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

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

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

1. INTRODUCTION

Polyurethane industry is one of the most intensively developing fields in the plastic industry. Nowadays, polyurethane materials play an important role in various primary areas of life, beginning from furniture, clothes and food packaging, through motorization to health care [1]. Since 2000 the world consumption of polyurethanes has been constantly growing. In 2004 polyurethanes represented 5 % of the worldwide polymer consumption [2]. Currently, they constitute 7,5 % (in 2015), what puts them at the forefront of the most consumed polymers [3].

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

The environmental advantages of the bioresources utilization represent the reduction of energy consumption during production, the greenhouse gases emission reduction, CO_2 emission reduction [9] and, in the term of polyesters, the biodegradability improvement [4, 7]. Figure 1 presents the comparison between bio-based and petrochemical-based components impact on the energy consumption (Figure 1a) and greenhouse gas emission (Figure 1b) in the example of the two primary components in the polyurethane polyester polyols synthesis – succinic acid and 1,3-propanediol. The degree of all of the presented advantages depends on the bioresources type and production method. In the certain cases, the biotechnological method of the chemical synthesis for polyurethanes allows for component obtainment with higher purity level than the petrochemical counterpart.

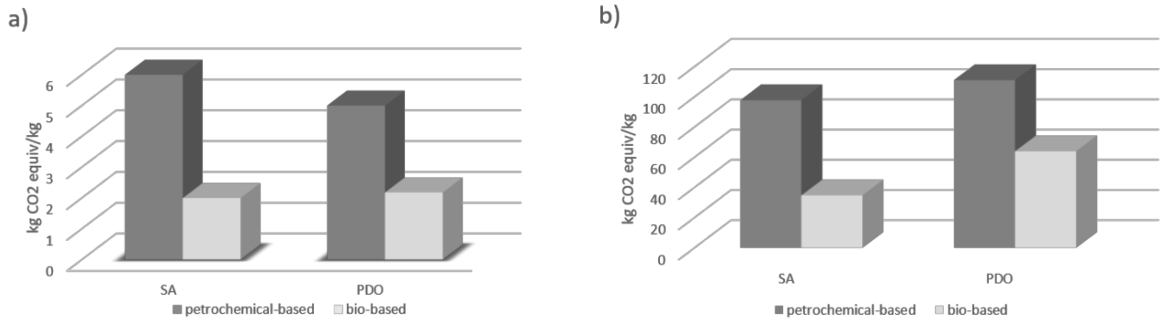
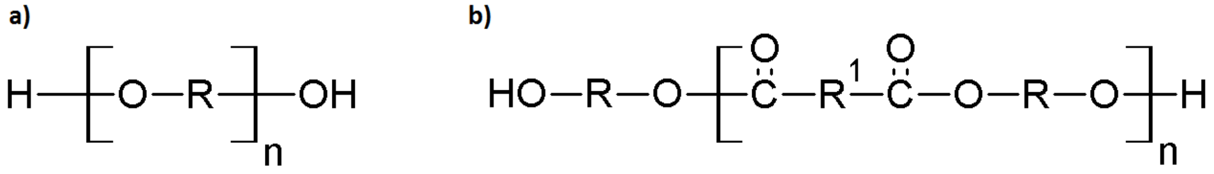


Figure 1 Impact of the bio-based components on the a) energy consumption and b) greenhouse gas emission in the example of petrochemical- and bio-based succinic acid (SA) and 1,3-propanediol (PDO).

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

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

Polyols constitute one of the two main components for polyurethane synthesis [2]. They can be grouped by a functional group which occurs in the macromolecular chain as polyether [10, 11], polyester [12] and polyether-ester polyols [13]. Polyols are usually liquid, reactive substances mostly terminated by the hydroxyl or partially amine groups [14]. These groups are responsible for the reaction with isocyanates [15]. The polyether polyols are characterized by the following general repeating unit and the molecular weight in the range from 2000 to 6500 g/mol (for elastic polyurethanes) (Figure 2a). They constitute ca. 80 % of the polyols globally used in the polyurethane synthesis [2]. The polyester polyols are characterized by lower molecular weight, in the range from 1000 to 4000 g/mol (for elastic polyurethanes) (Figure 2b) [2, 15]. They represent the second most important group with around 18 % of the polyols global usage. Both general formulae of the polyols mentioned above is given in Figure 2 a and b.



$$H\!-\!\left[O\!-\!R\right]_n\!-\!OH \qquad HO\!-\!R\!-\!O\!-\!\left[\overset{O}{\overset{\|}{C}}\!-\!R^1\!-\!\overset{O}{\overset{\|}{C}}\!-\!O\!-\!R\!-\!O\right]_n\!-\!H$$

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

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

The primary reaction of the polyester polyols obtaining is the polycondensation reaction between the carboxylic acid or carboxylic acid ester and the excess of the dihydroxyl alcohol [2, 14, 16] (Figure 3). This reaction can be divided into esterification reaction, namely, the direct esterification and the transesterification reaction, when the carboxylic acids or the carboxylic acid esters are used, respectively [17]. During reactions, beyond the polyester polyols, the by-products are produced. These by-products constitute water or alcohols, which hinders the polycondensation process towards the polyester polyols. To shift the reaction towards the main product, water and alcohols must be eliminated from the reaction system [2, 17–19].

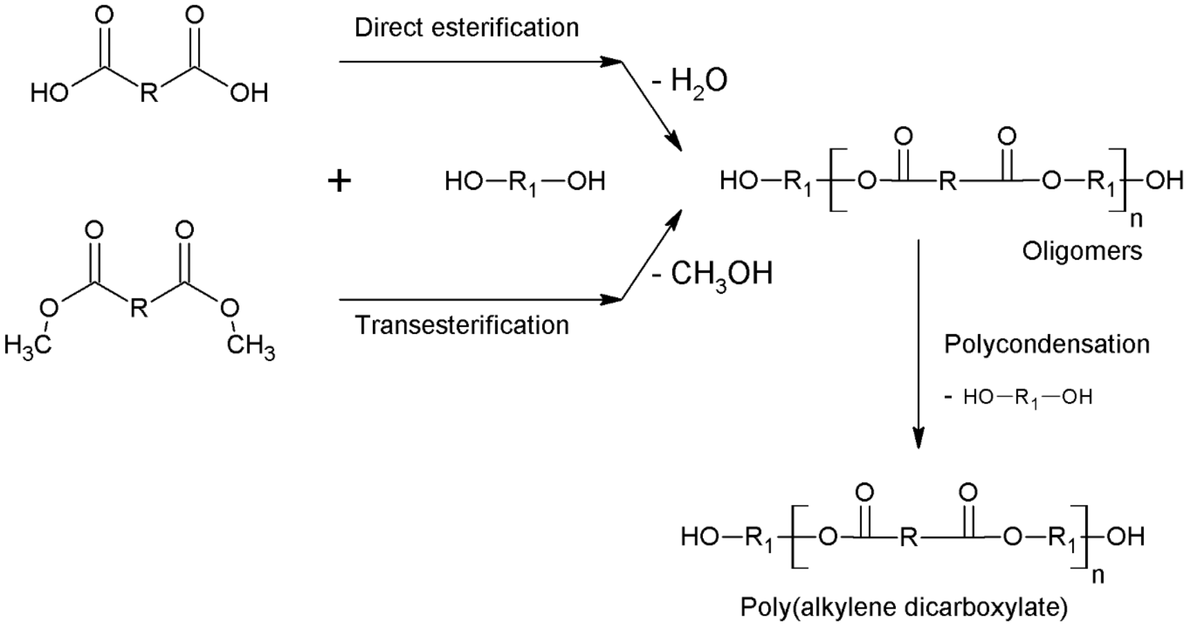


Figure 3 Scheme of the polycondensation reaction.

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

The polyurethanes obtained with the use of polyester polyols are less resistant to hydrolysis compared to the polyether polyols. However, it makes them more favorable due to the biodegradability [18, 26, 27]. Due to this, polyurethane materials produced based on polyester polyols can be submitted for different kinds of recycling processes. Through the secondary forces between polyester chains, they have more crystalline structure [2, 15]. Polyurethanes based on the polyester polyols have better thermal and fire resistance than the polyether-based PUR and superior solvent resistance [2, 15]. The polyether-ester polyols characterized by the hybrid of the polyester and polyether polyols properties [13, 28]. Due by the ester bonding in the molecular chain, the polyurethanes based on this kind of polyols undergoes biodegradation, when the ether bonding increased the mechanical resilience of the polyurethane materials.

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

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

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

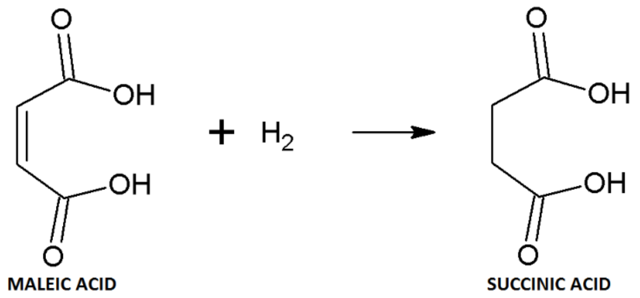


Figure 4 Scheme of the reaction between maleic acid and hydrogen leading to the succinic acid.

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

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

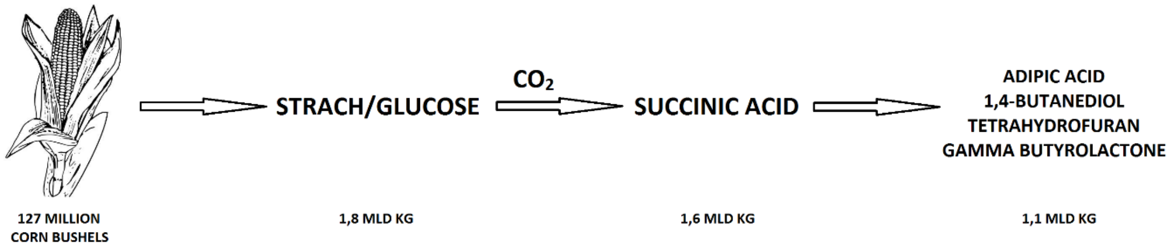


Figure 5 Steps of the corn fermentation process and opportunities to the resulting products utilization.

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

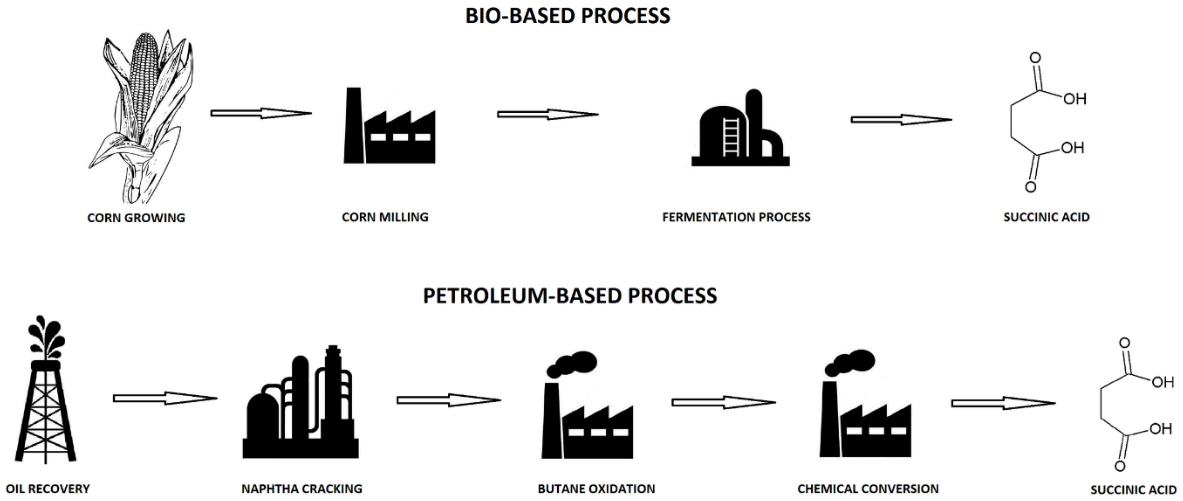


Figure 6 Scheme of the bio-based process and the petroleum-based process of the succinic acid obtaining.

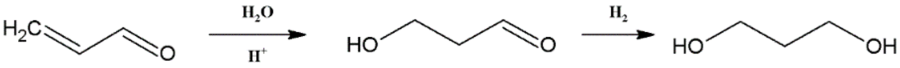
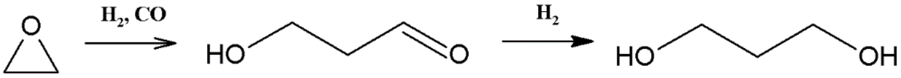
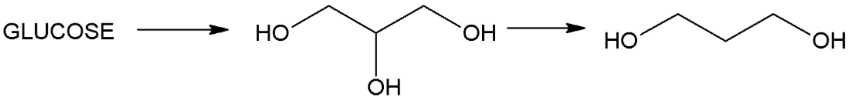
Figure 6 shows differences between the bio-based and petrochemical-based succinic acid preparations [37, 67]. It is clear that the biotechnological process of the SA production reduces the manufacturing stages in comparison to the petrochemical process. Moreover, each step in the petroleum-based SA production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

The reduction of the petrochemical sources utilization and growing interest in the bio-component usage leads to the economic volatility reduction [8]. The bio-based component usage generates alternative sources for polymer syntheses. The decreasing trend in the petroleum-based sources consumption was determined by the fossil fuel stocks depletion. Moreover, the increasing possibilities of the plant product usage or non-food residue utilization from the food industry allow improving the economic stability of the countries without access to the fossil fuels [71].

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

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

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	

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

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

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

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

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

Table 2 Selective properties of the bio-polyols obtained with the use of bio-based 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

Comparison between the two polyols mentioned above shows that there were no significant differences between the hydroxyl value, but, on the other hand, PDO-SA polyol revealed less acid value. Moreover, BDO-SA polyol discloses higher viscosity than PDO-SA, which leads to the difficulties in the industrial processes due to the requirement of higher temperature [6].

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

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

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

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

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

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

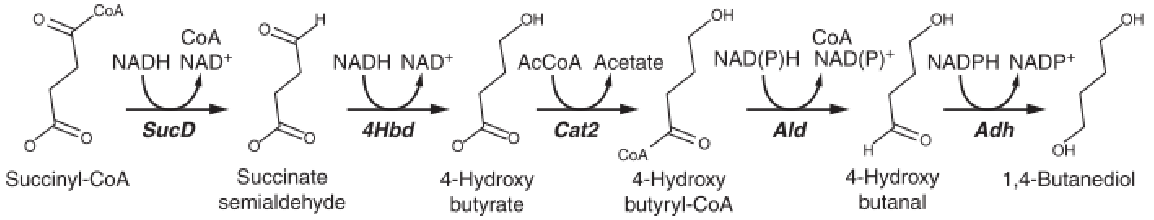
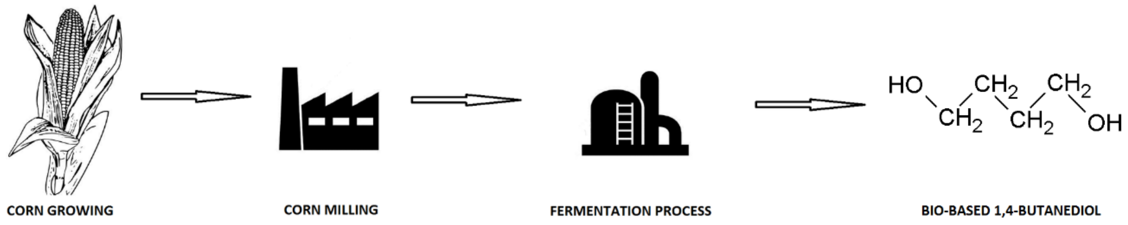
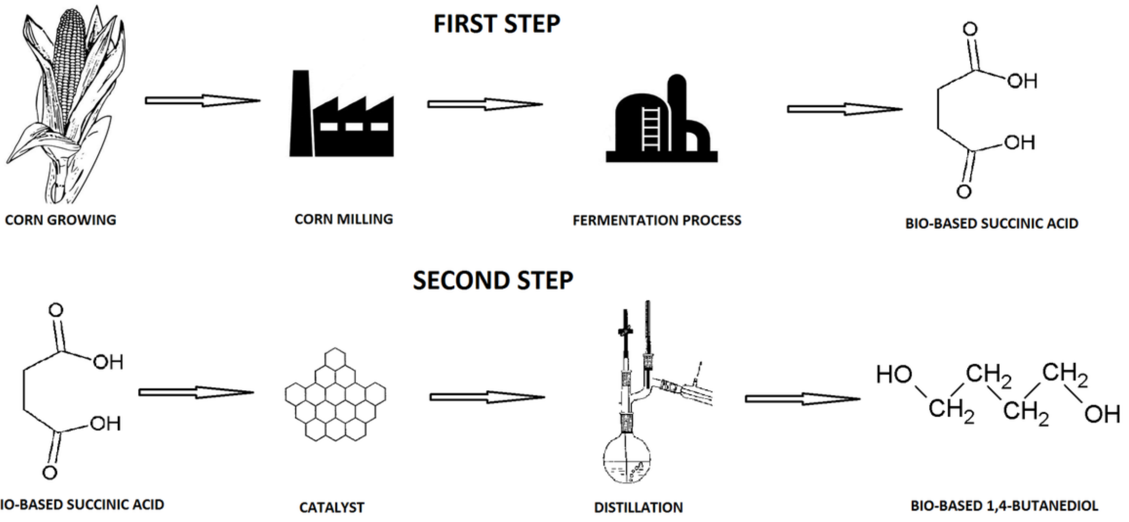


Figure 7 Biosynthesis of the 1,4-butanediol.

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 ^{o}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.

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 

Currently used petrochemical-based BDO was obtained from the fossil fuel stocks. There are many methods which leads to the petro-based 1,4-butanediol. The most important method for the BDO production since the last 20th century has been the hydrogenation process [72]. This method is based on the liquid phase hydrogenation of maleic anhydride [99] and leads to 1,4-butanediol [100].

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

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

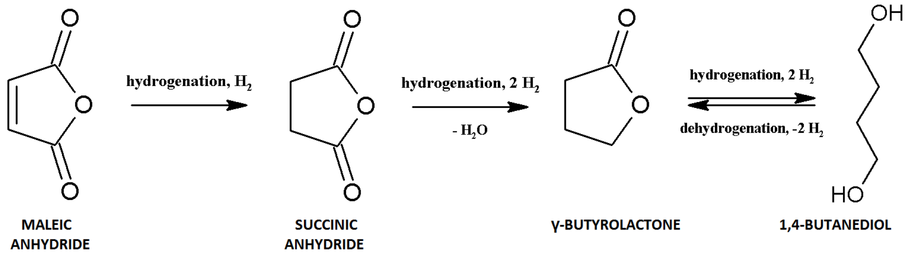
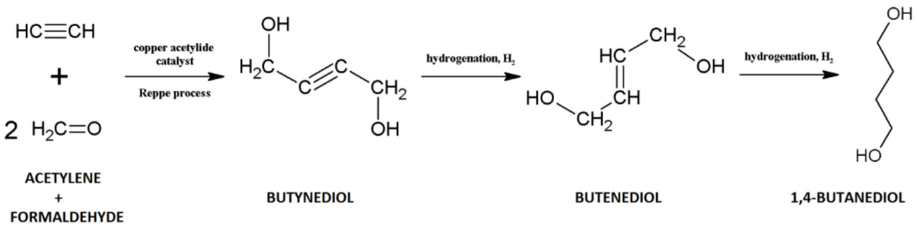
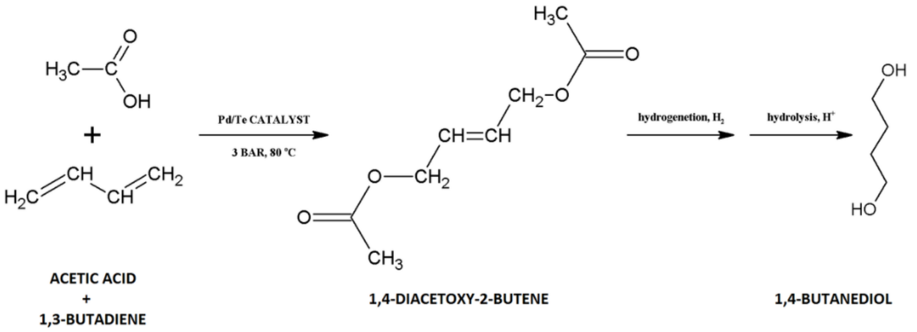
The BDO production is also possible with the use of butane. The butane oxidation reaction leads to the maleic anhydrate with the use of vanadyl pyrophosphate ($(VO)_2P_2O_7$), as the catalyst. When the maleic anhydrate is obtained, the hydrogenation process leads to the 1,4-butanediol forming [72].

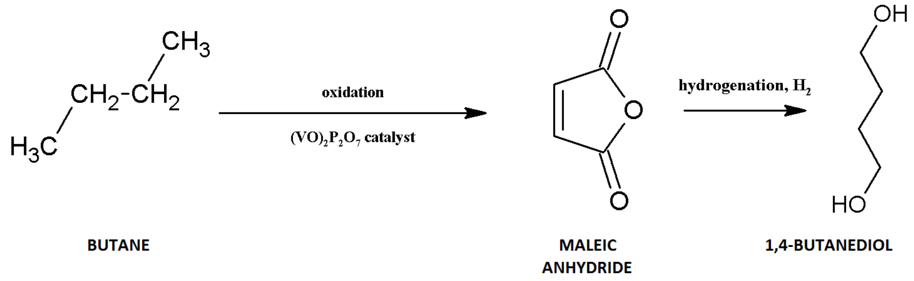
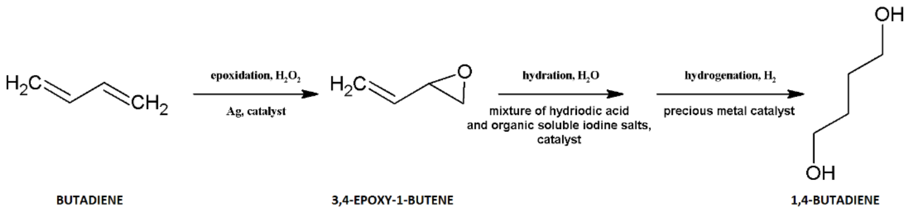
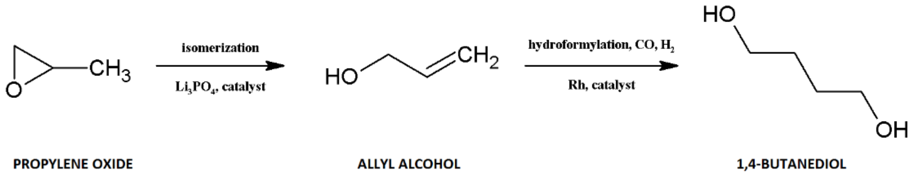
Eastman Chemical Company developed the commercial method for BDO production based on the butadiene epoxidation process. The butadiene epoxidation reaction leads to the 3,4-epoxy-1-butene using silver as a catalyst. In the next step, the product is hydrated and hydrogenated with the use of special catalysts,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

The LyondellBassell Company developed another, commercially used, a method for the BDO production [107]. This method is based on the hydroformylation process of the allyl alcohol via the hydroformylation technology licensed by the Kuraray Company [108]. In the first step, the propylene oxide is isomerized to the allyl alcohol by the lithium phosphate (Li_3PO_4) as the catalyst. The received product is subsequently hydroformylated by the rhodium catalyst in the triphenylphosphine and 1,4- diphenylphosphinobutane presence [72].

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

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

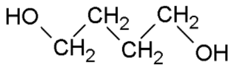
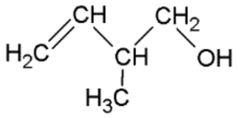
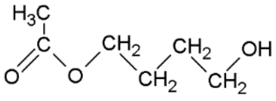
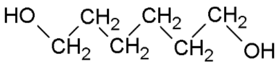
PETRO-1,4-BDO PRODUCTION METHOD	REACTION SCHEME
liquid phase hydrogenation (H_2) of maleic anhydride	
butynediol hydrogenation process (H_2) based on acetylene and formaldehyde (Reppe process)	
butadiene acetoxylation process (Mitsubishi Chemicals)	

butane oxidation (O₂) process	
butadiene epoxidation process (Eastman Chemical Company)	
allyl alcohol hydroformylation (CO + H₂) process (LyondellBassell Company)	

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

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

Table 6 Purity differences between bio-based BDO and petrochemical-based BDO [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

The test results proved the occurrence of differences between the bio-based and petrochemical 1,4-BDO. The biotechnological process of the 1,4-BDO production allows for more pure product obtainment. This fact leads to the reduction of the purification process. The smaller number of process steps leads to the costs cutting due to the reduction of the energy utilization. Moreover, it makes it possible to decrease the waste formation.

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

Table 7 Comparison between the poly(butadiene terephthalate) obtained with the use 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 [^{o}C]	45	44
Crystallization temperature during cooling T_c [^{o}C]	180	180
Crystalline melting point T_m [^{o}C]	224	224

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

2.4. Vegetable oil-based polyols.

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

A lot of scientists investigate the possibility to utilize the vegetable oil in the field of polymers [112–115]. Polyols based on the oils are characterized by a wide range of the molecular weight of the oligomers and usually substantial branching degree [116] what makes them suitable for the polyurethane foams industry. Non-food oil derivatives such as soybean oil [117–124], rapeseed oil [125, 126], palm kernel oil [127, 128], cottonseed oil [111, 129], castor oil [130–132] and many others are investigated on a large scale by scientists in the field of polymers. Wise prices and freely availability of soybean oil, palm oil, and rapeseed oil are the most attractive for large-scale industrial products. The results of the many types of research demonstrated that the vegetable oil polyols must be used in conjunction with petrochemical polyols in flexible foams, but they could be used as sole polyols in other applications. For the higher utilization in the polyurethane materials, natural oils have to be chemically modified due to the incompatibility in the polyurethane system [133]. This incompatibility results in a heterogeneous structure, physical instability, phase separation and in the sequel – poor properties [134].

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

The most commercially available polyols based on this type of vegetable oil constitute Honey Bee Biobased Soy Polyol [136] and Agrol [135]. Soyol bio-based polyols with a high bio-content ranging from 80.8% to 99%, revealed such properties as functionality ca. 2-3 and molecular weight between 1000-2000 Da. Their wide range of densities and reaction times make possible to their potential application as seating foam furniture, foam insulation, carpet backing, shoe soles or roof coatings. The soybean oil usage as polyol discloses cost less than the petroleum polyols which they replaced and their use benefits the agricultural business. Soybean polyols have very low volatile organic compounds content and produce less air pollution, acidification, smog formation and ecotoxicity versus petroleum. The researchers from Agrol team investigated that approximately 5.5 pounds of carbon dioxide equivalents are removed or prevented from entering the atmosphere for every pound of Agrol bio-based polyol [135]. They also claimed that 5% of petroleum-based polyether polyols replacement via soybean bio-based polyols will make it possible to 3.15 billion pounds of carbon dioxide removal from the atmosphere.

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

Castor oil is obtained from the seeds of Ricinus communis. This is a fatty acid and glycerin ester which ca. 90% of its fatty acids composed of ricinoleic acid. The seeds are highly toxic but the compounds responsible are not soluble in the oil. The oil was used in medicine and as a lamp oil but also as a precursor for plastics. The average functionality of castor oil is 2.7, so it is widely used as rigid polyol and coating. Because of low reactivity of castor oil, the focus has been directed to its derivatives. In the example, castor oil derivative with propylene oxide can be used in the polyurethane foam synthesis for adhesives, mattresses and automotive seats. Commercially available castrol oil-based polyols represent Polycin polyols (Vertellus), Lupranol Balance 50 (BASF) or Ulfcar Polem A (Nivapol). The advantages of the castor oil-based polyol employment in the polyurethane production constitute e.g. up to 25% of bio-mass in resulting polyurethane foam, less: energy and resource consumption, global warming potential and less SO_2 emission, so more ecologically friendly production processes [138]. The castor oil utilization characterized in the limited competition with food chain in comparison with other vegetable oils.

2.5. Bio-based diisocyanates for polyurethanes.

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

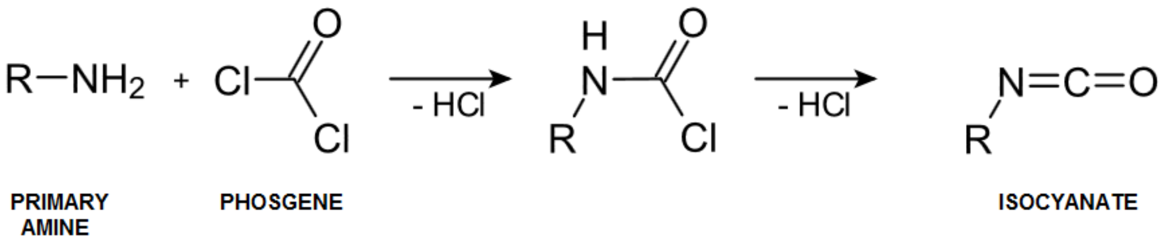


Figure 8 Scheme of the petrochemical-based isocyanate production process.

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

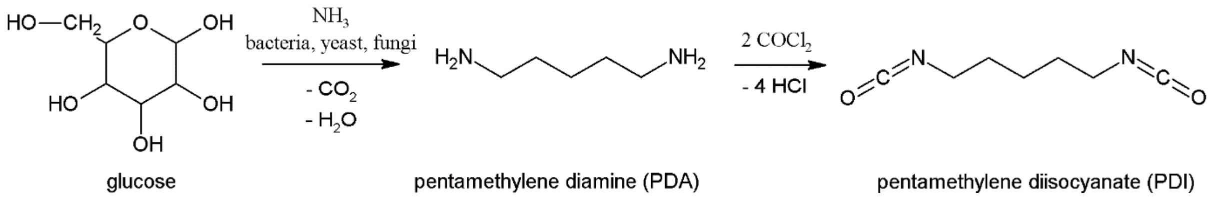


Figure 9 Scheme of the biotechnological production process of the pentamethylene diisocyanate (PDI).

Hojabri at al. [140] as first synthesized a new linear saturated terminal diisocyanate from oleic acid via Curtius rearrangement. The researchers established a synthesis of linear saturated terminal diisocyanate derived from fatty acids and prepared polyurethanes based mostly on lipid feedstock. The feasibility of utilizing this new diisocyanate for the production of polyurethanes was demonstrated by reacting it with commercial petroleum-based polyols and canola oil-based polyols, respectively. It was found that the fatty acid-based diisocyanate was capable of producing polyurethanes with comparable properties within acceptable tolerances [141–144].

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

2.6. Future perspective

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

There is a number of resources which can be successively used for the semi-product production for the polyurethanes syntheses. Extracted components from plant and wood biomass such as cellulose, hemicellulose or lignin, can be used as renewable carbon resources [1]. The difficulties in the catalyst selection for the biomass production and their conversion to the chemicals [146] pose one of the most important problems. Furthermore, a number of researchers investigated the problem associated with the catalysts deactivation and reuse possibility [147]. The catalysts usage in the biomass production and in the polymers synthesis provokes the several primary difficulties of good choice. The typical criteria of the good catalyst choice include the catalyst fouling, poisoning, and destruction [147]. The most important one can be caused by heavy oil components (asphaltenes) due to the bad process conditions [148]. Fouling is also caused by the destruction in overhigh temperature. Thermal decomposition of sugars leads to chemical substances which include the catalysts fouling [149]. These examples and others, make researchers work on the selective catalyst for the biorenewable chemicals [150].

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

The chemicals mentioned above constitute substrates for aliphatic polyester polyols production. In recent years the increasing interest is also visible in the term of aromatic monomers for polyurethane synthesis. The major sources for aromatic components derived from bioresources constitute carbohydrates and lignin. The most important examples, which revealed huge potential to polyester polyols and polyurethanes production processes employment, are 2,5-furandicarobxylic acid and vanillic acid [155]. The researchers investigated the polyesters based on aromatic bio-based monomer as furandicarboxylic acid as the bio-based alternatives of terephthalates. Such polymers as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) are thermoplastic polymers with excellent performance properties, but they all are petroleum-derived. Papageorgiou and co-workers [156–158] synthesized poly(butylene 2,5-furan dicarboxylate) (PBF) with the use of 2,5-furan dicarboxylic acid and 1,4-butanediol and studied its thermal properties with comparison with petrochemical poly(butylene terephthalate) and poly(ethylene terephthalate). Other compounds from aromatic bio-based monomers can be represented by 2,5-bis-(hydroxymethyl)furan [159], and 2,5-diformylfuran which are important monomers for polyesters, polyamides or polyurethanes. They are produced from 5-hydroxymethylfurfural, derived from dehydration of C6 sugars. Mou at al. [160, 161] investigated the synthesis of the three valuable monomers for polyurethane materials, 5,5′-dihydroxymethyl furoin (DHMF), 5,5′-bihydroxymethyl furil (BHMF), and 5,5′-bihydroxymethyl hydrofuroin (BHMH). Based on the obtained polyols the polyurethane materials were prepared and tested. The extensive literature on the bio-based polyester polyols, both types - aliphatic and aromatic, and constantly increasing a number of novel investigations proclaim the opportunity of fully bio-based polyols industrial employment in the future.

With triglycerides or fatty acid as starting materials, different chemical approaches have been explored to synthesize novel polyols and multi-isocyanate for polyurethanes. Cayli and Kusefoglu [162] synthesized soybean oil iodo isocyanate by reacting iodine isocyanate with double bonds in soybean oil triglycerides. Hojabri and co-workers [140] used oleic acid to produce 1,7-heptamethylene diisocyanate and 1,16-diisocyanatohexadec-8-ene. Oleic acid was first converted to diacids and then to diisocyanates. The researchers also prepared the polyurethanes for the comparative study of the materials properties. Polyurethanes based on 1,7-heptamethylene diisocyanate have similar physical properties as those made from petroleum-derived 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 for the polymer syntheses allowing for the complete replacement of the petrochemical based resources.

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Caption of Figures

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

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

Figure 3 Scheme of the polycondensation reaction.

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

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

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

Figure 7 Biosynthesis of the 1,4-butanediol.

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

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

Caption of Tables

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

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

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

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

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

Table 6 Purity differences between bio-based BDO and petrochemical-based BDO [99].

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