

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;

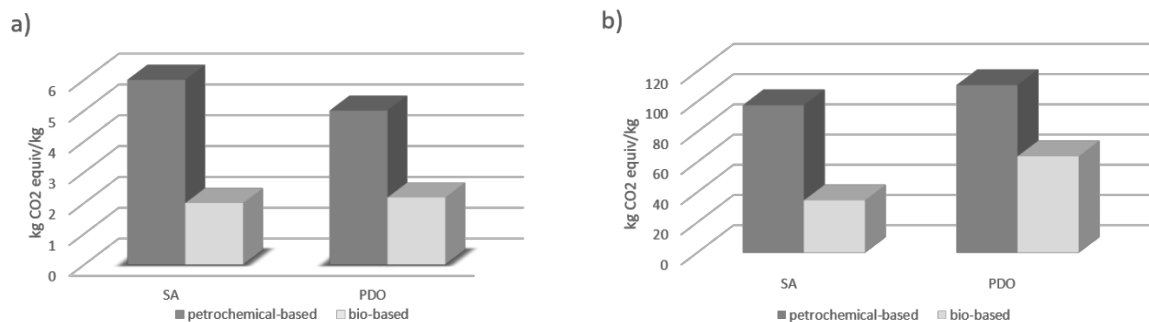
## 19 1. INTRODUCTION

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, CO<sub>2</sub> 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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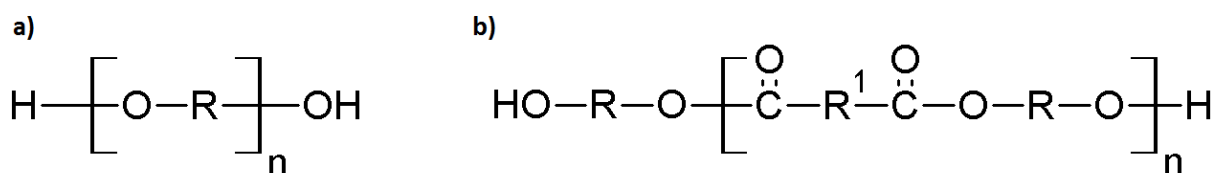
47 Figure 1 Impact of the bio-based components on the a) energy consumption and b)  
 48 greenhouse gas emission in the example of petrochemical- and bio-based succinic  
 49 acid (SA) and 1,3-propanediol (PDO).

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.

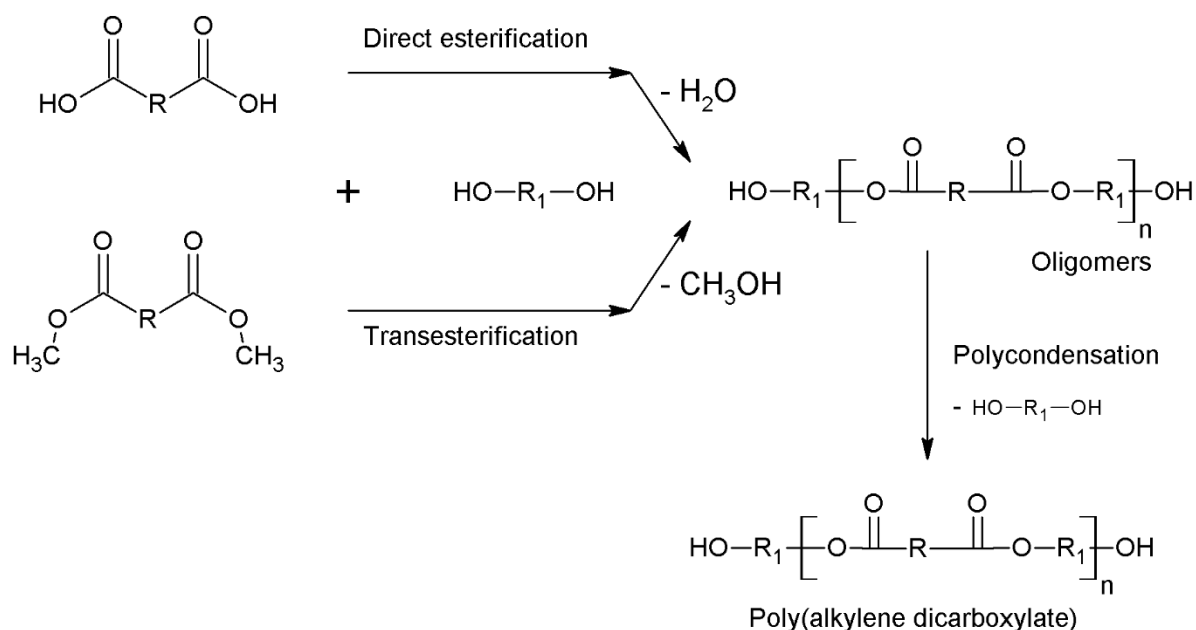


74  
 75 Figure 2 General formula of the a) polyether polyols and b) polyester polyols.

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].

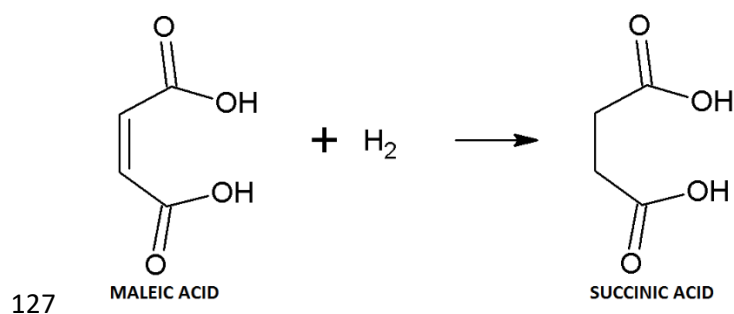
99 The polyurethanes obtained with the use of polyester polyols are less resistant  
 100 to hydrolysis compared to the polyether polyols. However, it makes them more  
 101 favorable due to the biodegradability [18, 26, 27]. Due to this, polyurethane materials  
 102 produced based on polyester polyols 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].

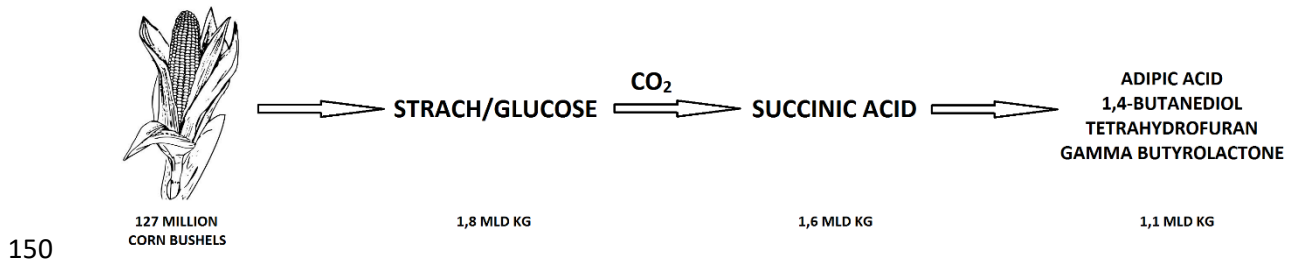


128 Figure 4 Scheme of the reaction between maleic acid and hydrogen leading to the  
129 succinic acid.

130 Succinic acid is a C<sub>4</sub> 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

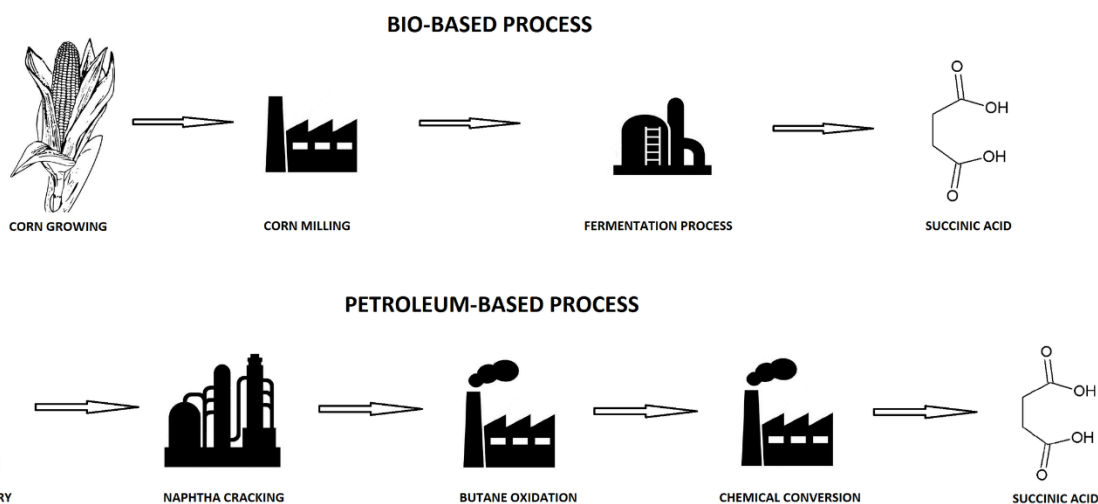
148 [65, 66]. The tests proved that using Coryne-type bacteria leads to significantly higher  
149 succinic acid productivity compared to Escherichia coli bacteria [34].



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].

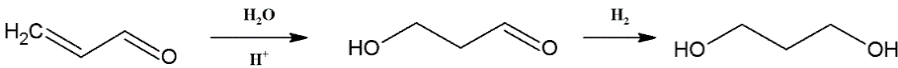
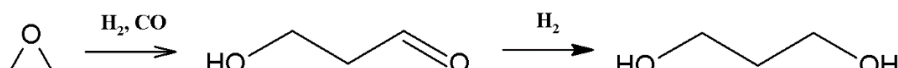
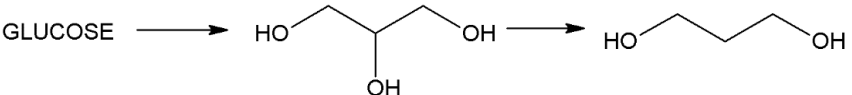
## 183 2.2. Bio-based 1,3-propanediol (Bio-based PDO) – bio-based glycol precursor.

184 At the end of the 20<sup>th</sup> 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	
Hydrocarbonylation of ethylene oxide	
Bio-based PDO	
Glucose fermentation	

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 <sup>3</sup> ]	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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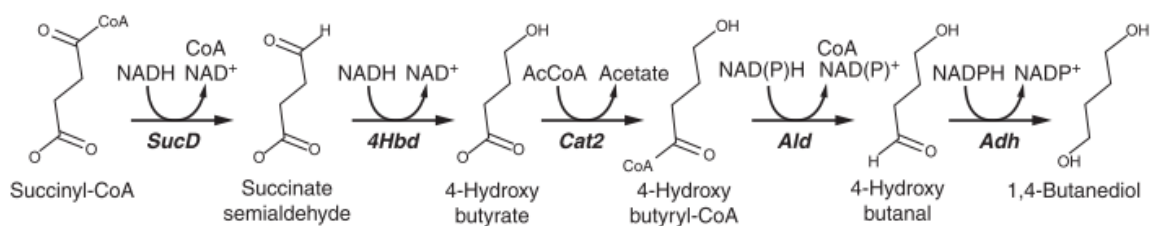
258 As can be seen from Table 3, with the similar hard segment content in all of the  
259 bio-thermoplastic polyurethanes, hardness increases with the growth of the chain  
260 length. The thermoplastic polyurethane with the 1,4-butanediol based polyol and 1,4-  
261 butanediol as the extender reveal 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.

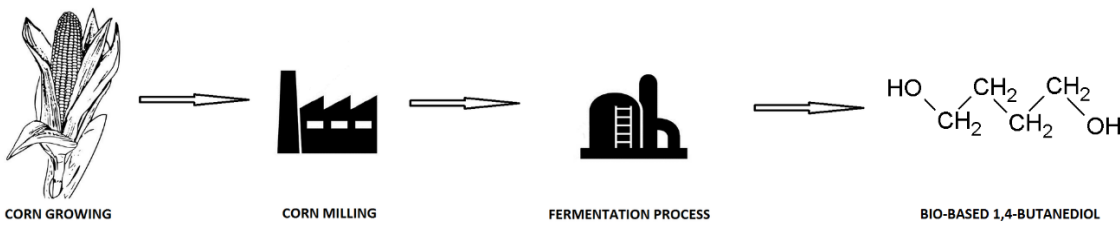
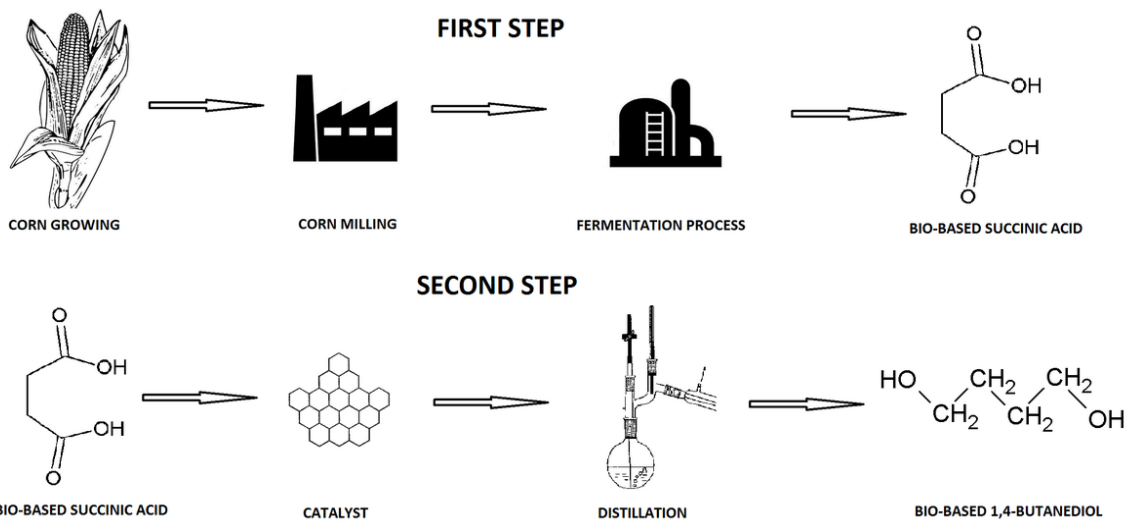
281 Some smaller companies like BioAmber [67] or Myriant [69] produced their bio-  
 282 based BDO by means of the bio-based succinic acid converting through the single  
 283 catalytic step [96–98]. Minh et al. [96] investigated the catalytic converting of the  
 284 succinic acid in 1,4-butanediol 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 20<sup>th</sup> 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].

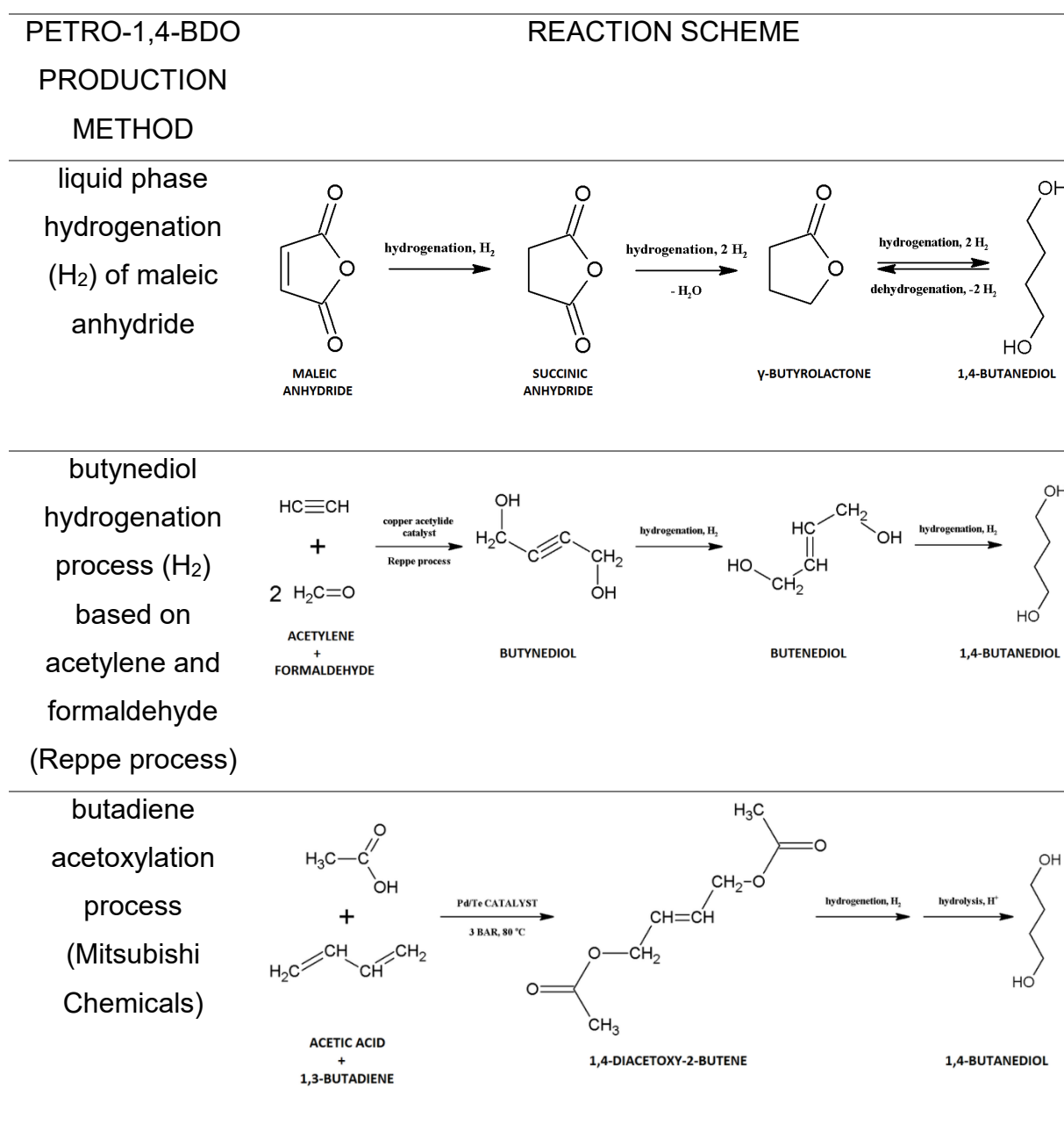
316 Eastman Chemical Company developed the commercial method for BDO  
317 production based on the butadiene epoxidation process. The butadiene epoxidation  
318 reaction leads to the 3,4-epoxy-1-butene using silver as a catalyst. In the next step,  
319 the product is hydrated and hydrogenated with 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.

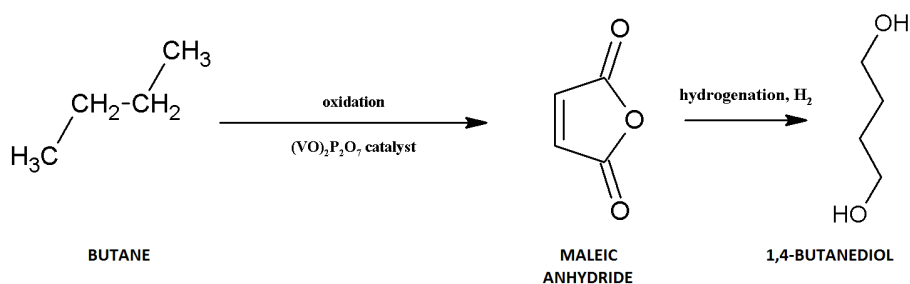
331 Table 5 Differences between the petrochemical-based BDO production methods.



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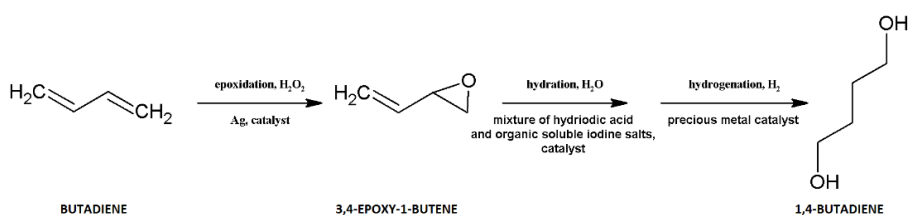
butane oxidation

(O<sub>2</sub>) process



butadiene  
epoxidation

process  
(Eastman  
Chemical  
Company)



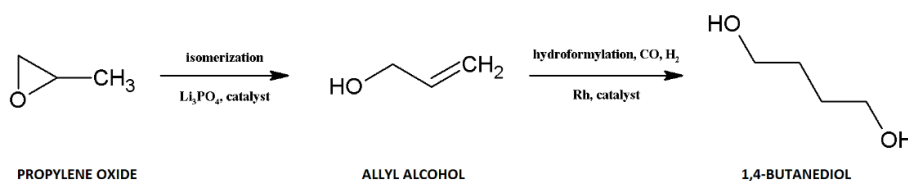
allyl alcohol

hydroformylation

(CO + H<sub>2</sub>)

process

(LyondellBassell  
Company)



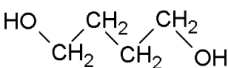
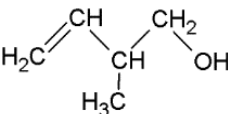
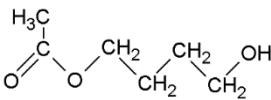
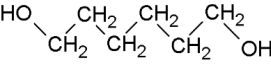
332

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 CO<sub>2</sub>-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.

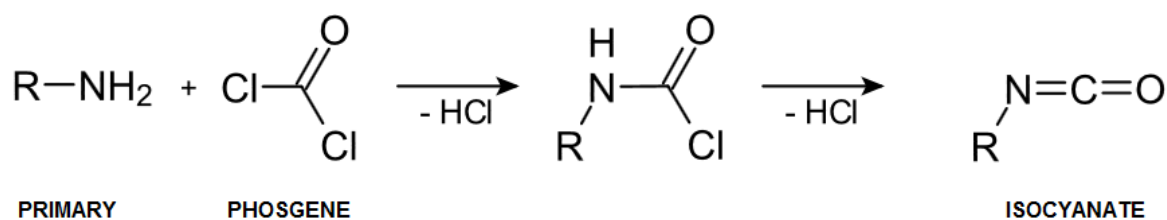
427 One of the cheapest from vegetable oil is the palm oil. It is extracted from both  
428 palm fruit and seed. Their crop requires less land and absorbs more carbon dioxide  
429 than other vegetable oil. Palm fruit and seed produces up to 10 times more oil per unit  
430 area than soybean, rape seed 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 SO<sub>2</sub> 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.

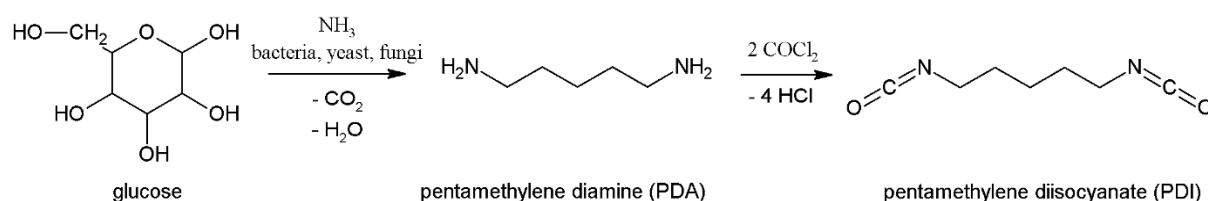


457

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 et al. [160, 161]  
538 investigated the synthesis of the three valuable monomers for polyurethane materials,  
539 5,5'-dihydroxymethyl furin (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 CO<sub>2</sub> and SO<sub>2</sub> 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.
- 1028 Table 5 Differences between the petrochemical-based BDO production methods.
- 1029 Table 6 Purity differences between bio-based BDO and petrochemical-based BDO  
1030 [99].
- 1031 Table 7 Comparison between the poly(butadiene terephthalate) obtained with the use  
1032 of two kinds of the 1,4-butanediol.
- 1033