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MICROWAVE ASSISTED LIQUEFACTION WITH CRUDE GLYCEROL AS A POTENTIAL METHOD OF BREWER'S SPENT GRAIN UTILIZATION

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Abstract. Brewer's spent grain was applied as a low-cost industrial type of lignocellulose biomass in a liquefaction process with crude glycerol. Influence of the reaction time and solvent:biomass ratio on the efficiency of the process, chemical structure and basic properties of obtained biopolyols was analyzed. Spectroscopic studies of the prepared polyols and solid residues shed light on the biomass degradation mechanism through application of microwaves and further reaction of degradation products with solvent particles.

Keywords: bio-based polyols, biomass liquefaction, brewer's spent grain, crude glycerol, microwave radiation.

1. Introduction

Liquefaction, next to combustion, pyrolysis and gasification, is one of the most common methods of biomass utilization. It is a very promising alternative for production of biopolyols, which could find application in production of plastics, mainly because of the renewable character of the biomass. According to Yamada *et al.* [1, 2] reaction pathways of biomass liquefaction reactions with different alcohols containing multiple hydroxyl groups (ethylene glycol, polyethylene glycol, glycerol) are quite similar and are based on cellulose solvolysis into glucose particles and other low molecular weight derivatives, which can be soluble in water or other solvents. These compounds can subsequently re-polymerize with themselves or react with solvent leading to oil-like compounds or mixture of particular compounds with vast range of molecular weight [3]. Thanks to the high content of hydroxyl groups present in the structure, they can be further successfully incorporated into production of different polymeric materials, such as polyesters, epoxy resins, phenolic resins or polyurethanes [4-6].

Proper selection of solvent for liquefaction process is crucial, because of its excess used in this process. Thus, it needs to guarantee possibly fast and effective decomposition of the material, but also has to show satisfactory properties as a potential polyol. That is why so many compounds have been analyzed as potential solvents for biomass liquefaction. According to literature data, among already investigated substances are phenolic compounds [7-9], supercritical ethanol [10] or subcritical water [11]. Nevertheless, two most popular compounds among the researchers are polyethylene glycol and glycerol, often used in combination in order to provide the proper degree of branching of resulting polyol [12-14].

Other consequence of solvent excess in the process is its very large use, which noticeably increases the cost of resulting polyols and successfully limits the application of biomass liquefaction in their manufacturing. Therefore, scientists and industry are very interested in alternative solvents, based on waste materials or renewable resources, which will make this process economically feasible. Such investigations are also associated with the ongoing green chemistry trends and law regulations, such as directives of European Union. Crude glycerol obtained from biodiesel production can be employed instead of pure glycerol, which will obviously decrease the cost of final product, because of the noticeable difference in price of these materials [15]. Application of this waste material is very attractive as a potential way of enhancing the ecological and economical aspect of the biomass liquefaction. Also it is really an actual trend, only few literature reports regarding incorporation of crude glycerol into the process have been published during last couple years [16-19].

Among the investigated types of biomassare wood [20, 21], corn bran, corn stover or corncobs [22, 23], wheat straw [24], soybean straw [18], cork [25], bamboo residues [26-28], palm kernel cake [29] or biodiesel production solid residues [30]. Many researchers have

paid a lot of attention to the liquefaction of neat biomass components, such as cellulose or lignin for better understanding of the whole process [31-33].

In presented work brewer's spent grain (BSG) was used as an industrial type of biomass generated during beer production. BSG is the major by-product of the brewing industry, generated in the mashing process [34]. It stands for ~85 % of the total by-products of beer manufacturing and assuming that for each hectoliter of produced beer, 20 kg of malts are used (for the most popular type of beer – light lager, exceeding 45 kg for strong stouts), 6.2 kg of brewer's spent grain is generated. According to the 2012 edition of The Brewers of Europe Beer Statistics Report [35], ~40 billion liters of beer are produced annually in Europe, giving around 2.5 million tons of BSG, which can be the interesting alternative for other types of biomass in the liquefaction process.

2. Experimental

2.1. Materials

Bio-based polyol was synthesized by liquefaction of brewer's spent grain with the mixture of purified crude glycerol and 1,4-butanediol. BSG was obtained from EnergetykaZłoczew sp. z o.o. (Poland) and used as the industrial type of biomass. Prior to liquefaction, BSG was mechanically grinded in co-rotating twin-screw extruder at 393 K in order to increase the surface area of biomass and facilitate the liquefaction process.

Crude glycerol was acquired from Bio-Chem Sp. z o.o. (Poland), while 1,4-butanediol was acquired from BASF company (Germany). Water content of these solvents was lower than 0.5 and 0.05 wt %, respectively.

2.2. Preparation of Bio-Based Polyol

As mentioned before, bio-based polyols were synthesized by liquefaction of brewer's spent grain with the mixture of purified crude glycerol (GLY) and 1,4-butanediol (BDO). Mass ratio of GLY to BDO was 1:4 and a ratio of solvents to biomass varied from 8:1 to 10:1. Analyzed reaction times were 1, 2, 5 and 7.5 min. All experiments were carried out at 393 K using microwave radiation of 350 W.

2.3. Characterization

The liquefaction extent was evaluated on the basis of the residue percent. Product of the liquefaction was diluted (more than 10 times) by methanol, stirred with a magnetic stirrer for 4 h and then filtrated through the filter paper in vacuum. Solid residue was washed with methanol and then dried in the oven at 373 K to a constant weight. The residue percent was calculated according to Eq. (1):

$$\%_{residue} = \frac{m}{m_o} \cdot 100\% \qquad (1)$$

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

Hydroxyl number of bio-based polyol was determined according to PN-93/C-89052/03. Samples of 0.5 g were placed in 250 cm^3 Erlenmeyer flasks with the acetylating mixture. Next, it was heated for 30 min, then 1 ml of pyridine and 50 ml of distilled water were added. Finally, resulting mixture was titrated using 0.5 M KOH solution in the presence of phenolphthalein until the color of mixture changed to pink. Hydroxyl values were determined according to Eq. (2):

$$HV = \frac{56.1 \cdot (V_{KOH}^2 - V_{KOH}^1) \cdot C_{KOH}}{m} \qquad (2)$$

where C_{KOH} – concentration of KOH; V^1_{KOH} and V^2_{KOH} – volume of KOH used to titration of analyzed sample and blind test, respectively; m – mass of sample.

Acid value of prepared polyol was determined according to PN-EN ISO 14104:2004. Samples of 1 g were placed in 250 cm^3 Erlenmeyer flasks. Next, 20 ml of acetone was placed into a flask and samples were stirred until their dissolution. Such prepared mixtures were titrated using 0.095 M KOH in the presence of phenolphthalein until the color of the mixture changed to pink. Acid values were determined according to Eq. (3):

$$AV = \frac{56.1 \cdot (C_{KOH} \cdot V_{KOH})}{m} \qquad (3)$$

where C_{KOH} – concentration of KOH; V_{KOH} – volume of KOH used to titration; m – mass of sample.

FT-IR spectrophotometric analysis was performed in order to determine the structure of the bio-based polyol and solid residues. 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.

3. Results and Discussion

3.1. Effectiveness of the Process

Fig. 1 presents the effect of the reaction time and solvent:biomass ratio on the liquefaction effectiveness. It can be seen that a residue percent is decreasing with a reaction time; however the rate of decrease is slowing after 5 min of the reaction. Reason of this phenomenon is the shift of the balance between degradation and re-polymerization processes occurring during lignocellulose biomass liquefaction. Degradation results in biomass decomposition to simpler, low molecular weight compounds which are reacting with solvents, simultaneously reducing the residue percent. The opposite effect, production of insoluble material, occurs through re-

polymerization of various compounds, such as glycol or glycerol glucosides and xylosides [36, 37]. At the beginning of liquefaction, degradation is a main process occurring, which results in rapid decrease of residue percent, however at the later stages, rate of re-polymerization is gradually enhancing, because of the rapid increase in the concentration of small molecules in the reaction system [24]. As a result, the balance between these two processes is shifted towards re-polymerization, which causes a slower decrease of residue percent with the increasing reaction time.

Obviously, solvent:biomass ratio is an important factor of the process, which has been repeatedly proven in the literature [38].Generally the residue percent is decreasing with decreasing the share of biomass in the reaction mixture, especially in case of smaller values of solvent:biomass ratio, however at higher values its impact becomes hardly noticeable [39]. Actually, effectiveness of liquefaction may even slightly decrease with increasing the share of solvent, which in case of glycerol has been confirmed by other researchers [18, 39]. Presented data suggest that increasing the ratio to 10:1 shows unfavorable influence on the biomass conversion, however at longer reaction times, this effect becomes negligible. Such phenomenon might be related to the high dilution of the biomass "solution" in applied solvents, which slows down the liquefaction process.

3.2. FT-IR Analysis of Prepared Polyols

In Fig. 2 there are presented FT-IR spectra of polyols produced by changing the reaction time. A signal (**a**) characteristic for stretching vibrations of O–H groups was observed at 3300 cm^{-1} [40]. The bands (**b** and **c**) at 2870 and 2940 cm^{-1} were attributable to the symmetric and asymmetric stretching vibrations of C–H bonds in CH$_2$ groups present in aliphatic chains and CH$_3$ end groups [41]. The absorption maxima (**d** and **e**) around

1730 and 1660 cm^{-1} could be attributed to the stretching vibrations of unconjugated C=O bonds and C=C bonds in hemicellulose or in the products of cellulose degradation, which occurs during subjection to a microwave radiation [42]. The absorption bands (**f** and **g**) at 1430 and 1375 cm^{-1} can be associated with CH$_2$ and HOC in-plane bending vibrations [43]. Signal (**h**) at 1335 cm^{-1} is related to the OH groups plane deformation vibrations, while the band (**i**) at 1220 cm^{-1} might be attributed to the stretching of C–O and C=O bonds [44]. In the range of 1170–1010 cm^{-1} there can be observed absorption bands (**j**, **k**, **l** and **m**) characteristic for vibrations of C–O–C ether groups, which intensity suggests that prepared polyol can be considered as polyether [45, 46]. Other signals (**n** and **o**) observed at 980, 945 and 830–850 cm^{-1} can be attributed to the out-of-plane vibrations of C=C and C–H bonds in aromatic rings present in the structure of used biomass [47].

Although FT-IR analysis was used for qualitative purposes and it can be seen that in the most regions spectra are overlapping, some differences in signal intensity can be associated with varying concentration of functional groups in the final product. It can be seen that in case of reaction lasting 1 min, there are no signals **d** and **e**, however they are appearing and their intensity is increasing with the elongation of reaction time. These signals are increasing with reaction time, because application of microwave radiation results in cellulose decomposition into small compounds, which can be subjected to oxidation, resulting in creation of ketone, aldehyde, carboxylic or ester groups [48]. Degradation of cellulose may also contribute to the slight increase of the intensity of signals related to stretching vibrations of O–H groups (**a**), C=O groups (**i**) and ether groups (**k**).

The FT-IR spectra of polyols produced with different solvent:biomass ratio are presented in Fig. 3. Detailed description of all the signals has been presented above. As it can be seen, with changing the biomass
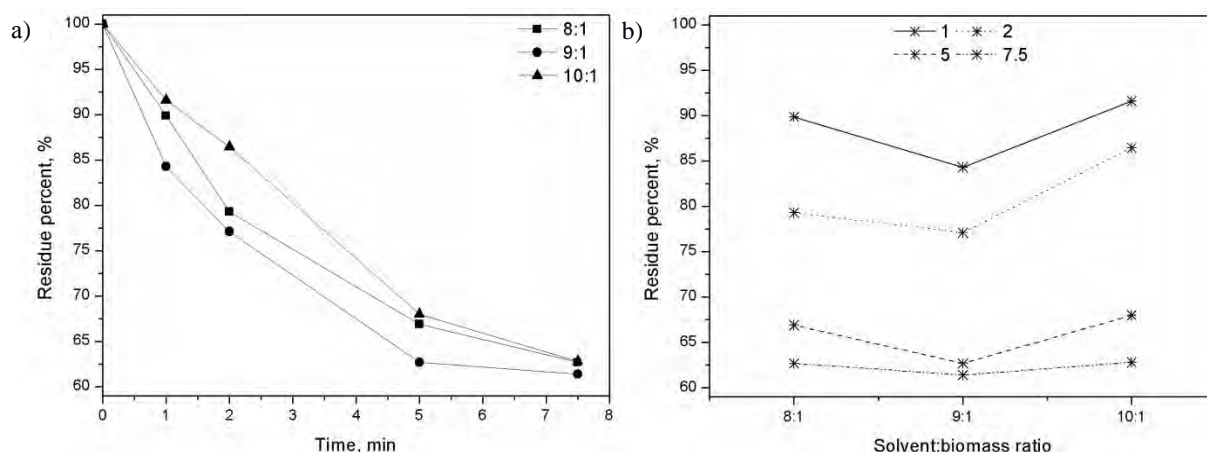

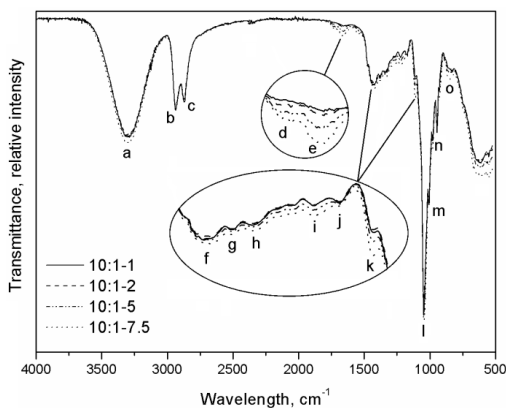**Fig. 1.** Effect of reaction time (a) and solvent:biomass ratio (b) on the efficiency of liquefaction process

Fig. 2. FT-IR spectra of polyols depending on the reaction time for solvent:biomass ratio 10:1
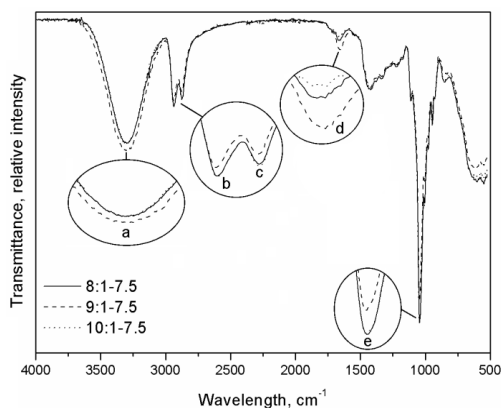

Fig. 3. FT-IR spectra of polyols depending on the solvent:biomass ratio for reaction time of 7.5 min
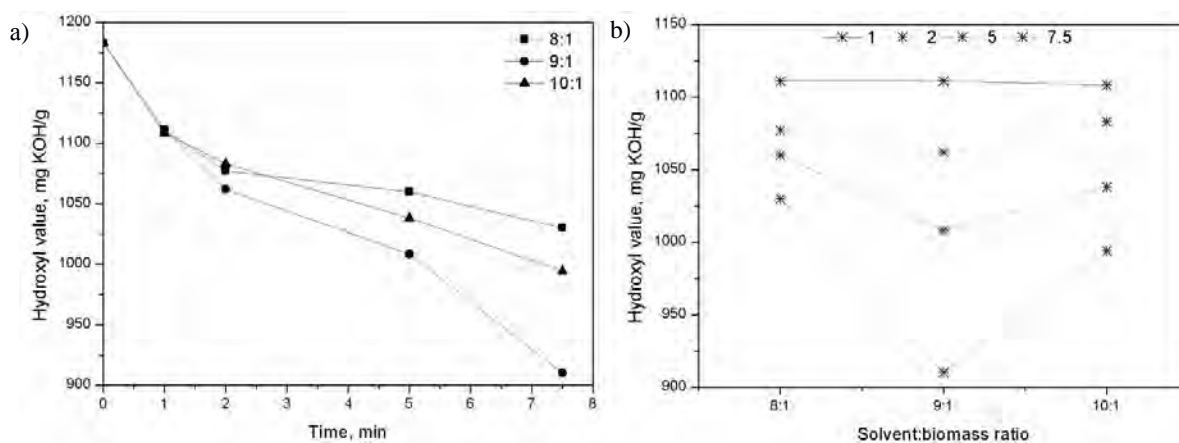

Fig. 4. Effect of reaction time (a) and solvent:biomass ratio (b) on the hydroxyl value of prepared polyols
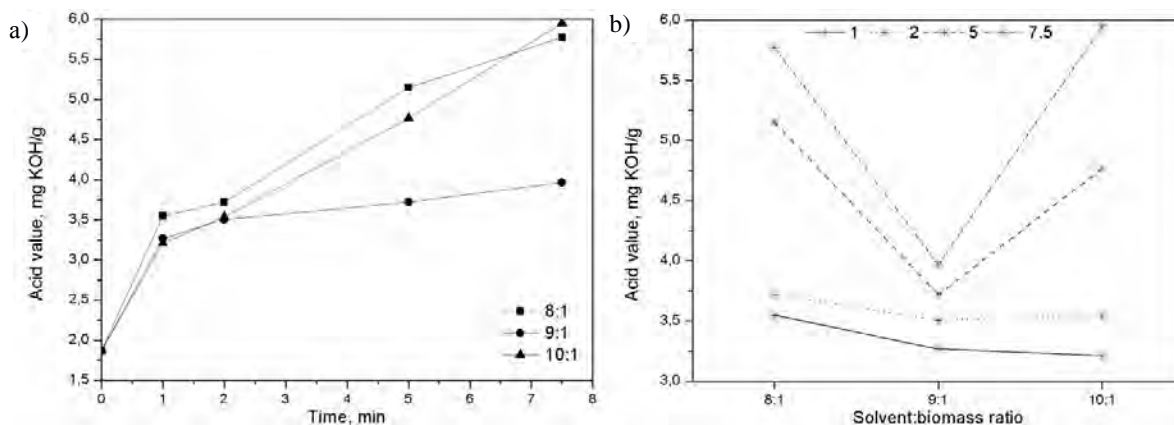

Fig. 5. Effect of reaction time (a) and solvent:biomass ratio (b) on the acid value of prepared polyols

content in the reaction mixture there are some slight differences in the intensity of particular signals. First of all it can be seen that the highest intensity of absorption band (**a**) characteristic for stretching vibrations of O–H groups was observed for 9:1–7.5 polyol, which is related to the differences in the yield of the process and degradation of cellulose present in biomass. The decrease of the intensity

of the signals (**b** and **c**) attributed to the symmetric and asymmetric stretching vibrations of methyl and methylene groups can be associated with the formation of branched structure and creation of methanetriyl groups (carbon with four single bonds, where one bond is to hydrogen) instead of CH_2 and CH_3 groups. Absorption band (**d**), characteristic for products of cellulose degradation due to

the applied microwave radiation, was slightly increased, also due to the differences in the yield of liquefaction. The biomass:solvent ratio 9:1 was found to be the most beneficial in this case, so the decomposition of cellulose material reached the highest level. This phenomenon resulted also in small decrease of the intensity of signal characteristic for C–O–C bonds, present in the glycosidic rings of cellulose, which were decomposed due to the microwave irradiation.

3.3. Hydroxyl Value of Polyols

Fig. 4 shows that the hydroxyl value (HV) of the liquefied brewer's spent grain decreases with the increasing reaction time, which is related to the chemical reactions between the functional groups of solvents and BSG components, such as dehydration or condensation reactions of liquefaction solvents and by thermal oxidative reactions that occur between solvents and biomass components [49]. Although, values of hydroxyl numbers of prepared polyols are significantly higher than those of commercially available polyols. Such big HVs are related to the initial HV of solvent mixture, which exceeded 1180 mg KOH/g, but also to the low yield of the process. Lower hydroxyl numbers could be achieved by incorporation of acidic catalyst, such as sulfuric acid, which has been repeatedly proven as an efficient catalyst for liquefaction without the assistance of microwave radiation [28, 33, 50]. Sulfuric acid is enhancing the decomposition of cellulose and hemicellulose into low molecular weight compounds, which can further react with solvents. Moreover, it is accelerating the oligomerization of solvent particles, which is decreasing the final hydroxyl value of resulting polyols [51].

Fig. 4 also shows that the lowest values of HV of the liquefied BSG are observed for 9:1 solvent:biomass ratio, which correlates nicely with the yield of the process for different ratios.

3.4. Acid Values of Polyols

Fig. 5 shows the changes of the acid value in a liquefied BSG. According to literature reports, the acid number of biopolyols tends to increase with increasing biomass conversion ratio due to the formation of acidic substances [52]. This is in agreement with the presented results, the acid value of prepared polyols is increasing with elongation of the liquefaction time. As mentioned before, cellulose present in BSG is subjected to solvolysis reactions during liquefaction, resulting in formation of glucose and other compounds, soluble in water or other solvents. One of these compounds can be levulinic acid, which can cause the increase of acid value of the product. Moreover, BSG contains hydroxycinnamic acids such as ferulic or *p*-coumaric acid, which may be successfully extracted from BSG, so they are probably also released during liquefaction process [53, 54]. Additionally, loss of glycerol decreases slightly the volume of the product and increases the concentration of acids.
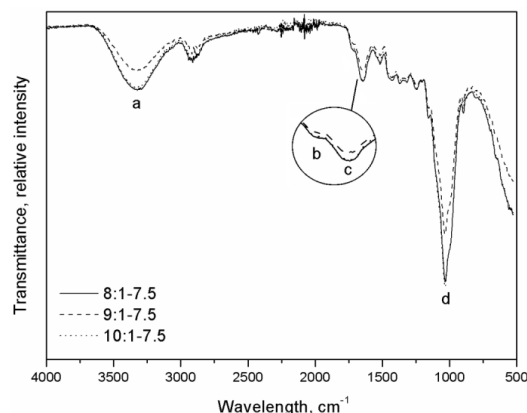
3.5. FT-IR Analysis of Solid Residues

Fig. 6. FT-IR spectra of solid residues depending on the solvent:biomass ratio for reaction time of 7.5 min

The FT-IR spectra of solid residues obtained with different solvent:biomass ratio are presented in Fig. 6. Detailed description of all the signals has been presented in Subsection 3.2. Changes in the intensity of absorption bands are related to the differences in yield of liquefaction. During the process degradation of carbohydrates occurs, because of the microwave irradiation and hydrolysis of biomass. As mentioned above, decomposition of cellulose material reached the highest level in case of 9:1 solvent:biomass ratio, which was also confirmed by the analysis of solid residues. Decrease of the intensity of the signal (**d**) characteristic for C–O–C bonds was observed, because of the cutting of cellulose chains by application of microwave radiation. Compounds generated during biomass decomposition are bonding with solvent particles leading to generation of polyols, subsequently changing the structure of solid residue. As a result, absorption bands (**b** and **c**), characteristic for stretching of unconjugated C=O bonds and C=C bonds present in the products of cellulose degradation due to the applied microwave radiation, were slightly decreased. Moreover, the lowest peak (**a**) characteristic for stretching vibrations of O–H groups was observed for 9:1–7.5 polyol, which can be associated with the higher amount of hydroxyl groups, which reacted with solvent particles during synthesis.

As it can be seen, changes in the intensity of absorption bands for solid residues correlate with these ones for obtained polyols.

4. Conclusions

Microwave assisted liquefaction of BSG with crude glycerol was investigated for various solvent:biomass ratios. Obtained biopolyols were analyzed in terms of

chemical structure, hydroxyl and acid value. Spectroscopic analysis indicated that biomass was degraded through application of microwaves and degradation products reacted with solvent particles. Although, efficiency of the process was quite low, that could be attributed to the purity of used glycerol. As a result, hydroxyl values of the products were in the range of 900-1050 mg KOH/g, which is too high for the production of polyurethane or polyester materials. Incorporation of proper catalyst, together with already applied microwave irradiation, should result in highly effective and rapid liquefaction of lignocellulose biomass. Together with the detailed analysis and optimization of process conditions it will result in development of potential method of BSG utilization, leading to generation of low-cost, value-added products, which can be further applied in plastics industry. Basing on presented results, further studies in that field should focus on three directions: enhancing the process efficiency through application of proper catalysts; optimization of the process conditions in order to obtain biopolyols with desired properties, allowing their successful application in plastics industry; further enhancement of ecological and economical aspects of biopolyols production by elimination of petroleum based solvents.

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МІКРОХВИЛЬОВЕ ЗРІДЖЕННЯ СИРИМ ГЛІЦЕРИНОМ ЯК ПОТЕНЦІЙНИЙ МЕТОД УТИЛІЗАЦІЇ ПИВНОЇ ДРОБИНИ

Анотація. Показано, що в процесі зрідження сирим гліцерином пивна дробина може бути використана як недорога лігноцелюлозна біомаса промислового типу. Досліджено вплив часу реакції і співвідношення розчинник:біомаса на ефективність процесу, хімічний склад і основні властивості отриманих біополіолів. За допомогою спектроскопічного аналізу отриманих поліолів і твердих залишків визначено механізм деградації біомаси внаслідок застосування мікрохвиль та подальшої реакції розкладання продуктів з частинками розчинника.

Ключові слова: біополіоли, зрідження, пивна дробина, сирий гліцерин, мікрохвильове випромінювання.