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

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7   ABSTRACT: Polyurethanes are one of the most developing branches of the polymers.

8   They consist of the two primary sources, such as the polyols and the diisocyanates.

9   So far, both of the main substrates have been obtained through the petrochemical

10   processes. The reduction of the petroleum based resources and ecological trend in

11   the chemistry, chemical technology, and materials engineering have generated the

12   increasing interest in the utilization of biorenewables in polymer syntheses. This paper

13   aims at giving comments of the environmental impact of the petrochemical-based

14   component replacement by the bio-based chemicals in the polyurethane synthesis.

15   KEYWORDS: Biopolymers; Bio-based Polyurethane; Bioresources; Environmental

16   impact;

17   1. INTRODUCTION

18   Polyurethane industry is one of the most intensively developing fields in the plastic

19   industry. Nowadays, polyurethane materials play an important role in various primary

20   areas of life, beginning from furniture, clothes and food packaging, through

21   motorization to health care [1]. Since 2000 the world consumption of polyurethanes

22   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 entirety, 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_2 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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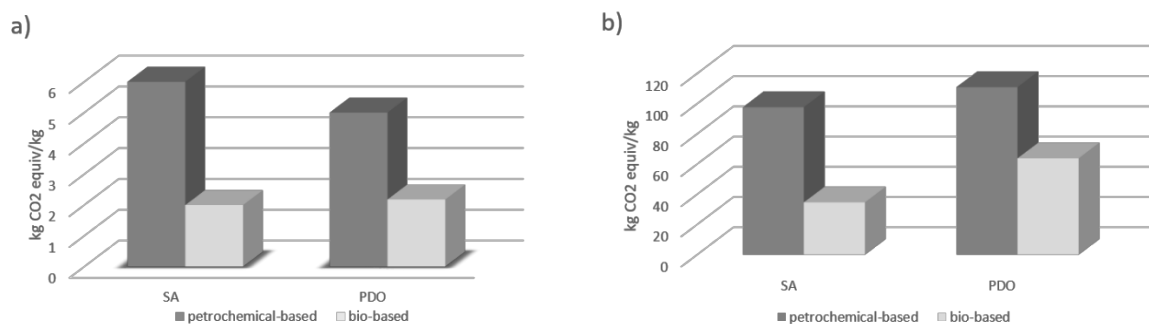
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47 Figure 1 Impact of the bio-based components on the a) energy consumption and b)

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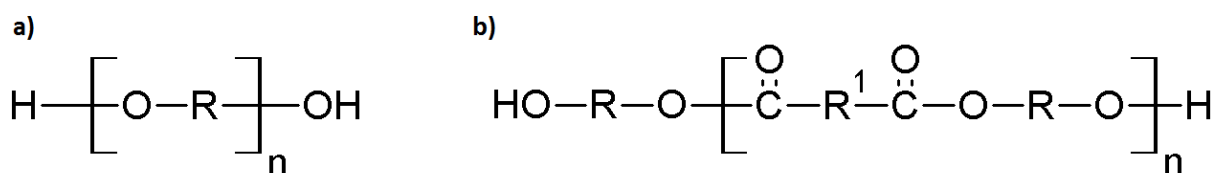
75 Figure 2 General formula of the a) polyether polyols and b) polyester polyols.

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

4

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].
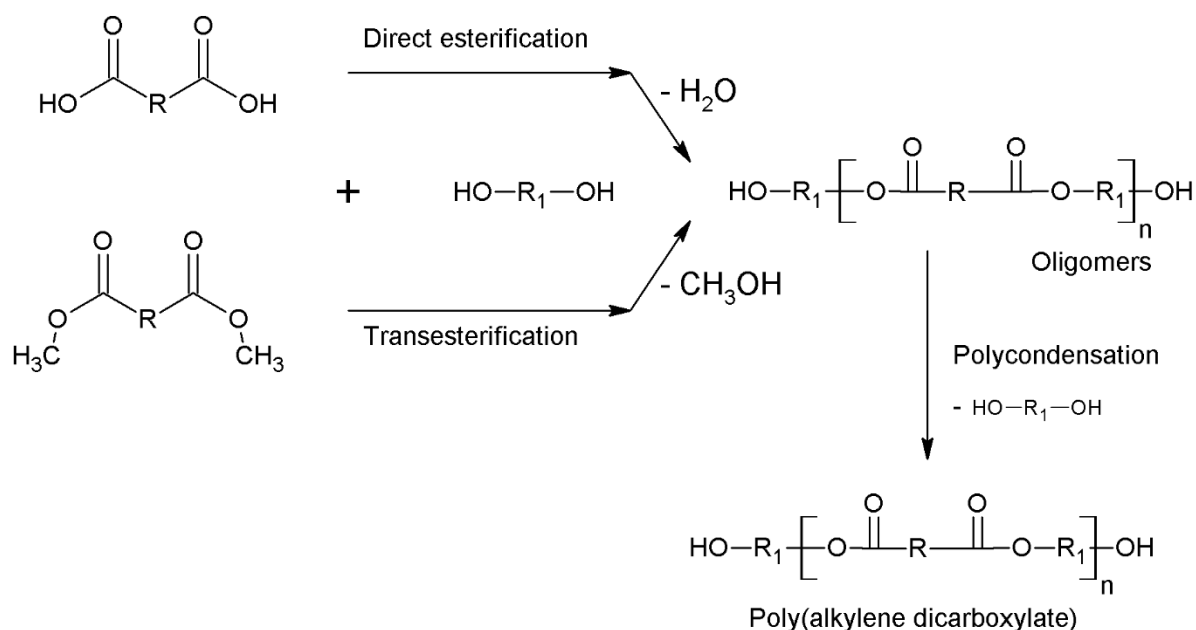
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91 Figure 3 Scheme of the polycondensation reaction.

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

5

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].
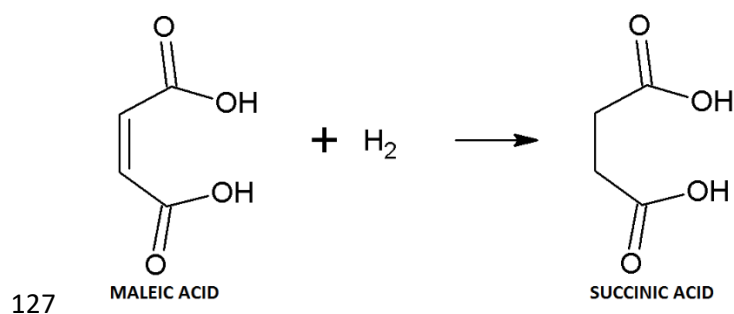
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MALEIC ACID   SUCCINIC ACID

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

Succinic acid is a C4 building-block chemical compound which recently has also been obtained by the corn fermentation [38, 39]. This biotechnological process makes it possible to produce bio-succinic acid production in the range from 5 000 tons per year at the price of 2.20 $/kg, to 75 000 tons per year at 0.55 $/kg [37]. The fermentation method proves economic advantages of the bio-succinic acid utilization due to the reduction of production costs coupled with the increasing production scale.
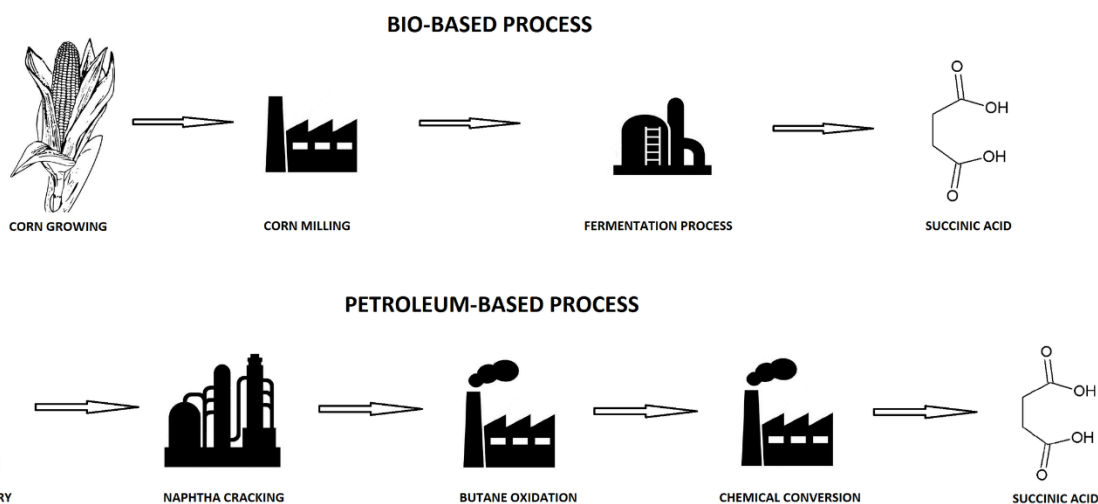
Figure 5 shows how to obtain the succinic acid with the use of fermentation method. This method consists of the corn fermentation of a large group of microorganisms such as fungi, yeasts [40] or Gram-positive bacteria [36]. The first identified and the most studied succinic acid over-producers were the Anaerobiospirillum succiniciproducens [41–45] and the Actinobacillus succinogenes [46–51]. They allowed to the succinic acid obtaining in the large scale [36]. Then, more attention was paid to the bacterium called Mannheimia succiniciproducens MBEL55E [52–55], due to its natural isolation from the bovine rumen [56]. Currently, the most important and applicable are the Escherichia coli bacteria [57–64]. Nevertheless, due to the economic disadvantages such as the high costs of this method, scientists in the field of bio-industries work upon other microorganisms applications [34]. The Mitsubishi Chemicals use the Coryne-type bacteria for the succinic acid production

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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].
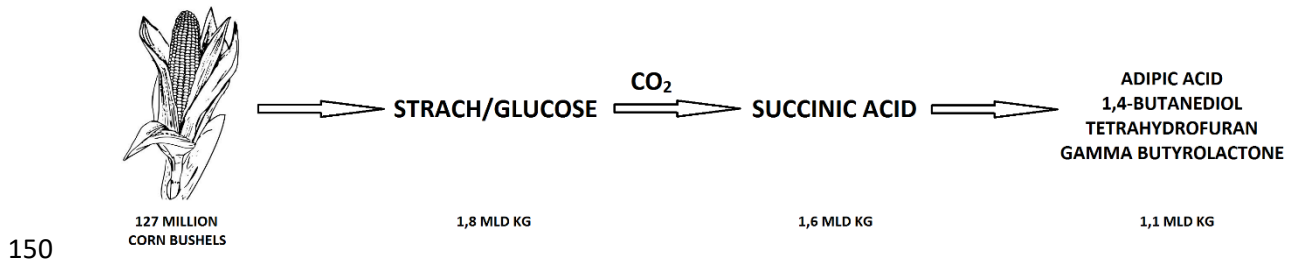
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151 Figure 5 Steps of the corn fermentation process and opportunities to the resulting

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].

BIO-BASED PROCESS

CORN GROWING → CORN MILLING → FERMENTATION PROCESS → SUCCINIC ACID

PETROLEUM-BASED PROCESS

OIL RECOVERY → NAPHTHA CRACKING → BUTANE OXIDATION → CHEMICAL CONVERSION → SUCCINIC ACID

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

9

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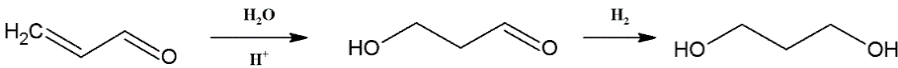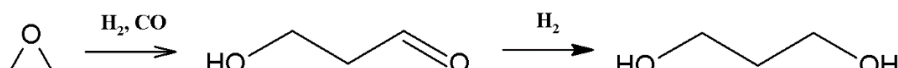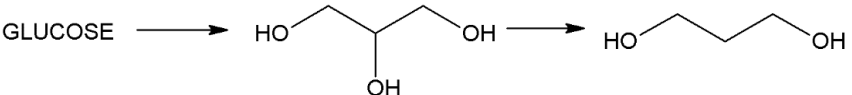
183 2.2. Bio-based 1,3-propanediol (Bio-based PDO) – bio-based glycol precursor.

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	
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].

11

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 fruendii
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 ^{o}C	4601	Solid
- 70.0 ^{o}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

13

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 [ºSh A] [ºSh D]	64	67.1	55
Tensile strength [MPa]	18.55	4.25	37.38
Elongation at break [%]	831	655.94	671
Resilience [%]	10	25.56	15

257

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].

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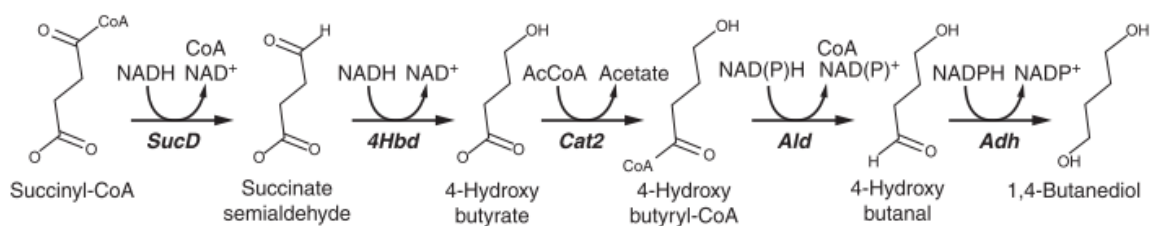
Figure 7 Biosynthesis of the 1,4-butanediol.

Some smaller companies like BioAmber [67] or Myriant [69] produced their bio-based BDO by means of the bio-based succinic acid converting through the single catalytic step [96–98]. Minh at al. [96] investigated the catalytic converting of the succinic acid in 1,4-butanediol using the modified Pd and Ru catalysts with the variable amounts of Re. The researcher investigated that the yield and selectivity were in the range from 62 to 66 %. The converting reaction was carried out at the temperature of 160 °C and the pressure of 150 bars. Kang et al. [97, 98] also studied the bimetallic catalysts as catalysts for the succinic acid conversion to BDO. They investigated the Re–Ru bimetallic catalysts supported on the mesoporous carbon and the mesoporous rhenium–copper–carbon composite catalysts. All the reactions needed high temperature and pressure, which indicates that the specific conditions are needed for the succinic acid conversion. Table 4 illustrates two methods of the bio-based 1,4-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
	CORN GROWING — CORN MILLING — FERMENTATION PROCESS — BIO-BASED 1,4-BUTANEDIOL
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
	FIRST STEP: CORN GROWING — CORN MILLING — FERMENTATION PROCESS — BIO-BASED SUCCINIC ACID; SECOND STEP: BIO-BASED SUCCINIC ACID — CATALYST — DISTILLATION — BIO-BASED 1,4-BUTANEDIOL

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].

17

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 anhydrate with the use of vanadyl pyrophosphate

314    $((VO)_2P_2O_7)$, as the catalyst. When the maleic anhydrate is obtained, the

315   hydrogenation process leads to the 1,4-butanediol forming [72].
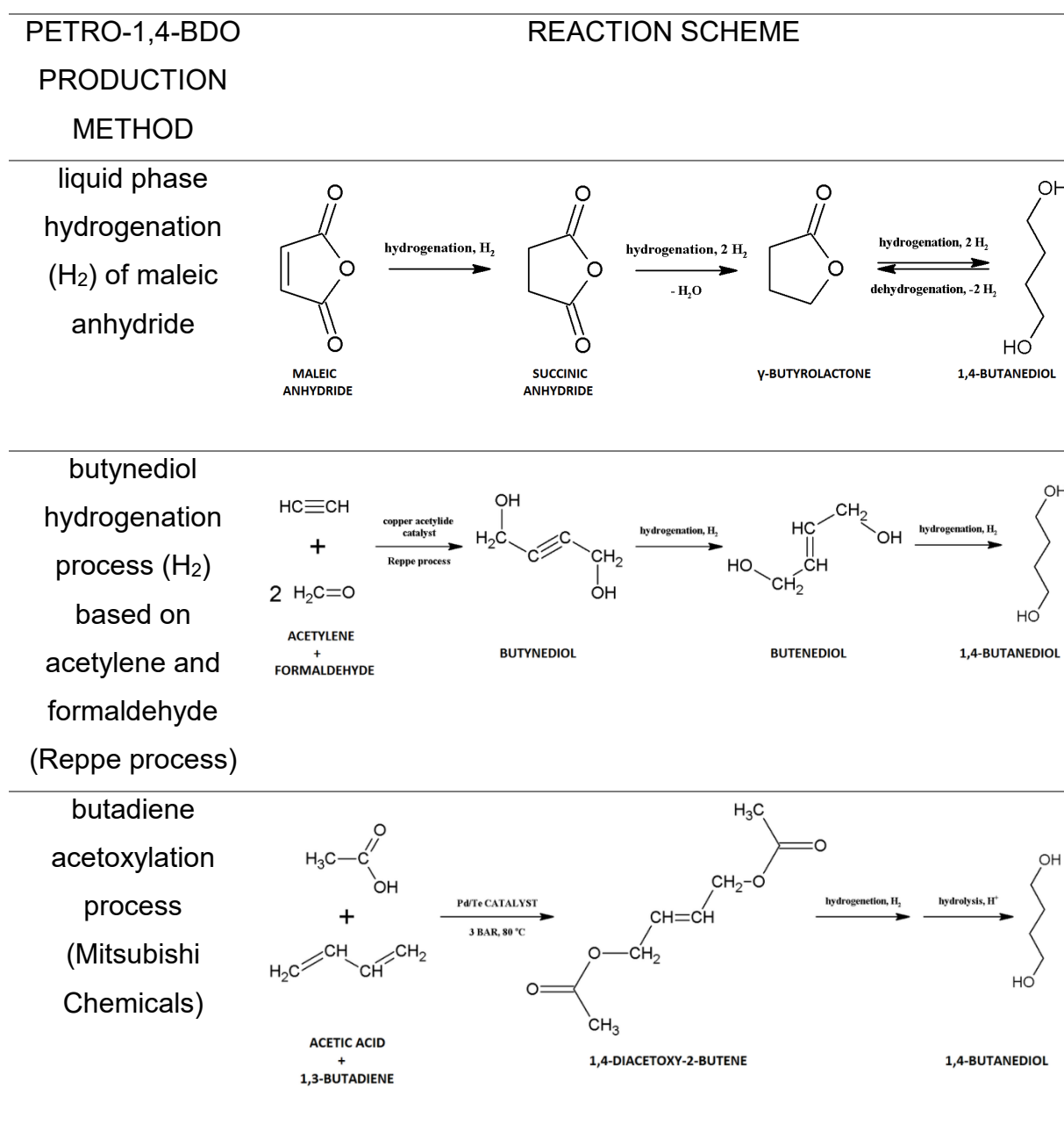
316   Eastman Chemical Company developed the commercial method for BDO

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

18

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.

PETRO-1,4-BDO PRODUCTION METHOD	REACTION SCHEME
liquid phase hydrogenation (H_2) of maleic anhydride	
butynediol hydrogenation process (H_2) based on acetylene and formaldehyde (Reppe process)	
butadiene acetoxylation process (Mitsubishi Chemicals)	

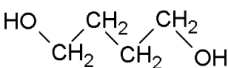| butane oxidation (O₂) process | BUTANE — oxidation (VO)₂P₂O₇ catalyst → MALEIC ANHYDRIDE — hydrogenation, H₂ → 1,4-BUTANEDIOL |
| butadiene epoxidation process (Eastman Chemical Company) | BUTADIENE — epoxidation, H₂O₂, Ag, catalyst → 3,4-EPOXY-1-BUTENE — hydration, H₂O, mixture of hydriodic acid and organic soluble iodine salts, catalyst — hydrogenation, H₂, precious metal catalyst → 1,4-BUTADIENE |
| allyl alcohol hydroformylation (CO + H₂) process (LyondellBassell Company) | PROPYLENE OXIDE — isomerization Li₃PO₄, catalyst → ALLYL ALCOHOL — hydroformylation, CO, H₂, Rh, catalyst → 1,4-BUTANEDIOL |
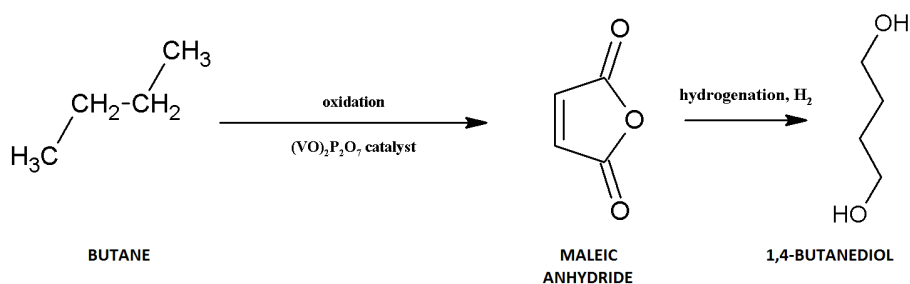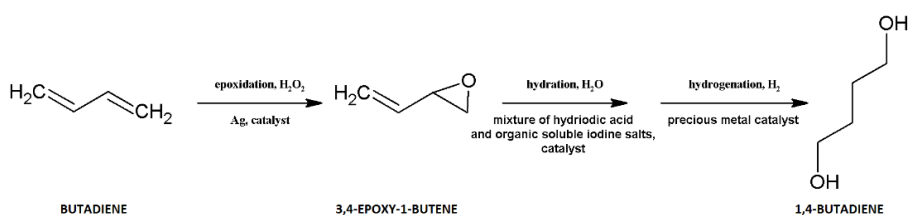
332
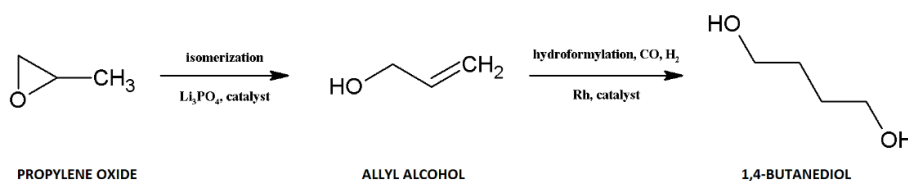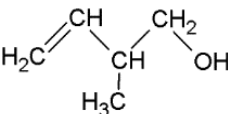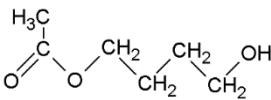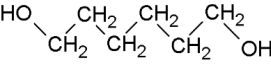
The comparison between the bio-based and petrochemical-based 1,4-butanediol production methods allowed to verify a number of advantages for the biotechnological method. First of all, the usage of the dextrose in the bio-based production method led to the 67% lower fossil energy usage and with up to 83% lower total CO_2-equivalent emissions/kg BDO [92, 94]. Relative to the petrochemical BDO production methods, where there exist many steps of the synthesis, the bio-based process decreases the amount of the steps. Moreover, biotechnological processes allow to reduce the catalyst demand and consequently decrease the difficulties in the catalyst recycling and reusing. Petrochemical processes generate the big amounts of chemical waste, which in the next step, must be submitted to reprocessing. The bio-based process

20

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	HO—CH$_2$—CH$_2$—CH$_2$—CH$_2$—OH	99.95	99.85
2-methyl-3-buten-1-ol	H$_2$C=CH—CH(CH$_3$)—CH$_2$—OH	-	0.10
1,4-butanediol, monoacetate	H$_3$C—C(=O)—O—CH$_2$—CH$_2$—CH$_2$—CH$_2$—OH	< 0.01	-
1,6-hexanediol	HO—CH$_2$—CH$_2$—CH$_2$—CH$_2$—CH$_2$—CH$_2$—OH	-	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

24

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

25

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 castrol 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_2 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

26

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].

472

glucose   pentamethylene diamine (PDA)   pentamethylene diisocyanate (PDI)

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-furandicarobxylic 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

29

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 (BHMH). 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 Kusefoglu [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

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

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

3. CONCLUSION

Due to the growing interest in the bio-based plastics and eco-friendly polymers, the researchers are working on new methods for polymer production from biorenewable materials. These activities allow to reduce the petrochemical processes, decrease the fossil fuels utilization and increase the usage of biorenewables. The reduction of the petroleum based resources and ecological trend in the chemistry, as well as chemical technology and materials engineering, contribute to the reduction of the energy consumption, which leads to the production efficiency by the decrease in the production costs while increasing the production scale. Moreover, the eco-friendly activities beget to the greenhouse gases production and CO_2 and SO_2 emission reduction. The major advantages include the decrease in the fossil fuel stocks utilization what leads to the economic volatility reduction and improve the economic stability of the countries without access to the fossil fuels. The growing interest in the field of the bioresources for polymer synthesis generates interest in the biorenewables. 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.

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