Due to the growing interest in the bio-based plastics and eco-friendly polymers, the
566 researchers are working on new methods for polymer production from biorenewable
567 materials. These activities allow to reduce the petrochemical processes, decrease the
568 fossil fuels utilization and increase the usage of biorenewables. The reduction of the
569 petroleum based resources and ecological trend in the chemistry, as well as chemical
570 technology and materials engineering, contribute to the reduction of the energy
571 consumption, which leads to the production efficiency by the decrease in the
572 production costs while increasing the production scale. Moreover, the eco-friendly
573 activities beget to the greenhouse gases production and CO₂ and SO₂ emission
574 reduction. The major advantages include the decrease in the fossil fuel stocks
575 utilization what leads to the economic volatility reduction and improve the economic
576 stability of the countries without access to the fossil fuels. The growing interest in the
577 field of the bioresources for polymer synthesis generates interest in the biorenewables.
578 Due to this activities, we can expect in the future yet more biorenewable substrates



579 for the polymer syntheses allowing for the complete replacement of the petrochemical
580 based resources.

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1006 Caption of Figures

1007 Figure 1 Impact of the bio-based components on a) the energy consumption and b)
1008 greenhouse gas emission in the example of petrochemical- and bio-based succinic
1009 acid (SA) and 1.3-propanediol (PDO).

1010 Figure 2 General formula of the a) polyether polyols and b) polyester polyols.

1011 Figure 3 Scheme of the polycondensation reaction.

1012 Figure 4 Scheme of the reaction between maleic acid and hydrogen lead to the
1013 succinic acid.

1014 Figure 5 Steps of the corn fermentation process and opportunities to the resulting
1015 products utilization.

1016 Figure 6 Scheme of the a) biotechnological process and b) petrochemical process of
1017 the succinic acid obtaining.

1018 Figure 7 Biosynthesis of the 1,4-butanediol.

1019 Figure 8 Scheme of the petrochemical-based isocyanate production process.

1020 Figure 9 Scheme of the biotechnological production process of the pentamethylene
1021 diisocyanate (PDI).

- 1022 Caption of Tables
- 1023 Table 1 Differences between the 1,3-propanediol industrial production methods.
- 1024 Table 2 Selective properties of the bio-polyols obtained with the use of bio-based
1025 succinic acid, bio-based 1,3-propanediol and petrochemical 1,4-butanediol.
- 1026 Table 3 Selective properties of the bio-based thermoplastic polyurethanes.
- 1027 Table 4 Differences between two methods of the bio-based BDO production.
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- 1031 Table 7 Comparison between the poly(butadiene terephthalate) obtained with the use
1032 of two kinds of the 1,4-butanediol.
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