Article

Solvothermal Liquefaction of Blackcurrant Pomace in the Water-Monohydroxy Alcohol Solvent System

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Abstract: Wet organic wastes are especially troublesome in valorization. Therefore, innovative solutions are still in demand to make valorization feasible. In this study, we tested a new transformation route of a blackcurrant pomace as a high-moisture industrial waste through a series of high-temperature and pressure solvothermal liquefaction experiments. The feedstock was directly converted under near-critical conditions of the binary solvent system (water/2-propanol). The goal was to examine the effect of conversion parameters (temperature, biomass-to-solvent ratio) on the change in the yield of resultant bioproducts, as well as the quality thereof. The experiments were conducted in a batch autoclave at a temperature between 250 and 300 °C. The main product of the transformation was liquid biocrude, which was obtained with the highest yield (ca. 52 wt.%) at 275 °C. The quality of biocrude was examined by ATR-FTIR, GC-MS, and elemental analysis. The ultimate biocrude was a viscous heterogeneous mixture containing various groups of components and exhibiting evident energy densification (ca. 145–153%) compared to the value of the feedstock. The proposed processing method is suitable for further development toward efficient valorization technology. More specifically, the co-solvent additive for liquefaction is beneficial not only for the enhancement of the yield of the desired product, i.e., biocrude, but also in terms of technological aspects (reduction of operational pressure and temperature).

1. Introduction

Blackcurrant (*Ribes nigrum*) is recognized as one of the most beneficial health-promoting fruit species. Its berries are rich in many valuable substances, such as polysaccharides, unsaturated fatty acids, vitamins, organic acids, and polyphenols like anthocyanins and flavonoids [1,2]. Particularly beneficial are polyphenolic compounds as desirable antioxidants. The global production of blackcurrant is mainly located in Europe. Poland is the largest producer of currants in the European Union and the second top producer worldwide. The production of currants in Poland reached almost 150 thousand tons in 2020, which accounted for over one-quarter of global production [3]. The consumption of fresh currants is limited, and a significant portion is subjected to further processing, e.g., towards blackcurrant juice concentrate [4]. The resultant residue, i.e., pomace, constitutes a mixture of leaves, peels, and seeds. Blackcurrant pomace is considered a wet residue since its moisture content is considerably high (59–69 wt.%) [1,5]. Naturally, elevated water content results in low biochemical stability of pomace and the possibility of rapid spoilage and rotting (*via* the growth of microorganisms, sometimes health-hazardous). Today, pomace generated by the food industry does not find a reasonable application route and is partially utilized as animal feed or fertilizer, while the majority is landfilled,

incinerated, or composted. According to Dhillon et al. [6], only 20% of pomace is retrieved as animal feed, while the rest is not effectively utilized. Taking into account the scale of production and processing of fruit and vegetables in Poland, new technologies for the advanced and sustainable transformation of this kind of waste are being intensively sought. Recently, new possibilities for the utilization of blackcurrant pomace towards value-added compounds have been considered. For instance, one of the new promising directions of application is the usage of dried blackcurrant pomace as healthy food ingredients, i.e., as colorants or antioxidant agents. Jurgoński et al. [4] suggested that extract from blackcurrant pomace may be useful for dietary supplementation, while Colombino et al. [7] concluded that it could be beneficial as an animal feed ingredient, increasing resultant meat quality. However, it must be kept in mind that, due to the heat of vaporization of water being high, the drying stage is energy-consuming. This stage alone can negatively affect the nutritional properties of resultant dry products compared to the raw material if drying is not carefully conducted [1,8,9]. Another method of blackcurrant pomace valorization, namely via thermochemical conversion towards biofuels and bioenergy, has been actively investigated in recent years. In the case of high-moisture content biomass, a particularly perspective route is the hydrothermal liquefaction (HTL) process conducted in the subcritical conditions of water. It allows for the omission of the drying step [10]. Water under its subcritical conditions is an excellent solvent, mainly because of the unique change in physicochemical properties. The ability of near-critical water allows for the solubilization of numerous groups of organic compounds and leads to a high reaction rate (due to lower diffusion limitations). Moreover, near-critical water has the capability to act as an acid or base catalyst for plenty of reactions. Overall, the hydrothermal liquefaction of organic matter allows for its effective conversion towards a high-energy-density liquid product called bio-oil or biocrude. Nevertheless, biocrude is a highly heterogenous product, and should not be considered as a drop-in biofuel, but rather as a semi-finished product. As such, it can be successfully used without upgrading for heat and energy generation. Then, it could be beneficial to rearrange the Polish energy system, being the most coal-based among the European Union countries, which should be supplied by clean alternatives and renewable energy sources.

In the last two decades, different types of wet raw materials, like microalgae [11], macroalgae [12], sewage sludge [13,14], wastes from the food sector [15], lignocellulosic biomass like pine wood [16], as well as its mixtures [17], have been processed via hydrothermal liquefaction towards different groups of bioproducts. Meanwhile, studies on the processing of fruit and vegetable pomace are less popular in the literature. Moreover, in the published reports, the authors noted somewhat moderate biocrude yield ranging between ca. 20–40 wt.%. The series of publications by Déniel et al. [5,18] reported a biocrude yield varying between ca. 24–30 wt.% for the hydrothermal liquefaction of blackcurrant pomace carried out between 290 and 335 °C. Anouti et al. [19] reported a similar oil yield (17–33 wt.%) from the conversion of blackcurrant pomace under subcritical water when various solvents were used for the bio-crude recovery procedure. In another report, Missaoui et al. [20] noted a low mass yield (ca. 20 wt.%) of liquid products obtained through the hydrothermal processing of olive pomace between 180 and 250 °C.

Recently, modifications to the hydrothermal liquefaction process have also been tested. It is often conducted by the introduction of organic co-solvents to water. The addition of monohydroxy alcohol or hydrocarbons serving as hydrogen donors positively impacts the increased yield of liquid products, and higher quality thereof. It was found that the addition of this monohydroxy alcohol creates favorable conditions for the efficient conversion of biomacromolecules contained in the biomass. The addition of alcohols to water under near-critical conditions causes alterations in the chemical nature of the reaction medium. As a result, it promotes the hydrolysis reaction and stabilization of formed intermediate products. Such a modification of hydrothermal liquefaction is commonly referred to as thermochemical liquefaction (THL) or solvothermal liquefaction (STL). Generally, there is a lack of reports concerning the processing of fruit pomace in the near-critical conditions of

a binary solvent system. However, the profound effect of the addition of monohydroxy alcohols as co-solvents for solvothermal liquefaction was reported in a handful of studies on other raw materials. For instance, a synergistic effect of alcohol and water was found in the case of processing microalgae [21], lignocellulosic biomass [22], and sewage sludge [23,24], resulting in a significantly higher biocrude yield compared to pure water. Ji et al. [21] noted a two-fold higher bio-oil yield (ca. 60 wt.% versus ca. 30 wt.%) in an ethanol-water co-solvent compared to pure water when low-lipid microalgae *Scenedesmus* sp. was converted. Furthermore, pine wood, as an exemplary lignocellulosic biomass, was transformed by Zhao et al. [22] in a mixture of methanol and water, and a noticeable increase in bio-oil was found, namely from ca. 24 wt.% to 55 wt.% for pure water and water-methanol (1:1), respectively. Furthermore, Han et al. [25], and Sebhat et al. [26] reported on conversion in binary solvent systems of microalgae and Kraft lignin, respectively. However, to the best of the authors' knowledge, there has been no scientific work reporting on the solvothermal liquefaction of any fruit pomace in binary solvent systems, which was the motivation for carrying out this work. It is untestable that the addition of an organic solvent as a reaction medium will increase the operating cost of the process. However, as outlined above, it may be well justified in relation to a significant increase in the process yield and the quality of the obtained biocrude (lower viscosity, higher selectivity toward valuable compounds). Additional technological difficulty in terms of the process of upscaling may be the recovery of the solvent and maintenance of the organic vapor-free environment, which can add to the cost (operational and investment) of the process. Since the use of the solvents is not yet well understood, it cannot be stated if its beneficial effect will mitigate the drawback related to its cost, so, in future research, this issue should be thoroughly investigated.

Therefore, the aim of the present study was to investigate the feasibility of the effective conversion of blackcurrant pomace towards biocrude via solvothermal liquefaction in the binary solvent system. Herein, industrial-origin blackcurrant pomace was transformed in near-critical conditions of the mixture of water and 2-propanol (1:1 *m/m*). Furthermore, the impact of the process variables (temperature, biomass-to-solvent ratio) on the obtained bioproduct yield distribution was studied. The feasibility of direct usage of as-received wet waste in solvothermal liquefaction was also investigated. For this purpose, the efforts outlined here were compared with the results obtained for initially dried feedstock with the loading of raw (wet) biomass. This brought new insight and could be more relevant for real conditions thanks to the simplification of the entire processing procedure. This in turn should pave the way for reducing this time- and energy-consuming step of the thermochemical transformation process. Finally, the composition of the biocrudes produced under various conditions was also analyzed. It was proven that the proposed approach based on solvothermal liquefaction in water/2-propanol mixture brings beneficial aspects in view of biocrude yield increment, its quality, and in terms of technological aspects. In this regard, the proposed technology may be a prospective and sustainable solution.

2. Materials and Methods

2.1. Raw Material

The raw material used in the present study, i.e., blackcurrant pomace, was left over from one of the largest industrial juice production facilities in Poland–Tymbark MWS company (Tymbark, Poland). The original feedstock was a mixture of residual seeds, leaves, stalks, and peels. Therefore, in order to randomize the feedstock, it was homogenized before thermochemical conversion. However, it was prepared in two different manners to investigate the effect of prior drying on the conversion of the tested feedstock. The first one, the so-called wet-feedstock, was prepared by grounding the wet raw material using a Fritsch Pulverisette 15 mill to a sieve fraction of ca. 2 mm. The second, the so-called dry feedstock, was prepared by drying the as-received pomace at 105 °C to remove moisture, and subsequently grinding to a particle fraction of <1 mm. The ultimate analysis was conducted using standard procedures.

2.2. Solvothermal Liquefaction Procedure

Solvothermal liquefaction (STL) tests were carried out in a 500 cm^3 Parr 4575A (USA) batch reactor. In each run, an amount of approximately 100 g of blackcurrant pomace slurry was used. The dry biomass-to-solvent ratio in the slurry was adjusted in a range of 1:19 (i.e., 5 wt.% of dry biomass in the slurry) to 1:4 (i.e., 20 wt.% of dry biomass in the slurry). In the present study, the solvent for liquefaction was a mixture of distilled water and 2-propanol (Avantor Performance Materials, 99.9%) kept at a constant ratio of 1:1 *m/m*. In using the wet feedstock, the amount of distilled water to be added was reduced by the moisture content contained in the raw material. Next, the slurry was placed in the reactor, which was subsequently carefully sealed. Prior to each experiment, a gas-tightness check was carried out by pressurizing the reactor with nitrogen (grade 5.0) to a pressure of p = 1 MPa. Before starting the trials, the reactor was pressurized with nitrogen (p_0 = 0.5 MPa) to keep operational pressure during experiments above saturation vapor pressure. The processing treatment temperature was set at 250, 275, and 300 °C. The reaction was realized under autogenous pressure, thus corresponding to the operational pressure ranging ca. 5–10 MPa (depending on processing temperature). The duration of heating necessary to reach the final temperature was approximately 30 min. The reaction time, representing the time interval between reaching the set temperature and the start of cooling down, was equal to 30 min. After the reactor was cooled to an ambient temperature (with each time precisely measured), the gas pressure was gauged, and a sample was collected. The autoclave was then depressurized, and the products were subjected to separation.

In order to separate and recover the bioproducts from the reaction mixture, the typical procedure of extraction with dichloromethane (DCM; Chempur 99.9%), followed by filtration under reduced pressure and solvent evaporation, was employed. Briefly, after each run, DCM was added to the as-received reaction mixture, keeping a constant ratio of DCM to the reaction mixture (1:1 *v/v*). It was aimed to maximize the recovery of conversion products, which partially stuck to the reactor elements (e.g., stirrer impeller, thermowell). Then, after carefully rinsing the reactor, the whole mixture was filtered and separated into liquid filtrate and solid residue left on the filter. Following filtration, the cake was dried at 105 °C until a constant mass was achieved to remove any residual solvents, weighed, and denoted as biochar. The resultant filtrate was placed into a separatory funnel, where it was split into the aqueous phase (top) and DCM phase (bottom). The water-soluble organics content was determined by placing two samples (ca. 2 cm^3) on the Petri dish and heating at 60 °C for at least 24 h to the constant mass. Then, the concentration of solid residue remaining after water evaporation was calculated as the average of both estimations and multiplied by the total volume of the aqueous phase. The dichloromethane, together with the 2-propanol (used as a co-solvent), was removed by using a rotary evaporator (Heidolph Instruments) working under reduced pressure. Finally, to obtain solvent-free biocrudes, the dense sample taken after the rotavapor was placed into the laboratory watch glass and put for a short time under the laboratory fume hood to remove residual solvents. The yield of gas products was calculated based on the ideal gas law, using the gas composition, temperature, and pressure measured inside the reactor. Finally, the following groups of products were separated: (i) biocrude as a mixture of DCM-soluble compounds; (ii) polar organics dissolved in the water phase; (iii) non-condensable (gas) products; and (iv) solid residue as biochar.

2.3. Analysis Methods of STL Bioproducts

2.3.1. Elemental Analysis (EA)

Carbon, hydrogen, and nitrogen contents in the studied blackcurrant pomace and resulting biochars and biocrudes were analyzed using a EuroVector EA3100 CHNS elemental analyzer (Eurovector, Pavia, Italy). The sulfur content in the raw material and the ultimate bioproducts was below the detection level (0.5 wt.%). The oxygen (O) content was individually determined using another EuroVector EA3100 unit (Eurovector, Pavia, Italy) equipped with a suitable pyrolysis reactor. Each run was carried out twice, and the final result represents the average value.

2.3.2. Infrared Fourier-Transform Spectroscopy (FT-IR)

The composition of the biocrudes was carried out by using mid-infrared Fourier-transform spectroscopy. The spectra were recorded on a Nicolet iS5 (Thermo Fisher Scientific Inc., Waltham, MA, USA) spectrometer equipped with an attenuated total reflectance device (ATR) with a diamond crystal and DLaTGS detector. Sixteen scans were recorded in a wavenumber region of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. The samples were analyzed without any preparation.

2.3.3. Gas Chromatography Coupled to Mass Spectrometry (GC-MS)

The composition of the volatile fraction of obtained biocrudes was analyzed using gas chromatograph (Agilent, model GC 7890B) coupled to mass spectrometer (Agilent, model MS 5977A, Agilent Technologies, Santa Clara, CA USA). The Agilent DB-17 capillary column (30 m × 0.32 mm × 0.5 μm) was used for the separation of compounds. The samples were prepared as 5 wt.% solutions in dichloromethane (Avantor Performance Materials Poland; HPLC grade). Additionally, samples were filtered through 0.2 μm PTFE syringe filters (Agilent) before injection. The obtained MS spectra were interpreted based on the reference MS library (chemical base G1034C). The share of the identified compounds was calculated as a ratio of its peak area to the sum of the peak area of all identified components. More specific information concerning the conditions of GC-MS analyses has been reported elsewhere [27].

The same GC-MS equipment was also used for qualitative analysis of aqueous phase organics. The analysis was only carried out for one measurement point; i.e., the test conducted at 300 °C and for the moderate biomass-to-solvent ratio (1:9). The sample was prepared by dissolving a sample of the aqueous phase (water + organics) in methanol (Avantor Performance Materials, 99.9%) and filtering a solution through a syringe filter.

2.4. Calculations

The yields of the ultimate *i* bioproducts (Y_i) were calculated as wt.% contributions with respect to the mass of dry matter of the starting biomass according to Equation (1).

$$Y_i = \frac{m_i^d}{m_{feedstock}^d} \cdot 100\%, \; [\text{wt.\%}] \tag{1}$$

where m_i^d refers to the mass (calculated on a dry basis) of different groups of bioproducts produced via solvothermal liquefaction; i.e., biocrude, biochar, gas phase, and aqueous phase organics.

HHV of the bioproducts from blackcurrant pomace was calculated based on the elemental composition according to the Dulong formula. The feedstock conversion ratio was calculated according to Equation (2).

$$\text{Conversion ratio} = 100\% - Y_{char}, \; [\text{wt.\%}] \tag{2}$$

Based on the calculated heating values and yields of bioproducts, energy recovery (ER) in the form of each group of products was also calculated following Equation (3).

$$ER_i = \frac{Y_i \cdot HHV_i}{HHV_{feedstock}} \tag{3}$$

ER_i—energy recovery in the form of STL group of products, where *i* means biocrude, biochar, gas phase, or water-soluble organics,
HHV_i—a higher heating value of *i*-group of products.

Similar to energy recovery, the *C* element distribution among the obtained different groups of products was also determined following Equation (4).

$$C_{share,i} = \frac{Y_i \cdot C_i}{C_{feedstock}} \tag{4}$$

$C_{share,i}$—the content of *C* element in the *i*-group of products,
$C_{i/feedstock}$—*C* element content in the *i*-group of products/feedstock, respectively.

3. Results and Discussion

3.1. Raw Material

The moisture content in the wet raw material was equal to ca. 67.5 wt.%, and, after grinding, it dropped to 44.4 wt.%. The ash content in the feedstock after grinding was equal to 3.1 wt.%. The characteristics of raw blackcurrant pomace, including elemental composition and ultimate analysis, are presented in Table 1. The carbon content of the tested pomace was 50.5 wt.%, and hydrogen was 7.1 wt.%, whereas the oxygen content was above 37 wt.% (all on a dry basis). These values are consistent with other reports in the literature related to blackcurrant pomace [5,19]. Feedstocks characterized by high moisture and low mineral matter contents (such as blackcurrant pomace) seem to be perfect raw materials to be processed under subcritical water (due to reduced issues with clogging the setup elements and/or saving energy for pre-treatment of raw material).

Table 1. Raw blackcurrant pomace characteristic.

Parameter	Value [wt.%]
Moisture content	67.5
Ash content [d]	3.1
Volatile matter content [d]	78.1
Fixed carbon content [d]	18.8
C [d]	50.5
H [d]	7.1
N [d]	2.7
O [d]	37.2

[d]—calculated on dry basis.

3.2. Effect of Process Variables on Bioproducts Yield Distribution

3.2.1. Temperature

The yield distribution of the resultant bioproducts of solvothermal liquefaction of blackcurrant pomace as a function of processing temperature for wet and pre-dried feedstocks is shown in Figure 1. Generally, it can be seen that the change in process temperature causes noticeable changes in the formation of different groups of products. In the whole range of tested processing conditions, the dominant group fraction was biocrude, with its yield ranging between 47 and 53 wt.%. The highest yield for both series was noted at 275 °C, which proves that a moderate temperature ensures a compromise between the occurring hydrolysis reactions of raw materials and a secondary decomposition of biocrudes. Compared to the work of Déniel et al. [5], who studied the hydrothermal liquefaction of blackcurrant pomace in a purely aqueous medium between 290–335 °C, the highest yield of liquid product (ca. 30 wt.%) was reported at 310 °C. In the investigated conditions, the co-solvent additive for liquefaction is beneficial not only for the enhancement of the yield of the desired product, i.e., biocrude, but also in terms of technological aspects. Namely, herein, the most beneficial conditions were obtained at an almost 50 °C lower temperature and a slightly lower pressure. It should be kept in mind that easing the processing conditions can be beneficial in view of the limitation of the strong corrosive activity of the reaction media on elements of the technological setup.
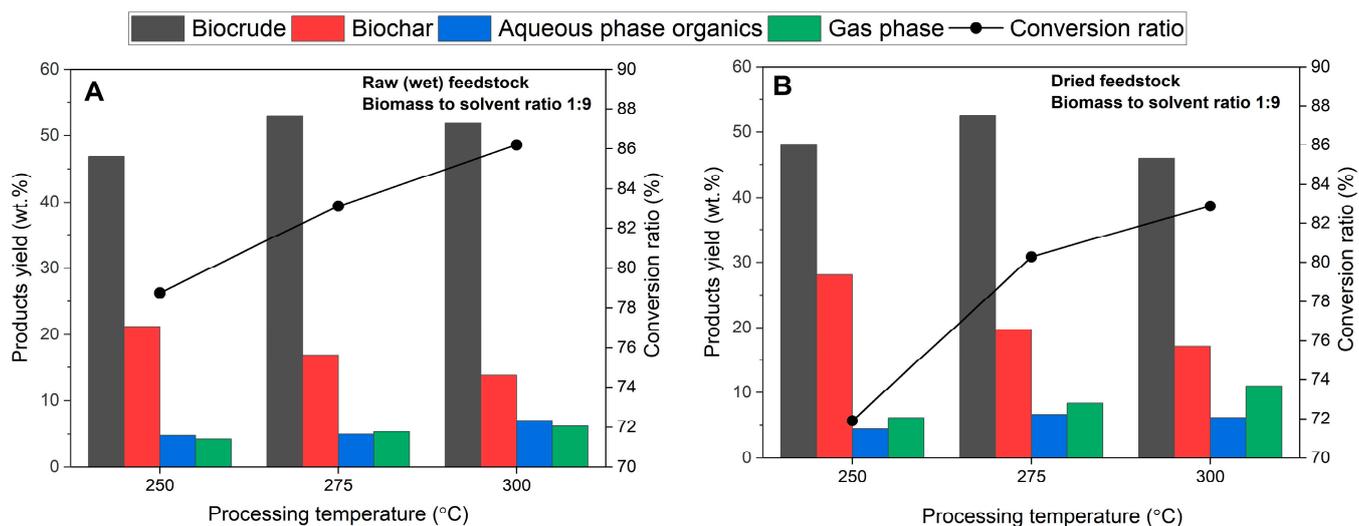
Figure 1. Effect of solvothermal liquefaction processing temperature on yields distribution of resultant bioproducts and conversion ratio tested for: (**A**) raw (wet) feedstock, (**B**) pre-dried feedstock.

Higher temperatures (cf. Figure 1) lead to a slight decrease in the liquid fraction yield in exchange for a minute increase in gas formation. This is the result of a secondary degradation of biocrude and aqueous phase organics occurring, which was also mentioned earlier [5]. The shift of reaction temperatures from 250 to 300 °C results in a gradual decrease in solid biochar yield from ca., as well as ca. 28 to 17 wt.% for wet and dried feedstock, respectively. The conversion ratio was relatively high, varying within the range of 78–86% and 72–83% for wet and pre-dried feedstock, respectively. This proves that solvothermal liquefaction in the mixture of water and 2-propanol ensures excellent conditions for the profound decomposition of original biomass matter. It can also be seen that direct subjection of blackcurrant pomace to the solvothermal liquefaction is possible, and the yields of the resultant biocrudes are even slightly higher. This can be linked to a change in the composition of the structure of the feedstock, which occurs at the drying stage. Moreover, when distilled water is used, the solubilization of some mineral matter contained in the raw material can occur. The presence of certain amounts of mineral matter in the raw material may likely contribute to catalytic transformations of the intermediates in secondary reactions.

3.2.2. Biomass-to-Solvent Ratio

The effect of the biomass concentration on the liquefaction of blackcurrant pomace was evaluated for various biomass-to-solvent ratios (i.e., from 1:19 to 1:4 m/m) at two different processing temperatures (i.e., 275 and 300 °C) and for wet and pre-dried feedstock (cf. Figure 2). The obtained results show that the increase in biomass loading entailed fewer regular changes in the distribution of products than temperature. Generally, similarly to the findings mentioned in Section 3.2.1, the dominant product was biocrude with the yield ranging between 42–53 wt.%. In the majority of tested conditions, the highest biocrude yield was noted for moderate biomass concentrations (1:9). It was also found that biochar yield rose with increasing biomass concentrations in the processed slurries. This observation was noted notwithstanding the studied temperatures and/or pretreatment application. The increased yields confirm that, for the highest biomass concentration, a significant fraction of the feed could remain either completely unaltered or as partially reacted matter of the raw material. These results are consistent with those found in the literature [5,10], and show a decrease in the liquid and solid fraction yield along with increasing biomass concentrations. The crescent biomass concentration also resulted in a reduction in the yield of aqueous phase organics by a few percent. Simultaneously, the change in the yield of the gaseous phase was rather irregular. It is worth noting that the optimization of biomass

concentration is a crucial variable to achieve the economic feasibility of the technology. As mentioned by Déniel et al. [5], an adjustment of the proper biomass-to-solvent ratio notably influences the energy consumption of the process. Generally, as concluded by Dimitriadis and Bezergianni [28], there is an optimal biomass concentration (usually around 15 and 20 wt.% in a mixture), being the midpoint between high biocrude yield and requiring moderate energy for the processing, which ensures economic benefits.
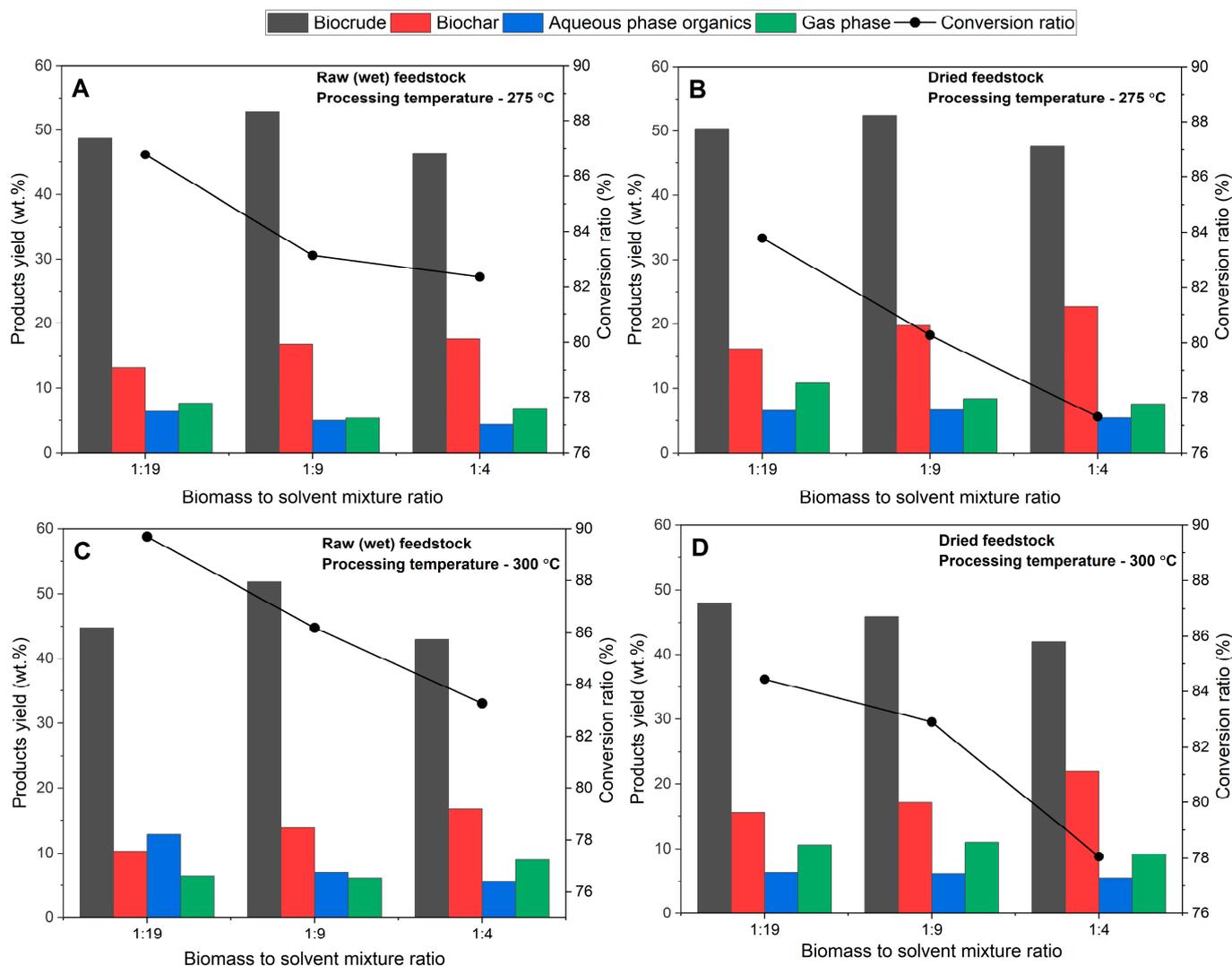

Figure 2. Effect of biomass-to-solvent ratio on yield distribution of bioproducts for tests carried out at different conditions: T = 275 °C, wet (**A**) and pre-dried (**B**) feedstock; T = 300 °C, wet (**C**) and pre-dried (**D**) feedstock.

3.3. Biocrude Composition

3.3.1. Elemental Composition

The biocrudes obtained through liquefaction in water and 2-propanol mixtures were highly viscous, dark brown liquids with an intensive odor. In Table 2, a comparison of the elemental composition of biocrudes obtained under various conditions is presented. The carbon content in the biocrudes is higher than for the feedstock and accounts for ca. 70 wt.%. The carbon content for biocrudes produced under various processing variables differs only slightly. The resultant biocrudes exhibit significantly higher energetic values compared to feedstock. Thus, solvothermal liquefaction in a binary solvent system caused distinguished energy densification. The HHV of the resultant liquids varied between 32.8–34.5 MJ·kg^{-1},

so this bioproduct can be used as a valuable fuel for heat generation. The relatively high energy density is the result of a noticeable increase in the C and H content (the latter: 8.8–10.0 wt.%) compared to raw material. Additionally, the oxygen content in liquids is much lower than in the original blackcurrant pomace.

Table 2. Elemental composition of biocrudes obtained from blackcurrant pomace.

Process. Cond.　　　 Element/HHV	250 °C		275 °C		300 °C
	1:9	1:19	1:9	1:4	1:9
C [wt.%]	69.68	69.80	69.60	70.35	69.34
H [wt.%]	10.29	8.81	9.63	9.55	8.97
N [wt.%]	1.48	2.48	2.37	2.39	2.38
O [wt.%]	18.55	18.91	18.40	17.71	19.31
HHV [MJ·kg^{-1}]	34.5	32.8	33.8	34.0	32.8

To depict the effect of processing temperature and biomass concentration in the slurry on the change of H:C, and O:C atomic ratios in the resultant biocrudes, a van Krevelen diagram was plotted (cf. Figure 3). When compared to dried blackcurrant pomace, a significantly lower ratio of O:C of all biocrudes could be seen. It proved the occurrence of an intensive deoxygenation reaction. Interestingly, the O:C was at a similar level for all of the studied samples and accounted for ca. 0.2. The H:C atomic ratio of all biocrudes did not noticeably differ from the raw material. However, for samples obtained at the highest temperatures and the lowest biomass-to-solvent ratio, the H:C quotient was lower, which suggests they underwent dehydration reactions during the transformation of blackcurrant pomace through liquefaction in near-critical conditions. It can be seen in Figure 3 that the drop in H:C gradually occurred along with an increase in reaction temperatures; i.e., from 1.77 to 1.55 when the temperature rises from 250 to 300 °C. Therefore, the deoxygenation route via decarboxylation/decarbonylation seems to occur more easily at lower processing temperatures, while dehydration is more intensive at higher temperatures. The opposite effect was noted for biomass concentration, where the highest H:C ratios were obtained for higher biomass concentration in the slurries.
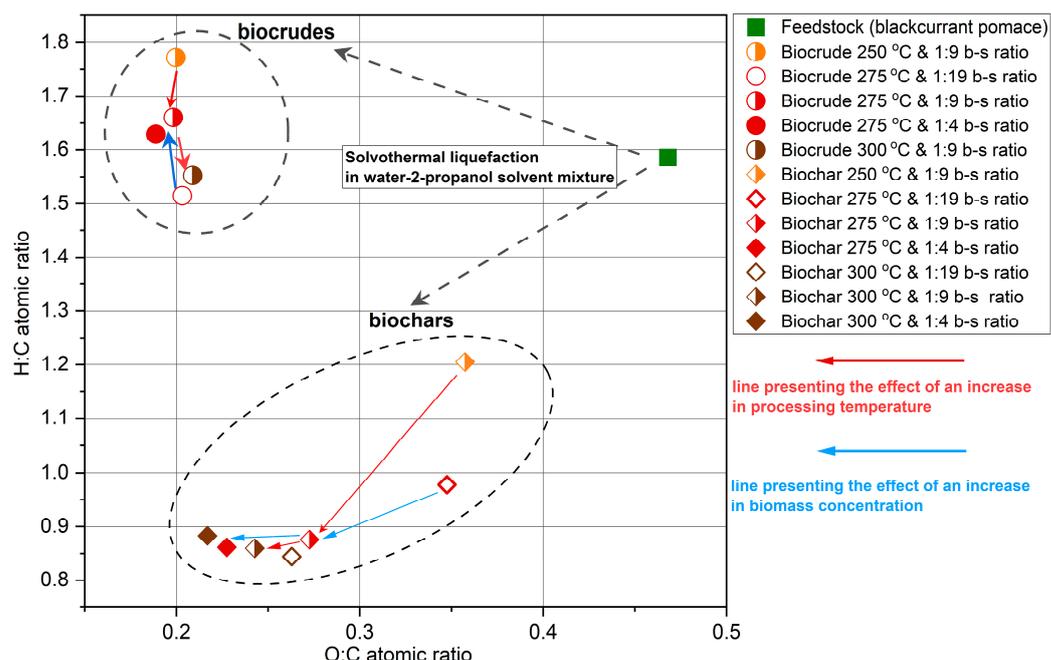

Figure 3. Van Krevelen diagram for biocrudes obtained from blackcurrant pomace at different processing conditions.

3.3.2. FT-IR

ATR-FT-IR analyses of the resultant biocrudes (cf. Figure 4) were carried out to assess the qualitative changes in composition between the samples acquired under various processing conditions. The shape of the absorption bands of collected spectra indicates the presence of numerous oxygen-containing compounds, as well as aromatic and aliphatic derivatives. The IR spectra recorded for the biocrudes obtained under various processing conditions reveal their mutual similarity. However, certain differences arising from higher temperatures are visible at a glance. The broad band at 3700–3000 cm^{-1} (centered at ca. 3343 cm^{-1}) might be assigned to the stretching modes of –OH species in various oxygenates; i.e., phenols, alcohols, esters, and carboxylic acids. The absorption centered at 3011 cm^{-1} can be ascribed to the presence of polycyclic aromatic compounds. However, its poor intensity suggests a minor share of such components in the samples. The spectral region of 3000–2850 cm^{-1} comprises the complex of four, partially overlapping absorption modes assigned to stretching vibrations of methyl and methylene groups (namely, 2967 and 2925 cm^{-1}–asymmetric vibrations of CH_3 and CH_2, respectively, and 2870 and 2855 cm^{-1}–symmetric stretching of CH_3 and CH_2, respectively). The relatively high intensity of these modes demonstrates the abundant share of various species containing aliphatic chains. The two intense sharp bands at 1740 and 1712 cm^{-1} are due to the presence of carbonyl moieties–mainly esters and carboxylic acids (these bands correspond to the stretching vibrations of C=O groups). The presence of esters is confirmed by the absorptions at 1160 and 1129 cm^{-1} (C–O stretchings). This is not surprising considering the chemical nature of the processed feedstock and the alcohol-containing liquefaction medium. It is interesting to analyze the bands at 950 and 816 cm^{-1} (=C–H out-of-plane bending and CH_2 rocking modes, respectively), which reveal a gradual decrease in intensity with a rising processing temperature. This is indicative of a gradually lower share of unsaturated compounds along with an increase in temperature. The close similarity of the spectra collected for different biomass concentrations (Figure 4B) discloses a negligible impact of this parameter on the qualitative composition of the obtained biocrudes.
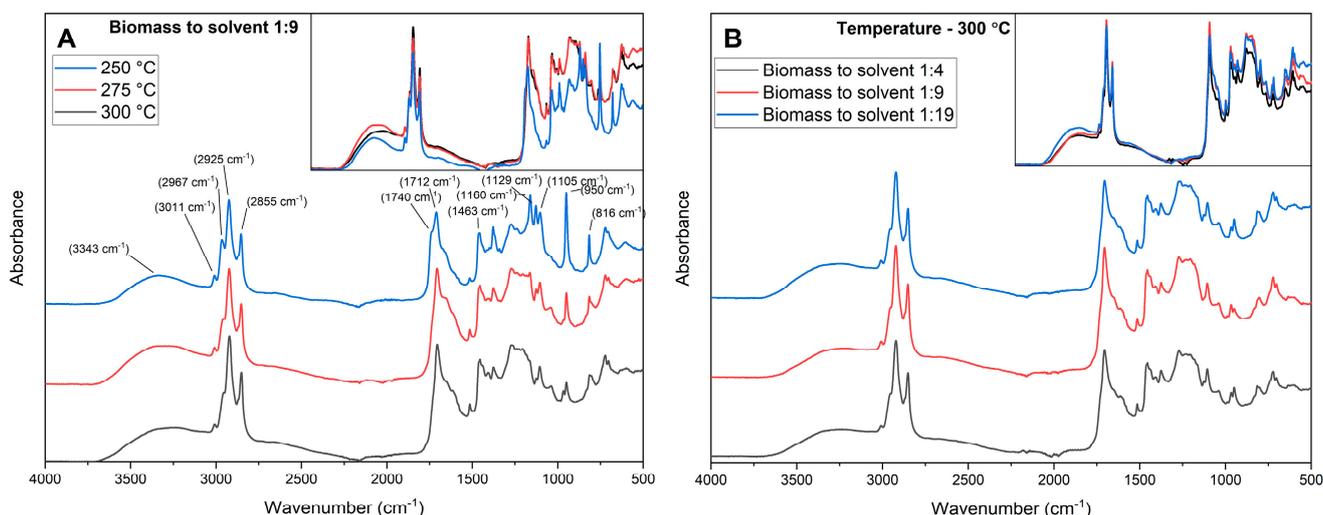

Figure 4. ATR-FTIR spectra of biocrudes obtained at different processing temperatures (**A**) and biomass-to-solvent ratios (**B**).

3.3.3. GC-MS

A qualitative analysis of the resultant biocrudes was carried out via gas chromatography coupled with mass spectrometry (GC-MS). In Table 3, a list of exemplary compounds with a sufficiently high threshold level of fitting to the MS library (75%) as a function of the processing temperature is gathered. Among the identified compounds, the main groups were various oxygen compounds, such as carboxylic acids and their derivatives, phenol derivatives, heterocyclic oxygen compounds, and nitrogen-containing species.

Table 3. Exemplary compounds identified in biocrudes obtained at different liquefaction temperatures for a biomass-to-solvent ratio equal to 1:9.

Compound Group	RT [min]	Compound	Relative Share [%]		
			250 °C	275 °C	300 °C
Carboxylic acids and derivatives	3.3	Acetic acid	3.40	2.33	1.02
	50.3	N-Ethyl-2-isopropoxycarbonylazetidine	3.55	2.11	0.93
	60.5	n-Hexadecanoic acid	6.27	8.43	11.29
	60.6	isopropyl palmitate	-	-	2.47
	66.5	9-Octadecenoic acid	2.83	8.13	12.63
	66.9	iso-Propyl 9,11-octadecadienoate	-	-	2.47
	67.2	9,12-Octadecadienoic acid	32.47	36.34	29.25
Other oxygen compounds	20.8	2-Cyclopenten-1-one, 2-methyl-	-	-	0.40
	24.8	2-Vinylfuran	-	0.38	0.45
	30.8	Phenol, 2-methoxy-	-	-	0.79
	34.2	Phenol, 4-ethyl-	-	-	1.22
	39.1	Phenol, 4-ethyl-2-methoxy-	-	-	0.63
	55.7	Hexadecyl octyl ether	1.31	1.45	1.39
	57.3	Cyclododecanemethanol	2.26	-	1.33
	57.5	1-Tetradecanol	0.92	0.84	-
	57.7	2-Cyclopropen-1-one, 2,3-diphenyl-	3.04	3.02	-
Nitrogen compounds	15.1	Pyrazine, methyl-	0.73	0.65	0.56
	33.0	3-Pyridinol	3.49	3.82	3.80
	33.8	2-Pyrrolidinone	-	0.66	1.11
	35.2	3-Pyridinol, 6-methyl-	0.39	0.58	0.68
	50.0	Quinoline, 6-methoxy-, 1-oxide	-	-	2.09
	75.62	9-octadecenamide	0.62-	1.67	1.89

The highest share was found for carboxylic acids, which could result from the degradation of seeds contained in the raw material. Interestingly, in the resultant liquids, 2-propanol derivatives (e.g., esters of propanol) were identified, which means that the added monohydroxy alcohol could act not only as a solvent but also as a reagent. For instance, it could stabilize some reactive intermediates. The presence of cyclic ketones and furan derivatives indicates the decomposition of polysaccharides (e.g., hemicellulose and cellulose). Under hydrothermal conditions, polysaccharides, such as hemicellulose or cellulose, are depolymerized into smaller monosaccharides. Following this, the formed hexoses and pentoses are susceptible to recombining into cyclic structures. Phenol derivatives were identified at the highest processing temperature, which proves the more intensive decomposition of the most thermally stable biopolymer; i.e., lignin. Nitrogen compounds come from the breakdown of proteins contained in the blackcurrant pomace. Moreover, the presence of N-containing heterocycles could suggest the occurrence of Maillard reactions between carbohydrates and amino acids, thermodynamically favored from 180 °C [29,30].

3.4. Other Groups of Bioproducts Composition

The biochars were dark-brown solid residues obtained after the isolation of liquid products, and they were mutually similar in appearance. However, some processed particles of raw material (e.g., seeds) were still observable in the products formed at lower processing temperatures. In Table 4, the elemental composition of the biochars produced under various processing conditions is presented. Firstly, it can be seen that carbon content was higher for all cases compared to raw blackcurrant pomace and varied between 57 wt.% and 63 wt.%. Generally, the increase in processing temperature, as well as the concentration of biomass in the slurry, caused a slight increase in carbon content. This is in line with the decrease of hydrogen and oxygen contents in solid residues, suggesting intensive dehydration of initial biocomponents. The produced biochars had noticeable heating values, ranging between 21.5–24.8 MJ kg^{-1}. Finally, the obtained results were also used to calculate O:C and H:C molar ratios, and the results were included in the van

Krevelen diagram shown in Figure 3. As can be seen, both ratios descend with an increase in processing temperature and concentration of biomass in slurry. However, the drop in the O:C molar is more pronounced than H:C.

Table 4. Elemental composition of biochars obtained from blackcurrant pomace.

Element	250 °C		275 °C			300 °C	
	1:9	1:19	1:9	1:4	1:19	1:9	1:4
C [wt.%]	56.91	57.59	57.96	61.20	58.56	60.01	63.20
H [wt.%]	5.72	4.69	4.23	4.39	4.12	4.30	4.65
N [wt.%]	1.99	2.66	3.11	3.85	3.15	3.45	3.40
O [wt.%]	27.12	26.69	21.07	18.56	20.53	19.42	18.28
HHV [MJ kg^{-1}]	22.60	21.44	21.91	23.69	22.05	22.99	24.79

Additionally, qualitative analysis of aqueous phase organics was conducted for the chosen samples. As can be seen in Table 5, both low-molecular and high-molecular compounds were present. Acetic acid was one of the main constituents among the identified water-soluble chemicals. It can be formed as a relatively stable product from the decomposition of primary sugars degradation products; e.g., via dehydration of HMF. The appearance of glycerin confirms that in the presence of 2-propanol, as a reaction media, triglycerides can undergo a transesterification reaction forming isopropyl esters and free glycerin. All of the compounds identified in the aqueous phase were species with a high content of heteroatoms, such as O, N, and S. These are products of hydrolysis of pristine biopolymers, building blocks present in raw blackcurrant pomace. However, a more detailed analysis of the aqueous phase should be the aim of future research.

Table 5. Exemplary compounds identified as aqueous phase organics at 300 °C and a biomass-to-solvent ratio of 1:9.

RT [min]	Compound	Formula	Relative Share [%]
2.79	4-Pentyn-2-ol	C_5H_8O	2.27
3.44	Acetic acid	$C_2H_4O_2$	29.06
4.21	Hydrazinecarbothioamide	CH_5N_3S	1.23
26.24	Glycerin	$C_3H_8O_3$	9.14
55.59	N-Benzyl-1H-benzimidazole	$C_{14}H_{12}N_2$	6.70
57.55	Sulfurous acid, cyclohexylmethyl isobutyl ester	$C_{11}H_{22}O_3S$	1.29
58.24	1,2-Benzenediol, O-cyclobutanecarbonyl-O′-cyclopropanecarbonyl-	$C_{15}H_{16}O_4$	20.13
60.36	Isophthalic acid, di(2-methylprop-2-en-1-yl) ester	$C_{16}H_{18}O_4$	1.93
60.87	Sulfurous acid, di(cyclohexylmethyl) ester	$C_{14}H_{26}O_3S$	1.87
62.28	2-Buten-1-one, 1-(6,7,7-trimethyl-2,3-dioxabicyclo)	$C_{13}H_{18}O_3$	1.33

The gas phase was analyzed in a previous work [31], where it was found that this product is mainly composed of carbon dioxide (87%) with minor shares of flammable compounds (i.e., hydrocarbons; 6.5%) and carbon monoxide (5.5%).

3.5. Energy Recovery and Biocrude Application Potential

The calculated energy recovery and carbon distribution among the obtained bioproducts formed during solvothermal liquefaction of blackcurrant pomace are presented in Figure 5. As can be seen, energy recovery in the form of the desired product, i.e., biocrude, varied between 73 and 81% of the energy accumulated in the raw material when the processing temperature was changed between 250 and 300 °C. Such high energy recovery proves that the proposed method may be promising for valorizing wet wastes like blackcurrant pomace and producing a valuable, alternative fuel. It is worth noting that the obtained biocrude is a highly energetic product. Compared to the energetic values of fossil fuels, the biocrude surpasses them by ca. 165%, 115%, and 72% with regard to lignite, hard coal, and heating oil, respectively. However, it is worth pointing out that further research on the characterization and utilization of biocrude should be the subject of future in-depth research.
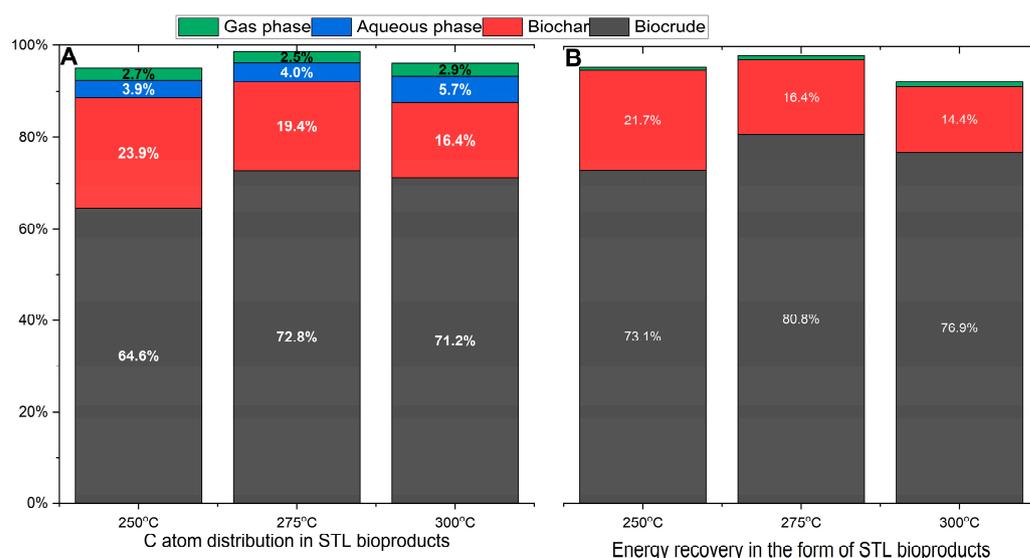
Figure 5. Distribution of C atom (**A**) and energy recovery (**B**) in the bioproducts of solvothermal liquefaction (STL) of blackcurrant pomace.

4. Conclusions

Poland is among the leading countries in the production and further processing of blackcurrant into juice concentrate, jams, etc. The leftover matter constitutes useless wet and unstable organic matter, which has not found any efficient disposal route thus far. Therefore, new technologies for effective conversion into value-added bioproducts are required. Herein, a new approach devised for the transformation of blackcurrant pomace via the application of solvothermal liquefaction in binary solvent systems (water/2-propanol) was proposed. It was proven that the addition of the mentioned organic co-solvent allowed for a significant increase in the production of the target product (biocrude). Moreover, the addition of this alcohol created favorable conditions for the efficient conversion of the biomacromolecules contained in the tested waste biomass. The addition of alcohols to water under near-critical conditions caused a change in the chemical nature of the reaction medium and, as a consequence, supported the hydrolysis reaction and stabilization of the formed intermediate products. The achieved biocrudes produced from blackcurrant pomace exhibited a noticeable increase in carbon content and HHV with regard to the raw material. This makes the resultant biocrudes attractive from the point of view of use as a source of energy or the prospective manufacturing of biofuel components through its downstream processing. A noticeable impact of the studied process variables, i.e., temperature and the biomass-to-solvent ratio, on the yield and quality of the resultant bioproducts was observed. It was also proven that blackcurrant pomace can be directly subjected to solvothermal liquefaction without pre-drying, which is more relevant for real conditions and brings certain advantages (i.e., saving time and energy) to the entire processing procedure. In summary, the proposed approach allows for effective and direct conversion of wet industrial wastes like blackcurrant pomace towards high-energy density biocrude. However, further research focusing on the upgrading of resultant liquid bioproducts should be undertaken.

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