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Liquefaction of macroalgae *Enteromorpha* biomass for the preparation of biopolyols by using crude glycerol

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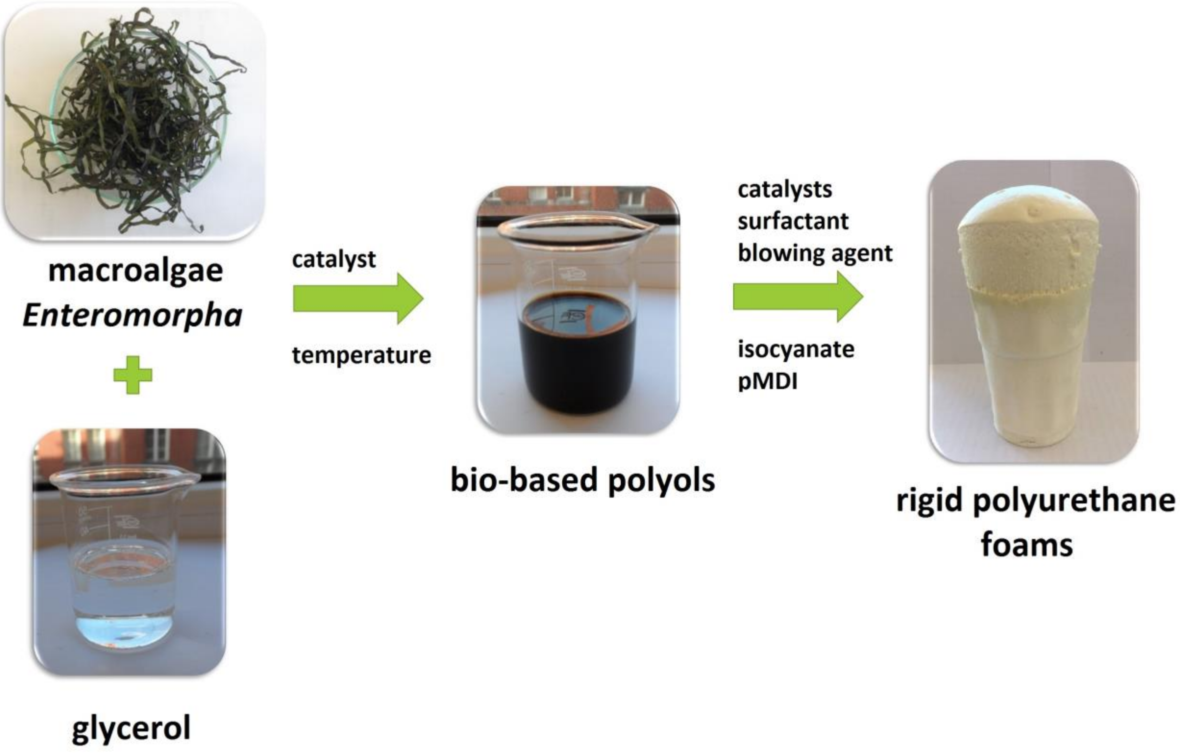
Graphical abstract



Highlights

- Biomass-based polyols were synthesized from macroalgae and crude glycerol.
- Six different biomass-based polyols were prepared.
- Bio-polyol displaying the most advantageous properties was obtained at 150°C.
- Using the biomass-based polyols, rigid polyurethane foams were fabricated.

Abstract

This article describes the liquefaction process of macroalgae Enteromorpha with the use of crude glycerol as a solvent and a reagent, aimed at obtaining of new bio-polyols, which are characterized with respect to their chemical structure, physical and thermal properties. Six different biopolyols were prepared. In order to optimize the liquefaction of algal biomass for the best bio-polyol properties, two catalysts (sulfuric or orthophosphoric acid) and three process temperatures (120-180°C) were applied. Bio-polyol displaying the most advantageous properties (hydroxyl number 590 mg KOH/g and 86% biomass conversion) was obtained at 150°C in the presence of sulfuric acid as a catalyst.

Keywords: Bio-based polyols, crude glycerol, algae liquefaction,

1. Introduction

Algae are a diverse group of tissueless, mainly autotrophic organisms. In general, they are photoautotrophs which utilize the energy of light to sustain biosynthetic processes. Algae present in water basins play the role of primary producers of organic matter and oxygen, while at the same time constitute a nutrition source for other organisms [1]. Algal biomass originating from the aquatic environment is a promising source of renewable energy and raw materials for the chemical industry. Algae have been utilized in the food and cosmetics industries for a long time [2,3]. At present, research related to this group of organisms focuses on the broader applications, mainly in connection to the alternative sources of energy [4].

The methods for converting algae into energy can be divided into two major groups, i.e. thermochemical and biochemical methods. Bio-oil, biochar and synthesis gas (syngas) are obtained as a result of thermochemical conversion. On the other hand, the biochemical conversion of algae leads to the production of biodiesel, biohydrogen, biomethane and bioethanol. The processes employed to manufacture the aforementioned products are presented in Fig. 1.

The most frequently applied processes in thermochemical conversion are gasification, pyrolysis and liquefaction. Minowa and Sawayama [6] described the gasification of microalgae *Chlorella vulgaris*. The algae containing 87.4% of water were converted into syngas with a high methane content (up to 37.5%) via catalyzed gasification at low temperature. The additional advantage of this method was the complete conversion of nitrogen from microalgae into ammonia that could be later used, in the form of reclaimed solution, as a nutrient for culturing the algae. Numerous publications about the algal biomass conversion via pyrolysis can be found in the scientific literature [7-9]. In this case, particular attention was paid to bio-oil produced via depolymerization and fragmentation of the main biomass components, i.e. cellulose, hemicellulose and lignin (the latter does not occur in algae). The described bio-oils displayed properties similar to those of crude oil and diesel fuel, while their combustion did not generate ash residue. Moreover, bio-oils generated from algal biomass had improved characteristics, i.e. higher nitrogen content and higher heating value compared to bio-fuels produced from lignocellulosic biomass [10]. Miao and Wu [11] obtained bio-oil via dry pyrolysis of microalga *Chlorella prothothecoides* at a temperature of 502 ^{o}C, with the conversion efficiency of 55.3%. The calorific value of this bio-oil equaled 39.7 MJ/kg. Zhang et al. [12] described the microwave-enhanced pyrolysis of algae that naturally occur in a lake in China. The authors stated that the described method is promising, while the optimal conditions of pyrolysis were as follows: microwave power source of 600W and the admixture of activated carbon (10%) added to powdered biomass as a catalyst and radiation absorbing agent. The heating value of bio-oil obtained under hydrogen and argon atmosphere reached 34.24 MJ/kg. Chaiwong et al. [13] described the conventional pyrolysis of microalgae *Spirulina*, and the main products of the reaction, i.e. bio-oil and biochar. Biochar, a substance obtained from the biomass with properties similar to those of charcoal, contains over 50% of carbon. It can be used not only as a renewable fuel, but also as a soil improving agent in agriculture. In the first stage of the study, the used biomass was characterized. Dry, powdered biomass was thermogravimetrically analyzed, and its composition was determined. The biomass mainly consisted of aliphatic hydrocarbons and a large amount of volatile compounds, which allowed the prediction of high efficiency of the bio-oil production via pyrolysis. The results of thermogravimetric analysis indicated that the decomposition of microalgal biomass occurs at a temperature lower than those of other types of biomass, such as corncobs, rice husks and wood shavings. Also, a relationship between the product-specific efficiency of pyrolysis and temperature was described. It was determined that the highest production efficiencies of bio-oil (ca. 45%), biochar (33%) and syngas (ca. 27%) occur at 550, 500 and 600 ^{o}C, respectively. The obtained bio-oil was characterized by the higher contents of water, oxygen and nitrogen in comparison to fossil fuels and bio-oil from wood biomass, while its calorific value was comparable to that of wood-derived bio-oil. The most investigated method for obtaining bio-oil from microalgae is hydrothermal liquefaction in supercritical water [14]. Its main advantage is the use of wet algal biomass, which has a positive economical effect and significantly simplifies the whole process. Hydrothermal liquefaction in supercritical water uses only 12% of energy that would have been needed to dry the algal biomass. The procedure is based on the decomposition and conversion of biomass (from 5 to 20%) in supercritical water at a temperature of 280-370^{o}C and a pressure of 10-25 MPa. In the published studies, the method was mostly applied at the established temperature for 60 min. Although, the reaction can be run for shorter time periods at increased temperatures to obtain higher efficiency of the process. For example, Yu et al. [15] produced a bio-oil with the efficiency of 39.4% for the process parameters equal 280 ^{o}C and 120 min, while Garcia Alba et al. [16] achieved the efficiency of nearly 50% for the conversion lasting only 5 min at a temperature of 375^{o}C. The process was conducted in the presence of either homogeneous catalysts, such as Na_2CO_3 and KOH, or heterogeneous catalysts, e.g. zeolites, and Pt, Pd or Ru deposited on activated carbon. As a result of the conversion, a bio-oil and solid, liquid and gaseous by-products were obtained . The bio-oil composition has been partially determined by using gas chromatograph and three classes of compounds were distinguished, namely, lipid derivatives, the derivatives of simple proteins, and water insoluble compounds (e.g. asphaltenes). The high nitrogen content (5-7%) in the produced bio-oil is problematic because large amounts of NO_x compounds will be generated in the case of that bio-oil combustion [17]. The thermochemical liquefaction of algae can also be conducted in organic solvents. Duan et al. [18] compared the conversion efficiencies of bio-oil from microalga *Chlorella pyrenoidosa* that were obtained with the use of ten organic solvents and water. The theoretical framework of this study was based on the fact that liquefaction in water results in the conversion of only 40% of carbon and 35% of hydrogen present in raw material into oil. Moreover, the bio-oil obtained due to conversion in water usually contains a large amount of oxygen, which lowers its calorific value and decreases its stability during storage. The application of organic solvents, which are characterized by lower values of dielectric constant, enables the dissolution or stability of non-polar intermediate products, and thus a better efficiency of the process. According to the authors, ethanol is the most suitable solvent for using in thermochemical liquefaction of microalgae because of the high efficiency of bio-oil production. In addition, ethanol can be obtained from the same raw material via biochemical conversion.

One of the newest ideas for the utilization of algal biomass is the preparation of bio-based polyols for the synthesis of polyurethane foams. The algae-derived oil is characterized by the properties similar to those of plant oils that have been used for many years as a substrate in the synthesis of biopolyols [19-21]. Pawar et al. [22] reported on the synthesis of biopolyol derived from algae from the genus *Chlorella*. The synthesis proceeded via oxidation with hydrogen peroxide and acetic acid, followed by the epoxide-ring opening reaction with the use of lactic acid or ethylene glycol. The obtained biopolyols were used to synthesize rigid PUR foams whose properties were similar to those of foams made from crude oil-derived polyols. Kim et al. applied a different approach to the synthesis of biopolyols from algae, i.e. [23] solvothermal liquefaction of microorganisms in polyethylene glycol and glycerol in the presence of sulfuric acid as a catalyst. The authors underlined that algae are a promising raw material for liquefaction because they do not contain lignin. Most of biomass types contain lignin which makes the liquefaction process more difficult. Moreover, microalgae contain a relatively high amount of free fatty acids which can be easily converted into monoglycerides. Such monomers can be used later for the synthesis of polyurethanes. In this study, the effect of specific reaction parameters, i.e. the ratio of polyethylene glycol to glycerol, temperature, reaction time, and the amount of biomass and catalyst on the properties of the final product was investigated. The following conditions have been described as optimal: the PEG/glycerol ratio of 6:4; reaction temperature of 190 ºC; reaction time of 60 min; 5 wt% of catalyst; and 20% of biomass.

Under these conditions, a biopolyol had been produced that was characterized by the hydroxyl and acid numbers of 650 and 9 mg KOH/g, respectively. The biomass conversion reached 88.5%.

In the present work, macroalgal biomass consisting of the genus *Enteromorpha* underwent liquefaction with the use of crude glycerol as a solvent. The influence of various parameters (reaction time, temperature and catalyst type) on the liquefaction efficiency was investigated. The process parameters were optimized, and the obtained bio-based polyols were characterized. The method for the synthesis of rigid polyurethane foams by using the produced biopolyols is described. The basic mechanical characteristics of the foams were also determined.

2. Experimental

2.1. Materials

Bio-based polyols were synthesized by the liquefaction of macroalgae from the genus *Enteromorpha* with purified crude glycerol. The algal biomass was collected in the Gulf of Gdansk (Baltic Sea). The refined crude glycerol was acquired from Bio-Chem Sp. z o.o. (Poland). The water content of the solvent was lower than 0.5 wt%, solvent density was 1.26 g/cm^3, and its hydroxyl number was 1000 mg KOH/g. The liquefaction process was catalyzed by a 95% aqueous solution of sulfuric(VI) acid, or an 85% aqueous solution of phosphoric acid, both purchased from Avantor Performance Materials Poland SA.

In order to synthesize polyurethane foams, the commercially available polyol Rokopol G441 and/or the biopolyol described in point 2.2 (coded S150) were used. Rokopol G441, a glycerine-based polyoxyalkylenetriol produced by PCC Rokita SA (Poland), is characterized by the hydroxyl number of 345 mg KOH/g and water content below 0.1%. The water content and the L_{OH} value of biopolyol S150 were 1.2% and 590 mg KOH/g, respectively. Polymeric methylene diphenyldiisocyanate (pMDI) was supplied by Borsodchem (Hungary). The content of free isocyanate groups in pMDI was 31.5%. Tin(II) 2-ethylhexanoate produced by Sigma Aldrich, and tertiary amines Dabco® 33LV and Dabco® 1027 (Air Products Europe Chemicals BV) were used as catalysts. Tegostab® B 8465 (Evonik Industries AG) was employed as a stabilizer of porous structure. Solkane® 365/227 (Solvay Chemicals) served as a physical blowing agent.

2.2. *Preparation of bio-based polyol*

Prior to liquefaction, algae were washed with water to remove inorganic salts, then dried and ground in a mill in order to increase the surface area of biomass and facilitate liquefaction. As mentioned before, bio-based polyols were synthesized by liquefaction of algae with purified crude glycerol. The mass ratio of solvent to biomass was 20:1. In order to accelerate the process, the catalyst (3 wt%) was added to the reaction mixture. The individual reactions were run at 120, 150 and 180°C for 5 h, with samples being collected every hour. The obtained polyols were neutralized with a 67% aqueous solution of sodium hydroxide, and then dried under vacuum.

2.3. *Preparation of rigid polyurethane foams*

Rigid polyurethane foams were obtained via a one-step method in a two-component system with the NCO/OH ratio of 2:1. The first component was prepared by mixing Rokopol G441 and biopolyol S150 (see chapter 2.2) at different weight ratios (100/0, 85/15, 70/30), and then adding catalysts, surfactant and blowing agent. The isocyanate pMDI was added to the prepared polyol mix at previously established mass ratio, and the reaction mix was stirred at 3000 rpm for 10 s. Next, the obtained foams were cured at 60ºC for 24 h. The detailed foam formulations are shown in Table 1.

2.4. *Characterization of bio-based polyols and rigid polyurethane foams*

The hydroxyl number of bio-based polyol was determined according to the standard PN-93/C-89052/03. Samples of 0.5 g were placed in 250 cm^3 Erlenmeyer flasks containing the acetylating mixture. Next, the samples were heated for 30 min, and 1 ml of pyridine and 50 ml of distilled water were added to each flask. Finally, the resulting mixture was titrated with a 0.5 M KOH solution in the presence of phenolphthalein until the solution turned pink. The hydroxyl values were determined according to formula (1):

$$\mathrm{HV} = \frac{56,1 \cdot (C_{\mathrm{KOH}} \cdot V_{\mathrm{KOH}})}{m_p} \quad (1)$$

The acid value of the prepared polyol was determined according to the standard PN-EN ISO 14104:2004. Samples of 1 g were placed in 250 cm^3 Erlenmeyer flasks. Next, 20 ml of acetone was added into each flask and the samples were stirred until complete dissolution of the reagents. Such prepared mixtures were titrated using a 0.095 M KOH in the presence of phenolphthalein until the solution turned pink. The acid values were determined according to formula (2):

$$\mathrm{AV} = \frac{56,1 \cdot (C_{\mathrm{KOH}} \cdot V_{\mathrm{KOH}})}{m_p} \quad (2)$$

where C_{KOH} is the concentration of KOH, V_{KOH} is KOH volume used for titration, and m_p stands for the sample mass.

The extent of liquefaction was evaluated on the basis of the percentage of residual biomass. The liquefaction product was diluted (more than 10 times) with methanol, stirred with a magnetic stirrer for 4 h, and then filtered through the filter paper under vacuum. Solid residue was washed with methanol and then dried in the oven at 100°C to a constant weight. Biomass conversion was calculated using the following equation (3):

$$\mathrm{BC} = 100 - \frac{m}{m_o} \cdot 100\% \quad (3)$$

where m is the weight of residual biomass, and m_o is the initial weight of biomass.

The viscosity values of the prepared polyols were determined by using an R/S Portable rheometer. The analysis was conducted at 25°C for the shear rates varying from 1 to 100 s^{-1}. The obtained results were analyzed by employing Rheo 3000 computer software.

FT-IR spectrophotometric analysis was performed in order to determine the structure of the bio-based polyols. The analysis was performed at a resolution of 4 cm^{-1} using a Nicolet 8700 apparatus (Thermo Electron Corporation) equipped with a snap-Gold State II, which allows for making the measurements in the reflection configuration mode.

The water content of the produced biopolyols was assessed by using Karl-Fischer titration. The samples were diluted with methanol and titrated with Fischer reagent. The measurements of biopolyol density were performed at 25°C by means of a pycnometer.

Oxidation Onset Temperature (OOT) Test. The OOT test was used to evaluate the effectiveness of antioxidants in biopolyols. The tests were performed under oxygen atmosphere using a NETSCH DSC F3 differential scanning calorimeter. The oxygen flow was maintained at 20 mL/min.

The biopolyol samples (12 mg each) were placed in open aluminum pans and heated from 35 to 250 °C, at a heating rate of 10°C/min. All the experiments were performed at least in duplicate. The OOT values were obtained by using NETZSCH Proteus Thermal Analysis software.

The thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 apparatus using 5 mg samples within the temperature range 100–500ºC under nitrogen atmosphere, at a heating rate of 15 °C/min.

The values of bulk density of the prepared foams were determined in accordance with the standard PN-EN ISO 845:2000, as the ratio of sample mass to sample volume. The sample mass was measured with an electronic analytical balance, with an accuracy of 0.1 mg. The sample volume was determined by measuring the dimensions of cylinder-shaped samples with an electronic caliper, with an accuracy of 0.1 mm.

The compressive strength of PUR samples was estimated in accordance with the standard PN–EN ISO 604:2006. The cube-shaped samples with the dimensions of 50x50x50 mm^3 were measured with a slide caliper, with an accuracy of 0.1 mm. The compression test was performed on a Zwick/Roell tensile tester at a constant speed of 10 mm/min to 40% deformation.

Dynamical mechanical analysis (DMA) was performed by means of a Q800 DMA instrument (TA Instruments) at a heating rate of 4 ºC/min, deformation frequency of 10 Hz, and for the temperature range from 25 to 270°C. The cylindrical samples were 13 mm long and 2.6 mm in diameter.

3. Results and discussion

3.1. Characterization of bio-based polyols

As described above, liquefaction was conducted at three different temperatures and with sulfuric(VI) acid and ortophosphoric acid as catalysts. The variation of hydroxyl number over time for the two catalysts used is presented in Fig. 2.

It is noticeable that the hydroxyl number values decrease with increasing temperature and reaction time for both catalysts. The polyols obtained after a 5 h liquefaction were characterized by hydroxyl numbers in the range between 320 and 950 mg KOH/g. The high hydroxyl numbers resulted from the presence of solvent, namely, glycerol containing three hydroxyl groups. A decrease in hydroxyl number during liquefaction was caused by the reactions of hydrolysis and alcoholysis. The reduction in hydroxyl value with increasing reaction time has been also reported by others [24]. When a significantly excessive amount of glycerol is used as a solvent during liquefaction, the condensation of glycerol may occur. Possible products, such as polyglycerol and water, can decompose the long chains of biomass [25]. This may in turn result in a temporary increase in hydroxyl number. Based on the obtained results, it was found that the use of sulfuric acid as a catalyst resulted in a more rapid reaction compared to the reaction catalyzed by ortophosphoric acid.

In Fig. 3 the changes in biomass conversion versus reaction time were plotted for the two catalysts used.

In the first stage of liquefaction, biomass undergoes degradation via decomposition to low-molecular-weight compounds, which react with the solvent. This results in a decrease of residual biomass content. Degradation determines the first stage of liquefaction, leading to the fast increase of process efficiency. In the following stages, the degradation products undergo repolymerization, which manifests itself by the presence of insoluble material composed of glycol or glycerol glucosides and xylosides as well as decreased rate of biomass conversion [26,27]. Based on the comparative analysis of biomass conversion to biopolyols with acid catalysts, i.e. sulfuric(VI) and ortophosphoric acids, it should be noted that the use of sulfuric acid resulted in a higher conversion, with a maximum of 90% reached after 5 hours. In Fig. 4 the variation of acid number over time is presented. The results of analysis demonstrate that the acid number of the obtained biopolyol mainly depends on the reaction temperature, and it is higher than those of commercially available polyols (max. 1 mg/g of sample). This finding is related to the application of acidic catalyst during liquefaction. An increase in the acid number value is connected to the increased efficiency of biomass conversion, which is accompanied by the formation of acidic reaction products. It was noted that in the case of synthesis catalyzed by sulfuric acid at the temperatures of 120 and 150°C, the acid number values did not vary with time. However, during the reaction conducted at the highest temperature (180°C) these values significantly increased over time, which was most likely connected to the abrupt increase in biopolyol viscosity followed by the elevated concentration level of acidic compounds in the sample.

Considering the results on the hydroxyl and acid numbers, and biomass conversion, it can be stated that sulfuric acid has a better catalytic effect on liquefaction than ortophosphoric acid. A similar conclusion has been reached by Pan et. all [28]. Based on rheological analysis, the viscosity values, flow curves and fitted mathematical models were obtained for the samples of polyols that had formed during the liquefaction catalyzed by sulfuric acid. Only the samples of polyols produced at the temperatures of 120 and 150°C were analyzed. The polyol sample obtained at 180°C was excluded from further analysis because of its high viscosity and thus unsuitability for commercial applications.

The flow curves of biopolyols obtained at different temperatures are shown in Fig. 5. The presented data indicates that polyols resulting from the liquefaction of algal biomass display the characteristics of a non-Newtonian fluid, as evidenced by nonlinear relationship between the shear stress and shear rate [29, 30]. The tangent of an initial angle of flow curve in relation to X axis is closely connected to the fluid viscosity, and can be described by the following equation [31]:

$$\tan\alpha = \eta_0 (4)$$

A decrease in the tan α value with the increasing temperature of liquefaction causes a decrease in fluid viscosity. The maximum shear stress values measured at 25°C in the samples obtained at 120°C and 150°C were 437.5 and 319.4 Pa, respectively. At 50 °C, the respective values reached 95.5 and 53.4 Pa.

The viscosity curves of biopolyols obtained at different temperatures and the fixed reaction time of 6 h are presented in Fig. 6. Based on the measurements performed at 25 and 50 °C, it was determined that the viscosity of polyol produced at 120°C deceased with increasing shear rate. This finding proves that the analyzed fluid has a pseudoplastic character. With increasing shear rates, the asymmetrical molecules in pseudoplastic fluids become gradually ordered. For the established flow, the molecules are parallel to the flow direction. At first, the viscosity of such fluid abruptly decreases. Then, the viscosity decreases at a lower rate until the molecules lined along the flow direction cannot be packed any closer to each other. Pseudoplastic fluids are considered synonymous for shear-thinning fluids because their viscosity decreases with increasing shear rate [32]. In the case of polyol obtained at 150 °C and tested at 25 and 50 °C, two types of fluid characteristics were observed in dependency on the shear rate. For the shear rates between 0-25 s^{-1}, the viscosity values increased, while for the shear rates above 25 s^{-1}, they remained constant. Within the lower range of shear rates, the viscosity curve of polyol resembles the shear-thinning curve of pseudoplastic fluid. For the shear rates above 25 s^{-1}, the polyol has a non-Newtonian character because its viscosity does not change with increasing shear rate.

The liquefaction of algal biomass by using waste glycerol resulted in the products that fit the Herschel–Bulkley and Ostwald de Waele rheological models. The equations were analyzed by means of Rheo 3000 software. The models and equation parameters obtained for the biopolyols are listed in Table 2. Based on the stability index R (for the values closest to 1), it was established that the Ostwald de Waele model is most suitable for the biopolyols obtained at 120 °C (tested at 25 and 50 °C) and 150 °C (tested at 25 °C). In the case of biopolyol S150°C tested at 50 °C, the Herschel-Bulkey model turned out to be the best fit. The flow behavior index in the Ostwald de Waele equation fitted to the data on biopolyol S120 was less than 1, which confirms the pseudoplastic character of this fluid and indicates its shear-thinning properties. In the case of biopolyol S150°C, the flow behavior index was greater than 1, which confirms the pseudoplastic character of this compound and points to its shear-thickening features.

Fig. 7 presents FTIR spectra of biopolyols obtained via reactions catalyzed by sulfuric acid at the temperatures of 120 and 150 °C, and the reaction components, i.e. glycerol and algal biomass. The band visible at 3300 cm^{-1} is characteristic for OH-stretching vibrations [33]. The absorption bands at 2940-2870 cm^{-1} can be attributed to symmetrical and asymmetrical CH-stretching vibrations originating from the CH_2 groups present in aliphatic chains, or the CH_3 groups [34]. The signal observed at 1720 cm^{-1} can be assigned to unconjugated C=C stretching bonds in the products of biomass degradation that had occurred at high temperatures [35]. The absorption bands at 1420-1333 cm^{-1} are attributable to CH_2 and HOC in-plane bending vibrations, while those at 1210 cm^{-1}, to CO and C=O stretching vibrations [36, 37]. The bands characteristic for the ether group vibrations are visible in the wavenumber range of 1170-980 cm^{-1} [38]. The remaining signals at 914-840 cm^{-1} can be possibly connected to C-H bonds that are present in the biomass structure [39].

FTIR analysis was used for qualitative purposes, however, a relationship between the band intensity assigned to the final products (i.e. S120 and S150) and the band intensity of raw materials should also be noted. In the polyol spectra, mainly the absorption bands characteristic for glycerol can be observed. This is due to the excess amount of solvent used during liquefaction.

The values of density, water content and pH of biopolyols obtained at the temperatures of 120 and 150 °C are listed in Table 3. It is noticeable that the reaction temperature did not significantly affects the product density. The water contents of the biomass used, glycerol and sulfuric acid were known (10, 0.5 and 5%, respectively) thus it was possible to calculate the theoretical water content of the produced biopolyol, i.e. ca. 1.06%. However, the products of the reactions conducted at 120 and 150°C contained 1.9 and 4.21% of water, respectively. The observed difference between the real water content and its calculated value is related to water formed as a by-product of liquefaction [40]. Moreover, there is an indication of another relationship, namely, an increase in water content of the product with increasing reaction temperature that can be connected to the higher efficiency of liquefaction. The results of Oxidation Onset Temperature (OOT) measurements in biopolyol samples are shown in Table 3. It was assumed that OOT is the point of intersection of two lines, i.e. the tangent line to the base line and the tangent line at the maximum rate point, the latter corresponding to the inflection point of oxidation peak. Based on the obtained results, it was established that the oxidative stability of biopolyols increases with increasing reaction temperature. During liquefaction, biomass decomposes to compounds with low molecular weights that react with the solvent, which in turn causes a decrease in the number of functional groups susceptible to oxidation.

The results of thermogravimetric analysis of biopolyols and raw materials are presented in Fig. 8 and Table 4. The thermal stability of liquefaction products increased with increasing reaction temperature. It was confirmed that the elevated reaction temperature results in a smaller amount of low-molecular-weight polyols displaying poor thermal stability, as previously observed in the case of

OOT data. The DTG curves of the analyzed biopolyols are positioned between the curves plotted for glycerol and algal biomass, which proves that algae liquefaction has taken place. The values of T_{max1} and T_{max2} for the obtained biopolyols are shifted towards higher temperatures, which is linked to better efficiency of liquefaction.

3.2. Mechanical properties of polyurethane foams

The values of bulk density, compressive strength, and glass transition temperature for the obtained rigid polyurethane foams are listed in Table 5.

There is a strong relationship between the bulk density and compressive strength of the analyzed rigid PU foams. It was determined that the compressive strength of the foam increases as its bulk density increases [41]. Due to this fact the foam formulations (see Table 1) were specifically chosen to obtain the final materials with the same density. The biopolyol S150-containing systems required lower amounts of both catalysts and blowing agent compared to the standard foam originating from crude oil-based polyol. This finding proves higher reactivity and the influence of biopolyol-derived water on the foaming process. In PU systems, water reacts with isocyanate groups, resulting in CO_2 formation and subsequent foaming of polyurethane [42]. A small increase in compressive strength was achieved by replacing crude oil-based polyol with bio-based polyol. In addition, an increase in the biopolyol share in the foam formulations resulted in a higher temperature of glass transition and a shift of storage modulus towards higher temperatures, as illustrated in Fig. 9. This is most likely due to higher cross-linking density of biopolyol-containing polyurethanes in comparison to those derived from crude oil-based polyol Rokopol G441.

4. Conclusions

The properties of algae-based biopolyols and subsequently produced rigid polyurethane foams confirmed that the application of algal biomass liquefaction for the preparation of novel polyols is possible. In this work, the effect of temperature and catalyst type on the properties of the obtained biopolyols was also investigated. Based on the values of hydroxyl and acid numbers, and biomass conversion calculated for the reaction of macroalgae *Enteromorpha* liquefaction with the use of crude glycerol, it was determined that sulfuric(VI) acid is a better catalyst than ortophosphoric acid. Further analysis consisting of FTIR spectroscopy, and the measurements of rheological and thermal properties revealed that the optimal liquefaction conditions are a 5-h reaction time and a temperature of 150 ºC. The biopolyols obtained under optimal conditions were characterized by a hydroxyl number and viscosity at 25 ºC of 590 mg KOH/g and of 1.6 Pa·s, respectively, while biomass conversion reached 86%. The rheological data were fitted to the Ostwald-de Waele and Herschel Bulkley models, which enabled the classification of biopolyol S150 as a Newtonian fluid for the shear rates larger than 25 s^{-1}. Biopolyol S150 was used in the preparation of rigid PU foams whose mechanical characteristics were later assessed. It was determined that the admixture of biopolyol resulted in the shift of glass transition temperature towards higher temperatures, and increased compressive strength. In summary, the presented results show that the application of biopolyols derived from macroalgae liquefaction has a high potential. The liquefaction of algal biomass positively affects the ecological and economical aspects. The use of crude glycerol and macroalgal biomass collected from beaches results in lowered production costs of reactive compounds that can be applied in polyurethane technology.

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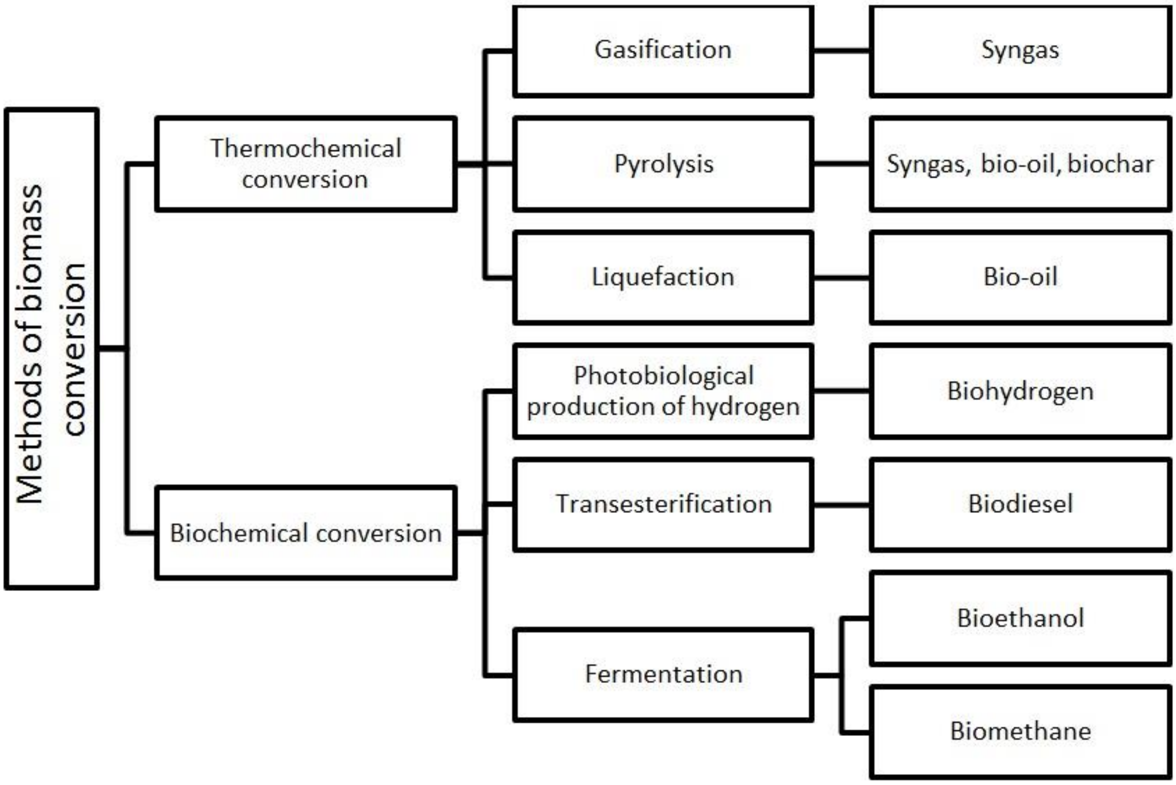

Fig. 1. Methods of algal biomass conversion. [5]

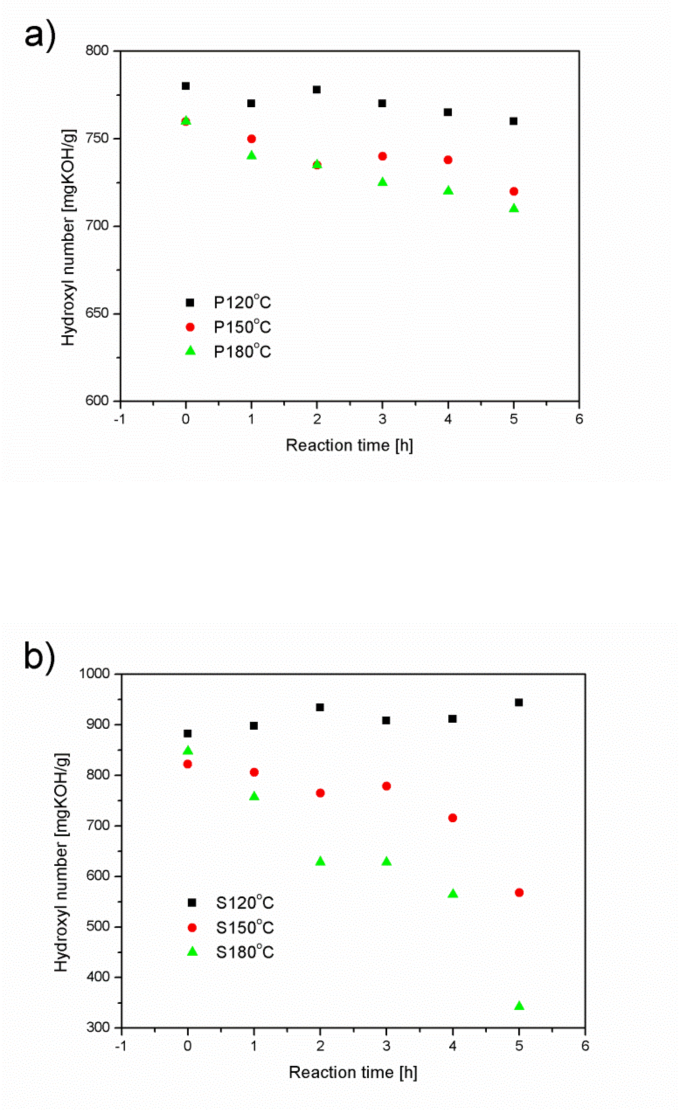

Fig. 2. Variation of hydroxyl number values during the reaction catalyzed by a) ortophosphoric acid, and b) sulfuric(VI) acid.

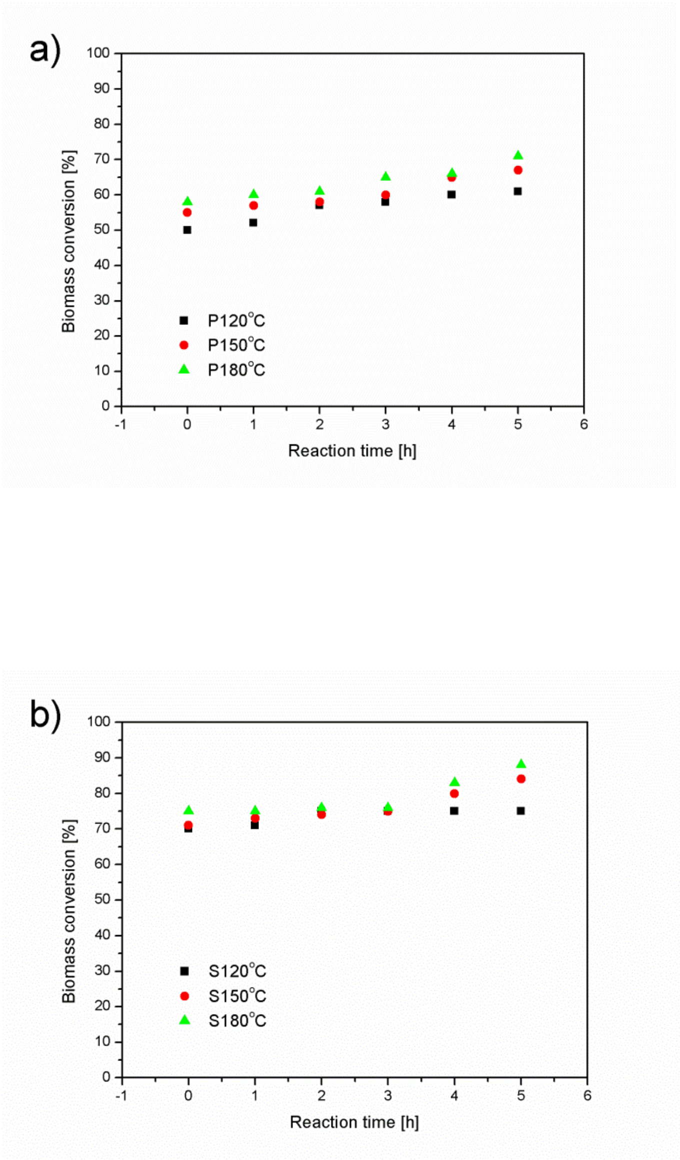

Fig. 3. Changes in biomass conversion during liquefaction catalyzed by a) ortophosphoric acid, and b) sulfuric(VI) acid

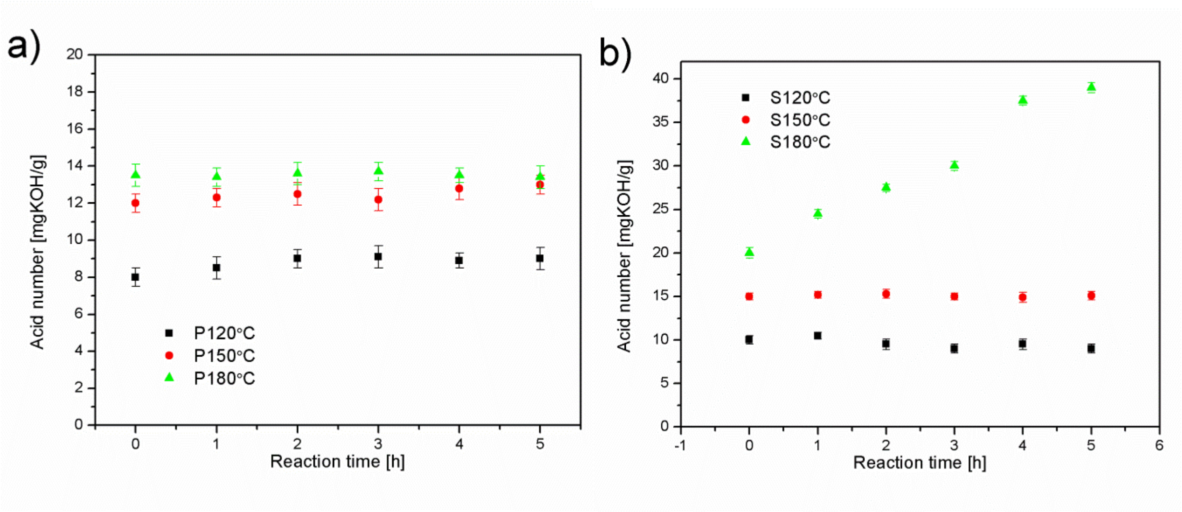

Fig. 4. Variation of acid number values during liquefaction catalyzed by a) ortophosphoric acid, and b) sulfuric(VI) acid.

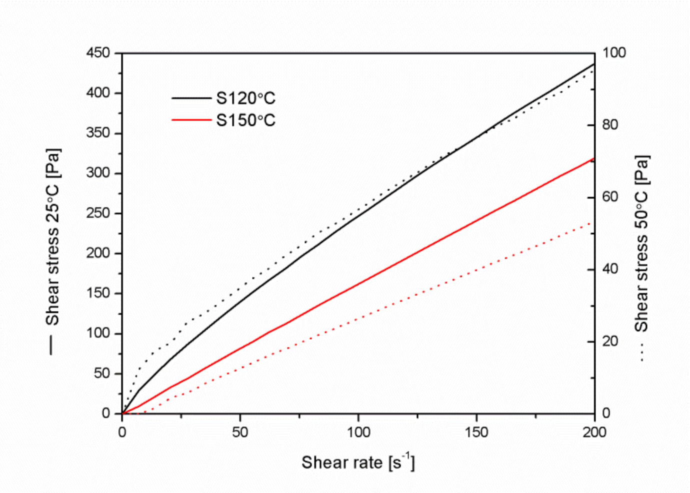

Fig. 5. Flow curves for biopolyols obtained with the use of sulfuric acid at the temperatures of 120 and 150°C.

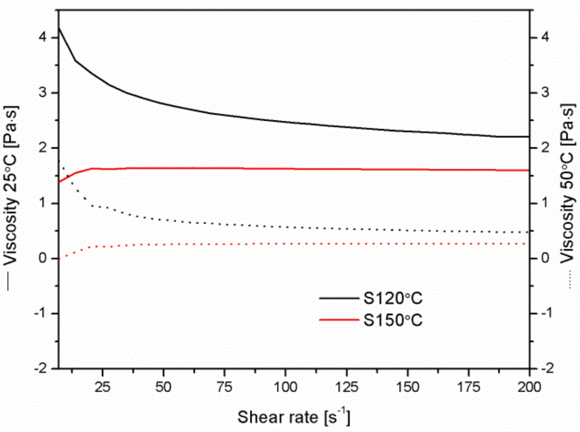

Fig. 6. Viscosity curves of biopolyols obtained via liquefaction conducted at 120 and 150°C for 6 h, with the use of sulfuric acid as a catalyst.

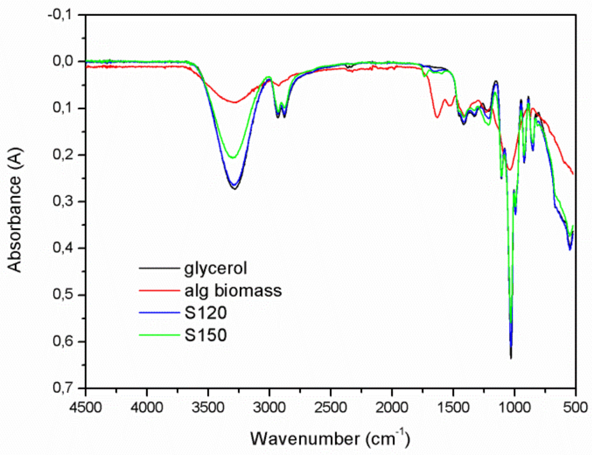

Fig. 7. FTIR spectra of biopolyols and the components used in their synthesis.

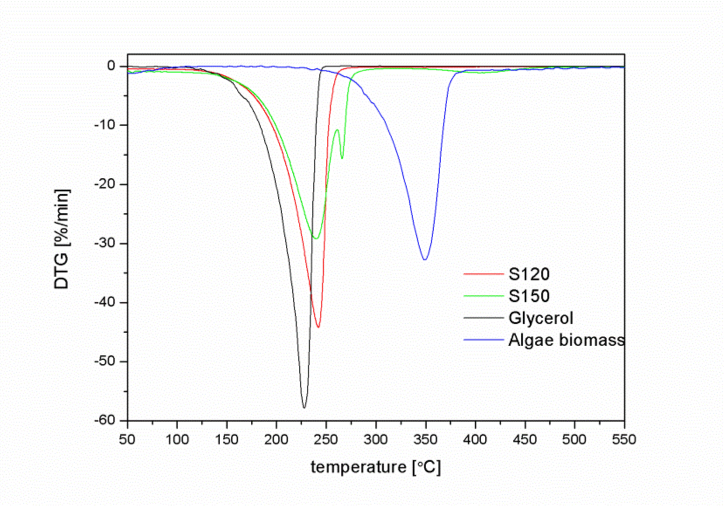

Fig 8 Differential thermogravimetric curves for glycerol, algal biomass and bio-based polyols.

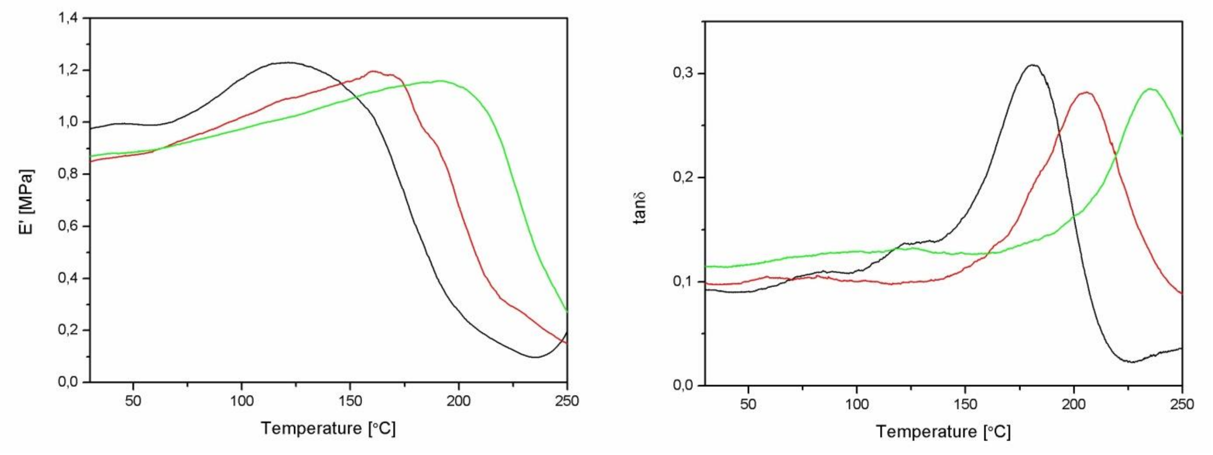

Fig. 9. Storage modulus (E′) and damping factor (tanδ) as a function of temperature plotted for rigid polyurethane foams.

Table 1. The composition of reaction mixture.

	Weight ratio of Rokopol G441 to biopolyol S150		
	100/0	85/15	70/30
	Foam’s symbol		
	100G0B	85G15B	70G30B
	Mass of the component [g]		
Component 1			
Biopolyol S150	0	2.4	4.5
Rokopol G441	17.3	13.7	10.5
Tegostab® B 8465	0.26	0.26	0.26
Tin(II) 2-ethylhexanoate	0.17	0.15	0.12
Dabco® 33LV	0.17	0.15	0.12
Dabco® 1027	0.17	0.15	0.12
Solkane® 365/227	4	3	3
Component 2			
pMDI	27.9	30.4	31.9

Table 2. Rheological models of the obtained biopolyols.

The Ostwald-de Waele linear functions				
Sample	Function	K [Pa·s^n]	n[-]	R^2
S120°C_25°C	$y=5.83\cdot x^{0.8079}$	5.8334	0.8079	0.9991
S120°C_50°C	$y=2.94\cdot x^{0.6436}$	2.9388	0.6436	0.9986
S150°C_25°C	$y=1.46\cdot x^{1.0189}$	1.4626	1.0189	0.9997
S150°C_50°C	$y=x^{0.7043}$	1	0.7043	0.9733

The Herschel Bulkley linear functions					
Sample	Function	τ_0 [Pa]	μ_{om}[Pa·s^n]	n[-]	R^2
S120°C_25°C	$y=6.17+4.59\cdot x^{0.8529}$	6.1735	4.5881	0.8529	0.9959
S120°C_50°C	$y=6.58+1.17\cdot x^{0.8129}$	6.5841	1.1666	0.8129	0.9973
S150°C_25°C	$y=1.67\cdot x^{0.991}$	0	1.6663	0.991	0.9995
S150°C_50°C	$y=0.21\cdot x^{1.0477}$	0	0.2053	1.0477	0.9978

Table 3. The properties of biopolyols obtained via liquefaction catalyzed by sulfuric acid.

Property	Sample	
	S120	S150
Density [g/cm^3]	1.38	1.4
Water content before drying [%]	1.9	4.21
Water content after drying [%]	1.1	1.2
OOT [°C]	153	165

Table 4. Thermogravimetric analysis of biopolyols, glycerol and algal biomass.

<table>
<tr><th rowspan="2">Sample</th><th colspan="7">Temperature °C</th></tr>
<tr><th colspan="3">T_5</th><th>T_{10}</th><th>T_{50}</th><th>T_{max1}</th><th>T_{max2}</th></tr>
<tr><td>S120</td><td colspan="3">130</td><td>174</td><td>230</td><td>242</td><td>-</td></tr>
<tr><td>S150</td><td colspan="3">159</td><td>183</td><td>233</td><td>239</td><td>266</td></tr>
<tr><td>Glycerol</td><td colspan="3">167</td><td>182</td><td>218</td><td>228</td><td>-</td></tr>
<tr><td>Algal biomass</td><td>254</td><td>295</td><td>347</td><td>-</td><td colspan="3">349</td></tr>
</table>

Table 5. Mechanical properties and the glass transition temperatures of rigid polyurethane foams.

Sample	Properties		
	Bulk density [kg/m^3]	Compressive strength [kPa]	Glass transition temperature [ºC]
100G0B	59±1.2	355±7.6	184
85G15B	61±1.4	358±6.8	205
70G30B	60±1.2	364±5.7	235