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Py-GC-MS Study on Catalytic Pyrolysis of Biocrude Obtained via HTL of Fruit Pomace

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Abstract: Herein, we proposed new two-stage processing of blackcurrant pomace toward a value-added, hydrocarbon-rich biocrude fraction. The approach consisted of thermochemical liquefaction of a wet-type organic matter into liquid biocrude followed by its upgrade by thermal and catalytic pyrolysis. Particularly, we put effort into investigating the effect of selected catalysts (ZSM-5 and HY zeolite) on the composition of the volatiles released during the pyrolysis of the biocrude. The latter was obtained through liquefaction of the raw material in the binary solvent system of water and isopropanol. The biocrude yield accounted for ca. 45 wt.% of the initial dry biomass. It was a complex mixture of various component groups with an abundant share of oxygenates, especially carboxylic acids and esters. Thereafter, the biocrude was subjected to a pyrolysis study performed by means of the microscale coupled pyrolysis-gas chromatography-mass spectrometry technique (Py-GC-MS). The dominant components identified in the catalytic pyrolytic volatiles were unsaturated hydrocarbons (both cyclic and aliphatic ones) and, to a lesser extent, oxygen and nitrogen compounds. The addition of the ZSM-5 and HY zeolite allowed us to attain the relative total share of hydrocarbons in the volatile fraction equal to 66% and 73%, respectively (in relation to identified compounds). Thus, catalytic pyrolysis over zeolites seems to be particularly prospective due to the promotion of the deoxygenation reactions, which manifested in the noticeable decrease in the share of oxygen compounds in the evolved volatiles. The developed innovative two-stage processing of blackcurrant pomaces allows for obtaining value-added products that could serve as chemicals, biocomponents, and self-contained biofuels as well as bioplastic precursors. The presented contribution brings some new insights into the field of valorization of residuals generated by the food industry sector.

Keywords: biomass; fruit pomace; blackcurrant pomace; hydrothermal liquefaction; pyrolysis; biocrude; bio-oil; sustainability; upgrading; bioproducts

1. Introduction

Commercial liquid fuels obtained by the processing of crude oil are the primary sources of energy in the transportation sector thus far. However, their common usage worldwide has resulted in the well-known negative aspects on the condition of the natural environment. Consequently, numerous extensive research devoted to the production of fully compatible biofuels and biocomponents obtained from biomass have been carried out over the last few decades [1]. This can be clearly proven by the gradually increasing number of scientific works in the field of bioliquid production optimization reported year-by-year [2]. Organic matter can be transformed into liquid bio-oil (commonly called biocrude) mainly via two alternative thermochemical conversion routes such as pyrolysis (conversion mainly of dry feedstock types) and hydrothermal liquefaction (HTL) (for wet-type feedstock). The composition and properties of the resultant liquid bioproducts depend on the process variables and the biochemical composition of the raw material [3]. However, in the literature, many valuable review works can be found reporting on the

effect of processing variables and feedstock type on the change in yield and quality of bioproducts for both technologies (i.e., pyrolysis [4–9]) as well as hydrothermal liquefaction [10–14] separately. The potential of biomass as a raw material for the production of biofuels depends mainly on its local availability, where the supplies depend largely on the agricultural model and the size of production in a given country. Additionally, vital roles are played by the availability and infrastructure for the further processing of crops, afforestation, and the amount of municipal and industrial waste. In Poland, among the different sources of biomass, it is particularly worth mentioning the organic waste generated by the food manufacturing sector as Poland is among the leading European countries in the production of various fruits and vegetables (e.g., blackcurrant, cherries, carrots, and apples) [15]. A significant part of these crops is further processed for juice and jams. The residual solid by-product left after fruit belt pressing (pomace) constitutes useless wet and chemically unstable organic matter, which could be effectively converted into value-added bioproducts using the two aforementioned thermochemical methods. Naturally, in the case of wet-type organic matter, more prospective is the transformation of pomace through hydrothermal processing. Hydrothermal liquefaction allows for the conversion of organic waste (biomass) in water as a reaction medium at elevated temperature (250–374 °C) and pressure (~5–22 MPa). The reaction medium pressure has to be kept above the water vapor pressure at a specific temperature, what enables keeping the medium in the liquid state. The beneficial changes of water's physicochemical properties under the sub-critical region (i.e., viscosity, density, ionic product, dielectric constant, and diffusion rate) allow for an effective conversion of troublesome organic matter into more stable bioproducts of a higher energy density [16,17].

It is worth emphasizing that the resultant biocrude from thermochemical processing is a biomass decomposition product—a crude-like oil. As a whole, the thermochemical products should be considered not as a final product, but as semi-finished products (intermediates) that require a further conversion and/or upgrade. On one hand, the heating value of biocrude is relatively high, reaching even up to 40 MJ·kg^{-1} [18,19]. On the other hand, its characteristics are still far from the standards established for conventional fuels such as diesel oil or gasoline. Biocrudes are highly heterogeneous in composition products that also exhibit low stability, which makes their direct usage highly limited or, often, impossible. Furthermore, it is important to highlight that biocrudes are fuels with a very wide range of boiling temperature and composed of compounds with molecular mass starting from several dozen up to even several thousand Daltons [20]. For example, the biocrude obtained via continuous hydrothermal liquefaction of microalgae *Scenedesmus* sp. contained compounds with a wide range of molecular masses ranging between ca. 100 and 3000 g mol^{-1} [21]. Similar molecular mass distribution was also reported for the biocrude derived from pine wood by the hydrothermal liquefaction [22]. The high content of high-boiling components entails unfavorable characterization of physicochemical properties such as high density, viscosity, low stability, and tendency to form solid products (e.g., via re-polymerization). In comparison with conventional liquid fuels, the biocrudes are also characterized by a significantly higher content of oxygen compounds. The oxygenates are often highly reactive and contribute to the low stability of the alternative fuel during its storage, transportation, or processing.

Consequently, the low quality of biocrudes and their disadvantageous set of properties contribute to a narrow range of viable commercial direct applications. Thus, it is clear that these products should be subjected to refining processes that not only change the composition and improve the physicochemical properties but also broaden the application potential of the ultimate bio-product. A number of methods have been developed to enhance the quality and application potential of bioliquids. Among them, the following can be mentioned: thermochemical processes (e.g., hydrotreatment, catalytic (hydro)cracking), physicochemical treatments (e.g., distillation, blending or electrochemical treatment), or chemical methods (solvent extraction, transesterification, biological methods) [2]. There have been some valuable reviews discussing the progress in upgrading methods [23–25].

Among them, one of the most prospective is cracking or catalytic cracking. During processing, the decomposition of oxygen-rich compounds contained in biocrude occurs, which results in products with lower molecular weights. Processing over catalysts (e.g., zeolites) additionally allows for the intensification of deoxygenation and the increase in the share of hydrocarbons. The upgraded biocrude has a group composition closer to conventional liquid fuels as well as in terms of physicochemical properties, chemical composition, and operational parameters (calorific value, cetane number, oxidative stability).

Herein, we proposed, for the first time, a new, two-stage processing approach of blackcurrant pomace consisting of the thermochemical liquefaction of the raw material in a combined water-organic medium toward biocrude followed by the pyrolytic decomposition of the latter (see Figure 1). The first stage allows for the effective conversion of wet-type residual organic matter toward a more stable biocrude with a higher energy density. The addition of isopropanol as a co-solvent to the reaction medium allows for an increase in liquid fraction yield as we previously reported [26]. In the literature, only research regarding the processing of blackcurrant pomace in the aqueous medium can be found [27,28], so the postulated modification allowing for almost double the yield of biocrude without lowering the quality thereof can be particularly valuable. In the postulated approach, we investigated the possibility of converting the highly heterogeneous main product containing high-molecular compounds via thermal and catalytic fast pyrolysis. The latter technique allows for troublesome heavy fractions to be cracked into lighter fractions exhibiting better application potential (e.g., biocomponents or chemicals). The residual group of bioproducts generated in the first and second stages of the proposed concept (e.g., biochar, non-condensable gas fraction) can be used as an internal source of energy and heat within the technology. It is worth emphasizing that the light liquid fraction offers better flexibility in finding the most beneficial application route and can be considered as a source of value-added chemicals. To the best of our knowledge, as of today, there has been a lack of research on the utilization of fruit pomace through a two-stage approach similar to that investigated herein. Indeed, there are other two-stage approaches such as focusing on the conversion of biochar obtained from different kinds of organic wastes (e.g., cherry pomace [29] or brewery spent grains [30]), but the new concept presented in this contribution has not hitherto been exploited. Moreover, the present research also brings new insights into the evaluation of the physicochemical properties of HTL biocrude as well as its conversion via fast pyrolysis over ZSM-5 and HY zeolites. While the application of zeolites in the pyrolysis process of raw materials (biomass, plastics) can be found in the literature quite often [31–33], there is a lack of research regarding the application thereof to upgrade the bio-oils or biocrudes. It is noteworthy that the implementation of such technologies also allows for a reduction in the emission of greenhouse gases to the atmosphere and helps to alter the diversification of energy sources used in the energy system. This is particularly important in light of the Polish energy system, which is currently mainly based on fossil fuels (lignite and hard coal).
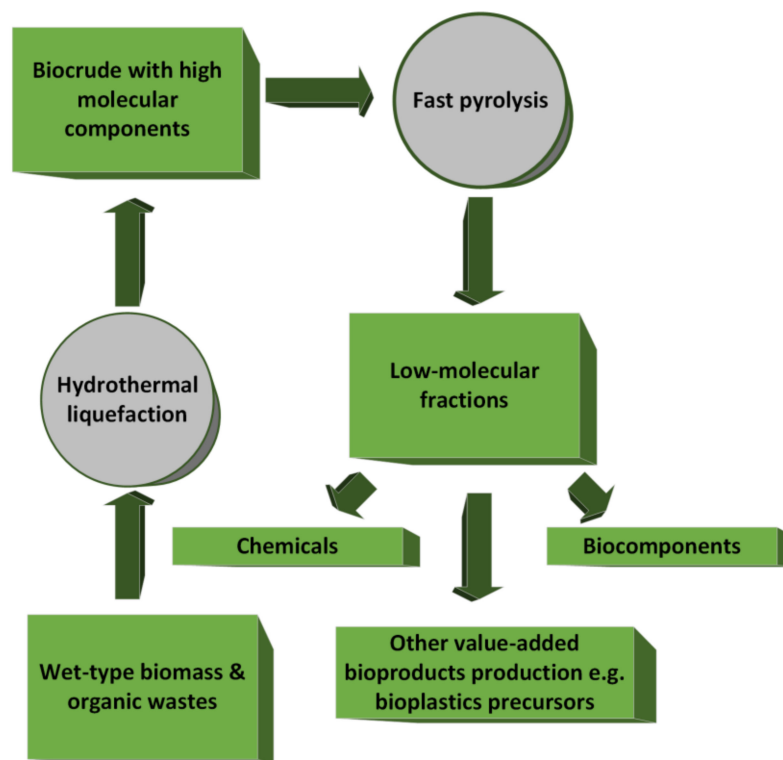
Figure 1. The proposed approach for two-stage processing of waste fruit pomace via hydrothermal liquefaction followed by the fast pyrolysis of biocrude toward value-added products.

2. Materials and Methods

2.1. Materials

The biocrude used in this study was obtained by the conversion of blackcurrant (*Ribes nigrum*) pomace. The tested waste material was supplied by an industrial juice production company—Tymbark MWS (Tymbark, Poland). The pomace is a highly heterogeneous mixture of different residual particles of the shredded plant (seeds, leaves, stalks, and peels), so the first step was grinding it by using a cutting mill (Fritsch Pulverisette 15). The obtained mesh fraction was ca. 2–3 mm. The moisture and ash contents in the raw material after grinding were equal to 44.1 and 3.1 wt%, respectively. The raw material was subjected to a hydrothermal liquefaction test without preliminary drying.

The catalysts used for catalytic pyrolysis investigation (i.e., ZSM-5 and HY zeolites) were commercial products. ZSM-5 was supplied by Acros Organics, while the HY zeolite was purchased from Alfa Aesar (720 m^2 g^{-1}; 60:1 mole ratio SiO_2:Al_2O_3). Isopropanol (p.a.), dichloromethane (DCM, p.a.), acetone for GC-MS analysis (HPLC grade), and acetone for solid residue analysis (p.a.) as well as NaOH (p.a.) and phenolphthalein (2 wt% solution) as an indicator for TAN determination were supplied by Avantor Performance Materials.

2.2. Biocrude Production via Thmochemical Liquefaction

The production of biocrude from blackcurrant pomace was carried out by hydrothermal liquefaction in mixed solvents. The test was carried out in a batch autoclave (Parr Instrument, Moline, IL USA) equipped with a dedicated controller (Parr Instrument, USA). The operational volume of the batch reactor was 0.5 dm^3. The total mass of the slurry subjected to processing was ca. 250 g. Herein, the studied biocrude was produced in the subcritical region of the mixture of water and isopropanol at a mass ratio of 1:1. The test was conducted in the following conditions: (i) temperature—275 °C; (ii) biomass concentration (on the dry state)—10 wt%; (iii) residence time—30 min; and (iv) paddle stirrer speed—400 rpm. The pressure was generated autogenously and varied between 75–80 bar. The actual amount of water in the starting slurry was the cumulative mass of

water contained in the raw feedstock and the portion of distilled water added to keep the intended biomass to solvents ratio. The selected conditions were chosen based on our previous work [26].

The separation and recovery of the resultant groups of bioproducts were performed according to the standard procedure based on the solvent extraction with DCM, followed by vacuum filtration and solvent evaporation. The detailed procedure was described elsewhere [34]. Ultimately, the isolated bioproducts were: (i) liquid biocrude; (ii) aqueous phase organics; (iii) solid residue; and (iv) non-condensable gas fraction. The yield of the latter was calculated based on the Clapeyron equation using processing parameters and gas composition. The composition of the gas phase was analyzed using a gas chromatograph (GC-SRI, model 302, SRI-Instruments Inc., Las Vegas, NV USA) equipped with FID and TCD detectors. The HTL test was carried out twice and the final product was prepared as a mixture of biocrudes from both runs after we ensured that their compositions were mutually similar.

The yield of each group of products (i.e., biochar, biocrude, gas phase, and water-soluble organics) was calculated based on their mass regarding the mass of dry feedstock. The difference was considered a loss. The variation in closing the mass balance could be linked with the loss of some organics during the evaporation of solvents, some solid residues leftover on small elements of the batch autoclave as well as issues in the quantification of formed water as a product. Additionally, we calculated the C and H element distributions in certain HTL groups of products as a ratio of the product of yield and C/H content in each group of products to C/H element in dried raw material.

2.3. Biocrude Characteristics

The elemental composition (C, H, N) in the raw material and the resultant biocrude was determined using a EuroVector EA3100 CHNS elemental analyzer. The oxygen content was determined by the difference (i.e., by subtracting from the unity the content of other elements as well as ash). Each presented result is an average of at least two analyses. HHV of the analyzed bioproducts was determined based on elemental composition according to the Dulong formula.

The composition of the obtained HTL biocrude was investigated by means of mid-infrared Fourier transform spectroscopy. The spectra were collected on a Nicolet iS5 (Thermo Fisher Scientific Inc., Waltham, MA USA) spectrometer equipped with an ATR accessory with a diamond crystal. The spectrometer was assembled with a DLaTGS detector. The spectrum of biocrude was acquired in a 400–4000 cm^{-1} spectral range at a resolution 4 cm^{-1}.

The analysis of the light fraction of biocrude (i.e., being evaporable up to ca. 300 °C as the GC technique allows) was also conducted based on gas chromatography (Agilent Technologies, model: GC 7890B) coupled to mass spectrometry technique (Agilent Technologies, model: 5977A) with electron ionization (EI). The GC-MS analytical set was equipped with a DB-17 capillary column (30 m × 0.32 mm × 0.5 μm). The sample was prepared as 5 wt.% solutions in acetone. Moreover, before injection, the solution was filtered through 0.2 μm PTFE syringe filter. The analysis was performed at a split ratio of 15:1. The injector temperature was set at 250 °C. The ion source temperature was 230 °C, electron ionization was set at 70 eV, and spectra were scanned from 33 to 400 m/z with a frequency of 3.9 scans per second. The obtained MS spectra were interpreted based on the reference MS library (chemical base G1034C) and only peaks with high enough compatibility with the MS library (>70%) were considered for analysis. The relative share of compounds or group of compounds was calculated as a ratio of peak area of a given compound related to the cumulative peak area of all detected components. The compounds were identified using an integration procedure, and additionally manually verified with the MS library.

In order to determine the physicochemical characteristics, the set of basic parameters, (i.e., viscosity, density, water content, pH, Total Acid Number (TAN), oxidative stability, ash and solids content) for the resultant biocrude was also assessed. The dynamic viscosity

of biocrude was measured using the Brookfield Ametek DV-1 rotational viscometer. The measurement was performed at temperatures ranging between 10 °C and 40 °C using the dedicated high viscosity materials spindle (RV-07). The assessment was conducted under changing rotation frequency ranging between 1.5 and 60 rpm. The pycnometer method was used to determine the density at the same temperatures as for viscosity. The kinematic viscosity was determined as the ratio of the dynamic viscosity with respect to the density. Measurement of the water content in the tested biocrude was carried out using the Karl Fischer method (i.e., coulometric titration technique), according to the standard ASTM D4928 (Moisture Titrator MKC-501, Kyoto Electronics Manufacturing, Kyoto, Japan). The pH of the biocrude was measured using an integrated electrode. Calibration was performed just before the measurement. TAN is the number of milligrams of sodium hydroxide (NaOH) required to neutralize the acids present in one gram of biocrude. The TAN determination was carried out by dissolving 50 mg of a sample in 10 mL of isopropyl alcohol, and then colorimetric titration with 0.05 M NaOH solution in the presence of phenolphthalein as an indicator. The ash content was determined as the residue after the oxidation of biocrude in an open crucible at 815 °C in an electric muffle furnace under static air atmosphere. The solid content was determined as the amount of biocrude insoluble fractions in the selected solvent (i.e., acetone). Thermooxidation stability at 140 °C was tested according to the standard PN-EN 16091: 2011 method using the Petrooxy apparatus (Petrotest, Berlin, Germany). All analyses were repeated three times, and the presented values were calculated as the average value of all performed measurements.

2.4. Fast Pyrolysis Tests—Py-GC-MS

The study focused on the upgrading of HTL biocrude by thermal and catalytic fast pyrolysis, so experiments were conducted by means of coupled analytical techniques Py-GC-MS. The tests were carried out using a pyrolyzer unit (CDS Analytical, Oxford, PA USA, model 5200) connected to an analytical setup GC-MS consisting of a gas chromatograph unit (Agilent Technologies, Santa Clara, CA USA, model 7890B) and a mass spectrometer (Agilent Technologies, model 5977A). The experiments were conducted in the following three different manners: (i) thermal processing without the catalyst; (ii) catalytic test over ZSM-5; and (iii) HY zeolite. In the case of catalytic study, the catalyst/biocrude mass ratio was equal 1:1. For tested conditions, other processing variables were kept fixed: (i) temperature—500 °C; (ii) heating rate—50 °C s^{-1}; (iii) residence time at final temperature—30 s; and (iv) inert atmosphere—helium (grade: 6.0). All tests were conducted in the direct mode so the analytes that evolved during each measurement were transferred for analysis to the GC-MS immediately after starting to heat the filament of the pyroprobe. To avoid condensation of the released volatiles, the transfer line was kept constant at 300 °C.

For all tests, the sample (ca. 1.00 mg) was placed in a quartz boat, which was then transferred to a platinum coil filament. Additionally, the residues after the samples' pyrolysis were also weighed. The mass of samples and residues was controlled by using a Mettler-Toledo microbalance model WXTS3DU. Before commencing the procedure, the reaction zone was purged with an inert gas (He, grade: 6.0) for a few minutes. The GC-MS analysis was conducted in split mode with the ratio 50:1. The injector temperature was set at 300 °C. The Agilent HP-5MS capillary column of dimensions of 30 m × 0.25 mm × 0.25 μm was used for separation. The temperature regime of the GC analysis was as follows: (i) isothermal held at 40 °C for 7 min; (ii) next heating to 250 °C at a rate of 4 °C min^{-1}; (iii) and last isothermal stage at 250 °C for 5 min. The compounds and their peak areas were found by their integration. For analysis, we considered the peaks with a height not less than 0.2% of the highest one. The MS spectra were identified based on the reference MS library (chemical base G1034C). The identification of compounds was also supported by applying the deconvolution procedure as well as manually checking with the MS library. We only considered the compounds that had a sufficiently high threshold of matching with reference compounds in the MS library (>70%). The details of the procedure have been described elsewhere [35].

3. Results and Discussion

3.1. Biocrude Production

The distribution of the yield of bioproducts received after the hydrothermal liquefaction of blackcurrant pomace is presented in Figure 2. As can be noted, the major group of products was liquid biocrude, which accounted for ca. 45 wt% with regard to the dried biomass subjected to conversion. A moderate yield (25 wt%) was noted for a solid residue called biochar. Relatively low yields were noted for aqueous phase organics and non-condensable gas fractions. It is worth noting that the biocrude yield as a target product was higher compared to other works in the literature. For instance, Déniel et al. [27] reported lower biocrude yields produced from blackcurrant pomace through HTL in an aqueous medium ranging between 24 and 30 wt%. Thus, it is worth emphasizing here that the addition of isopropanol as the co-solvent is beneficial in light of reaching a higher efficiency of conversion in the case of this kind of organic residue. Additionally, it was proven here that there is a possibility of producing biocrude from wet-type organics with high yield, omitting the preliminary biomass drying.
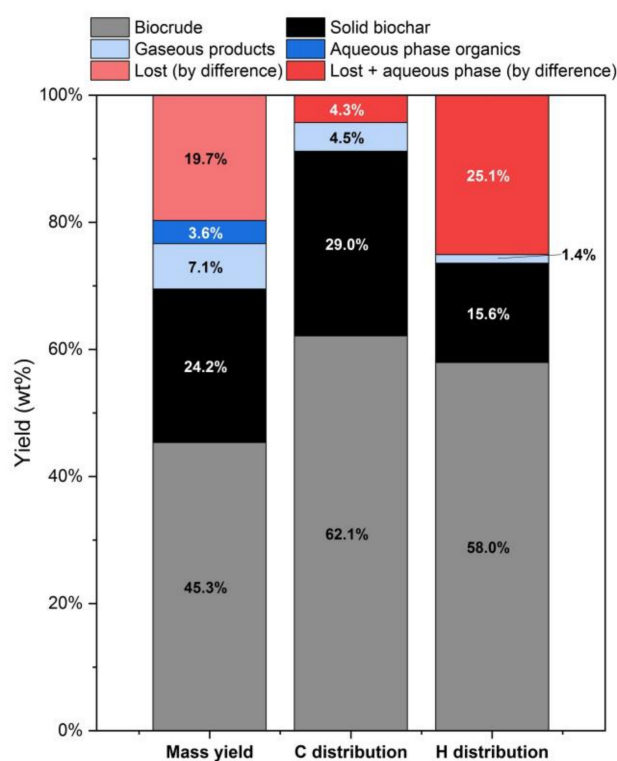

Figure 2. Mass yields of given product fractions, and respective C and H distributions in HTL bioproducts in the present contribution.

The distribution of C and H elements in the obtained groups of products through hydrothermal liquefaction of blackcurrant pomace in the present contribution is also presented in Figure 2. The highest carbon recovery was revealed by the biocrude, which constituted ca. 62.1 wt% of carbon contained in the dry pristine feedstock. It is worth noting here that the carbon balance closure was high (95 wt%). The hydrogen balance closure was lower (ca. 80%), which could prove that the loss calculated from the mass balance closure is possibly linked with the water potentially formed during the HTL processing, but hard to quantify.

In Table 1, a comparison of the elemental compositions of raw blackcurrant pomace with the resultant HTL biocrude is presented. The carbon and hydrogen contents in the biocrude were noticeably higher than that for the feedstock and accounted for approx. 70 wt.% and 9 wt%, respectively. This affects a noticeably higher energetic density of the

resultant biocrude compared to the raw material. The HHV of the liquid accounted for ~33 MJ kg^{-1}, while for dried blackcurrant pomace, it equalled 20.8 MJ kg^{-1}. Thus, higher energy density makes the resultant biocrude much easier for transportation and storage, which undoubtedly produces closer opportunities for its use in industrial reality. It is also worth mentioning that the H/C mole ratio between pomace and biocrude stayed almost unchanged, while O/C decreased more than twice. Hence, it can be concluded that thermochemical decomposition occurs preferentially via the decarboxylation/decarbonylation route.

Table 1. Elemental composition of blackcurrant pomace as feedstock and biocrude obtained via its hydrothermal liquefaction in mixed solvents.

Element/Parameter [a]	Unit	Feedstock		HTL Biocrude	
C	wt%	50.54	±0.67	69.25	±0.53
H	wt%	7.13	±0.15	9.11	±0.14
N	wt%	2.72	±0.17	2.38	±0.22
S	wt%	0.22	±0.06	n.d.	-
O	wt%	36.57	±0.82	19.25	±0.47
H/C	mol mol^{-1}	1.679	±0.013	1.579	±0.033
O/C	mol mol^{-1}	0.543	±0.019	0.209	±0.007
HHV	MJ kg^{-1}	20.78	±0.59	33.07	±0.26

[a] calculated on dry basis; n.d.—below the level of detection, i.e., <0.1 wt%.

We also analyzed the composition of the gas phase evolved during the thermochemical liquefaction of blackcurrant pomace. As can be seen in Table 2, the dominant constituent was carbon dioxide, which accounted for 87.2 wt% of the released gas phase. This proves that the decomposition of the investigated residues occurs mainly on the decarboxylation route. However, the presence of carbon monoxide (5.47 wt%) also confirms that some decarbonylation reactions can also take place. The total share of flammable components was rather negligible, but it is worth noting the highest share of propene (6.55 wt%). It could be the reason for the dehydration of isopropanol used in this experiment as a co-solvent.

Table 2. The composition of the gas phase evolved through the liquefaction of blackcurrant pomace in this contribution.

	Gas Components						
	CO_2	CO	H_2	CH_4	C_2H_6	C_3H_6	C_3H_8
Mean value (wt%)	87.21	5.47	0.32	0.33	0.04	6.55	0.08
SD	±0.02	±0.01	±0.01	±0.02	±0.01	±0.03	0

3.2. Biocrude Composition and Properties

The resultant biocrude was a highly viscous, dark color liquid product similar in appearance to heavy fractions derived from crude oil (e.g., heavy heating oil). The performed GC-MS and FT-IR analyses depicted in Figure 3A,B, proved that our biocrude was a complex mixture of organic compounds containing heteroatoms—mainly oxygen and to lesser extent nitrogen. As can be seen in Figure 3A, which depicts the group fraction of the light fraction of the biocrude, the highest share accounted for carboxylic acids (55.7%) and esters (19.7%). These compounds originated from the degradation of lipids accumulated mainly in the seeds contained in the feedstock. The relatively high amount of esters could be the result of undergoing transesterification reactions between triglycerides and isopropanol added as a co-solvent to the HTL reaction medium. However, the high share of esters is more probably the result of the esterification reaction between the co-solvent and carboxylic acids formed after the hydrolysis of triglycerides. The presence of phenol derivatives is a consequence of the degradation of lignin. The share of this group as well as other groups of oxygenates (ketones, aldehydes) were rather minor and accounted for ca. 3.1% and

1.7%, respectively. It is likely that lignin could not completely undergo decomposition or could exist in the form of higher molecular compounds forming heavy boiling fractions. Protein degradation products were transformed mainly to nitrogen compounds, which accounted for ca. 13.7%. Complex compounds with high molecular mass or exhibiting various functional groups accounted for ca. 6.1%, but it is worth noting that this was due to the limitation of the applied gas chromatography technique (cf. Experimental Section). What is particularly worth noting here is the lack of hydrocarbons in biocrude. This is a significant drawback to this product considering its intended energetic purpose.
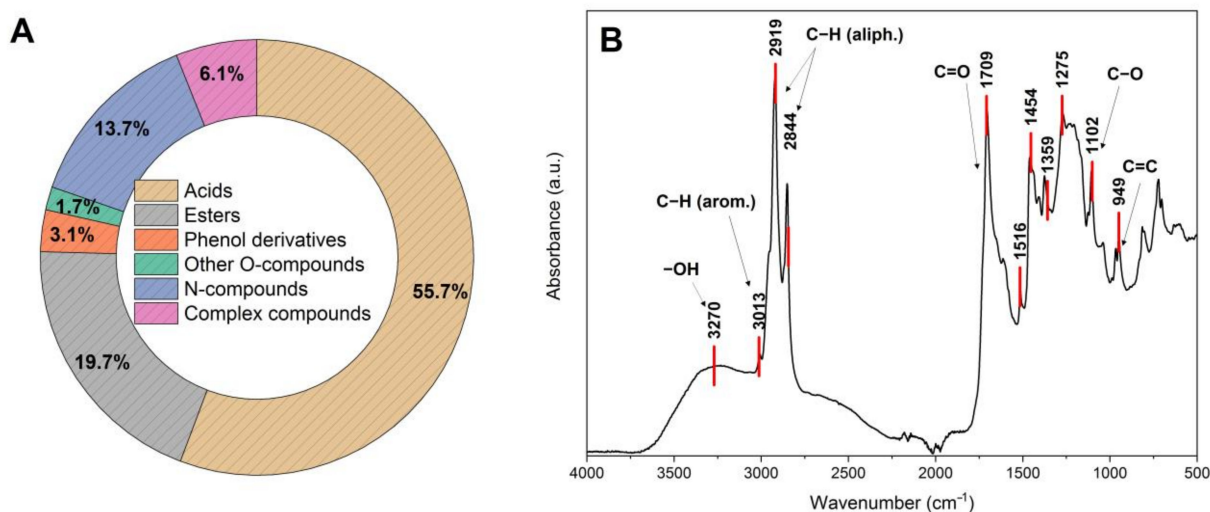

Figure 3. Composition of the resultant HTL biocrude from blackcurrant pomace based on (**A**) GC-MS analysis, (**B**) ATR-FTIR analysis.

The above discussion regarding the composition of biocrude was also supported by the mid-infrared spectroscopy. As shown in Figure 3B, the presence and intensity of particular absorption bands indicated the domination of numerous oxygen-containing compounds in aliphatic and aromatic structures. The presence of carboxylic acids, esters, and phenols can be confirmed by the presence of a broad band assigned to the stretching vibrations of the hydroxyl group between 3500–3000 cm^{-1}. The aliphatic structures were corroborated by the relatively intensive stretchings of the methyl and methylene groups between 3000–2850 cm^{-1}. More intensive were the modes characteristic for CH_2 groups (i.e., at 2919 and 2844 cm^{-1}) than CH_3, which could prove the domination of long-chain unbranched aliphatic species typical for fatty acids and their derivatives. The presence of aromatic structures can be confirmed by the absorption centered at 3013 cm^{-1} (C–H vibrations in aromatic structures) as well as absorption modes between 1500–1400 cm^{-1}. The oxygen-containing moieties can also be proven by the intensive sharp band around 1709 cm^{-1} as well as the one between 1160–1100 cm^{-1}, which can be assigned to the carbonyl groups and C–O stretchings, respectively.

Additionally, in Table 3, the exemplary compounds within all groups identified via GC-MS analysis were collected. It is worth noting the significant amount of isopropanol derivatives. This proves that the addition of alcohol to the reaction medium also acts as a reagent during conversion on the hydrothermal liquefaction route. The highest content constituted saturated and unsaturated C16 and C18 carboxylic acids and their corresponding derivatives—isopropyl esters. Among the other oxygen compounds, we found lower amounts of organics such as cyclic ketones, which were likely the products of the transformation of saccharides. The detected nitrogen compounds were mostly heterocyclic aromatic species such as pyrazine derivatives (methyl pyrazine or pyridinol). Finally, it is worth mentioning that a noticeable amount of detected compounds could not be susceptible for analysis because of the too low volatility of obtained biocrude.

Table 3. Exemplary compounds identified in biocrude obtained from the conversion of blackcurrant pomace.

Group	RT (min)	Name	Formula	Relative Area (%)
Acids	5.7	Propanoic acid	$C_3H_6O_2$	0.32
	60.4	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.22
	66.6	9-Octadecenoic acid	$C_{18}H_{34}O_2$	15.39
	67.2	9,12-octadecadienoic acid	$C_{18}H_{32}O_2$	28.51
	67.9	9,12,15-Octadecatrienoic acid, (Z,Z,Z)-	$C_{18}H_{30}O_2$	3.04
Esters	12.6	Isopropyl 2-hydroxypropanoate	$C_6H_{12}O_3$	1.08
	30.5	Pentanoic acid, 4-oxo-, propyl ester	$C_8H_{14}O_3$	0.48
	60.6	Hexadecanoic acid isopropyl ester	$C_{19}H_{38}O_2$	3.60
	64.9	9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	0.73
	66.3	Octadecanoic acid isopropyl ester	$C_{21}H_{42}O_2$	3.79
	66.9	9,12-Octadecadienoic acid isopropyl ester	$C_{21}H_{38}O_2$	7.52
	67.7	9,12,15-Octadecatrienoic acid, isopropyl ester	$C_{21}H_{36}O_2$	1.63
Phenol deriv.	24.8	Benzene, ethoxy-	$C_8H_{10}O$	0.50
	30.8	Phenol, 2-methoxy-	$C_7H_8O_2$	0.68
	34.1	Phenol, 4-ethyl-	$C_8H_{10}O$	0.69
	39.1	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0.57
Other O-cmpd	25.1	Butyrolactone	$C_4H_6O_2$	0.41
	27.7	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	0.36
	74.5	2,3-Butanediol, diacetate	$C_8H_{14}O_4$	0.55
N-cmpd	15.1	Pyrazine, methyl-	$C_5H_6N_2$	0.64
	33.1	3-Pyridinol	C_5H_5NO	4.75
	33.8	2-Pyrrolidinone	C_4H_7NO	1.04
	35.2	3-Pyridinol, 6-methyl-	C_6H_7NO	0.74
	50.3	N-Ethyl-2-isopropoxycarbonylazetidine	$C_9H_{17}NO_2$	2.29
	61.4	1,2,5-Oxadiazole-3,4-dicarboxamide	$C_4H_4N_4O_3$	0.86
	64.3	3,6-Diisopropylpiperazin-2,5-dione	$C_{10}H_{18}N_2O_2$	0.73
Complex cmpd	69.7	l-Valine, n-propargyloxycarbonyl-, pentadecyl ester	$C_{24}H_{43}NO_4$	0.72
	70.4	Benzenamine, N-(4-pyridinylmethylene)-	$C_{12}H_{10}N_2$	0.56
	71.5	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolopyrazine	$C_{14}H_{22}N_2O_2$	0.80
	71.6	9H-Carbazole, 9-(1-naphthalenyl)-	$C_{22}H_{15}N$	0.23
	85.2	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)-	$C_{14}H_{16}N_2O_2$	1.15

Table 4 presents the comparison between the physicochemical properties of the studied biocrude and diesel oil as the reference conventional engine fuel. Determination of physicochemical properties allows assessing the application potential and the main limitations in the case of biocrude direct usage. On this basis, the possible routes of its downstream processing can be designed to improve its quality to the transport fuel class. The tested biocrude indicates high density and viscosity, falling within the ranges reported previously in the literature [28].

It is worth mentioning that these high values are one of the major limitations of the application of biocrude to fueling the reciprocating combustion engines. For instance, too high density and viscosity can cause issues with the operation of fuel pumps and injectors as well as disrupt or even block the combustion process because of difficulties in its vaporization and spraying during fuel injection. As a consequence, it may also lead to incomplete and imbalanced combustion, resulting in releasing pollutants into the atmosphere (e.g., CO, unburnt by-products compounds, soot, and PM).

Thermo-oxidative stability is a parameter that allows for oxidation reactions to be simulated during fuel storage and transport. As seen in Table 4, the biocrude's oxidation stability is vastly lower compared to diesel oil. The biocrude exhibits more than twice a shorter time of oxidation compared to diesel oil under the same conditions (29 min

vs. 68 min, respectively). This can be due to the abundant content of various oxidation-prone compounds (i.e., organic acids, aldehydes, ketones, or phenols in the biocrude). The oxidation process of these compounds leads to the formation of various types of products causing changes in composition and properties. Those compounds also favor the occurrence of secondary reactions (polymerization and polycondensation), which results in the formation of high molecular compounds (e.g., resins and gums forming sediments) negatively changing the physicochemical properties of the biocrude. The resulting products can damage pumps, block filters, and fuel lines as well as lead to the corrosion and degradation of various engine components.

The low pH of the biocrude is mainly caused by a high concentration of organic acids in the freshly obtained product. Additionally, the progressive ageing of the fuel can affect the increase in acidity. The low pH value of biocrudes has been reported previously in the literature [36]. This fact is also confirmed by the total acid number (TAN) of biocrude. The high acidity may cause some operational and exploitation issues (e.g., due to intensification of the corrosion of materials in a distribution setup or engine fuel supply system. In addition, the oxidation process takes place over time and the chemical instability during storage further intensifies these negative effects (the *snowball effect*), which can critically limit the possible storage time and usability of fuel.

On one hand, the ash and moisture contents in the tested biocrude are relatively low compared to the pyrolysis bio-oils. On the other hand, the solid deposits, determined as the fraction insoluble in acetone, were very high and proves the complex and heterogeneous chemical composition of the obtained biocrude and the presence of both polar and non-polar compounds.

Based on the physicochemical characteristics of the obtained biocrude, it can be concluded that the main limitations of the direct use of biocrude as a transport fuel are too high a density, viscosity, and acidity as well as high heteroatom (O,N) content. Those values are out of the limits of the standards for conventional liquid fuels. Biocrude characteristics are the closest to the heavy fuel and/or heating oils used for fueling big marine propulsion units. Thus, the direct application of biocrude should be limited to heat generation in industrial boilers and furnaces, or as fuel in the aforementioned low-speed diesel engines used in watercrafts. However, increasing the potential of biocrude requires improving its quality in the upgrading processes toward the reduction in heteroatoms content and producing more homogenous fractions. Then, resultant high-quality components can be applied as biocomponents or chemicals, which can partially or completely substitute conventional fuels such as gasoline or diesel oil.

Table 4. Physicochemical characteristics of obtained HTL biocrude and standard requirements for the reference conventional fuels.

Parameter	Unit	HTL Biocrude [a]	Diesel Oil [b]	Heavy Heating Oil [c]
Density, 15 °C	kg m^{-3}	1114 ± 17	820–845	>890
Kinematic viscosity, 40 °C	mm^2 s^{-1}	558 ± 20	2–4.5	—
Dynamic viscosity, 40 °C	cP	625 ± 16	—	<800 [e]
Oxidative stability, 140 °C	min	29.81 ± 0.15	67 [a]	—
Water content	wt%	0.08 ± 0.03	0.02	<1.0
pH	—	4.15 ± 0.09	—	—
TAN	mg NaOH g^{-1}	80 ± 4	—	—
Solids content	wt%	10.21 ± 1.77 [d]	0.0024	<0.5
Ash content	wt%	0.07 ± 0.01	—	<0.2

[a] Determined in the present study; [b] Requirements according to the standard PN-EN 590; [c] Requirements for heavy heating oil type C3; [d] Determined as a fraction insoluble in acetone; [e] Determined at 50 °C.

3.3. Biocrude Upgrading through Thermal and Catalytic Pyrolysis over ZSM-5 and HY Zeolites

The effect of thermal and catalytic conversion of HTL biocrude via fast pyrolysis was investigated using the Py-GC-MS technique. In Figure 4A, we depicted the chromatograms of analytes evolved after the thermal and catalytic pyrolysis of biocrude over ZSM-5 and HY zeolites. For the sake of comparison, we also present the chromatogram acquired for the raw biocrude in Figure 4B. It can be seen that fast pyrolysis of the biocrude allowed for noticeable conversion of compounds contained in the raw biocrude. It can be seen at glance that the raw biocrude had a lower number of the detected compounds. There is mainly an intensive set of peaks in the range of RT = 50–70 min, which correspond mainly to fatty acids and respective esters. There were also several other peaks, but with significantly lower abundance. The thermal conversion without the addition of the catalyst resulted in the partial decomposition of the originally contained fatty acids and esters (RT = 50–60 min, Figure 4A), which resulted in the detection of lighter compounds. However, compared to catalytic pyrolysis, the pyrolysis over both tested zeolites resulted in a much higher number and abundancy of lighter compounds that could be noticed. This suggests the activity of both zeolites in cracking of the organics. In the case of the catalytic pyrolysis of biocrude, almost one hundred and fifty compounds could be identified, while in the case of thermal raw biocrude processing, only less than half of them were detected. However, the pyrolysis chromatograms noted for both runs over zeolites exhibited a mutual qualitative similarity, but some quantitative differences could be seen. The subjected zeolites allowed for the profound conversion of organic acids and esters abundantly presented in the raw biocrude.
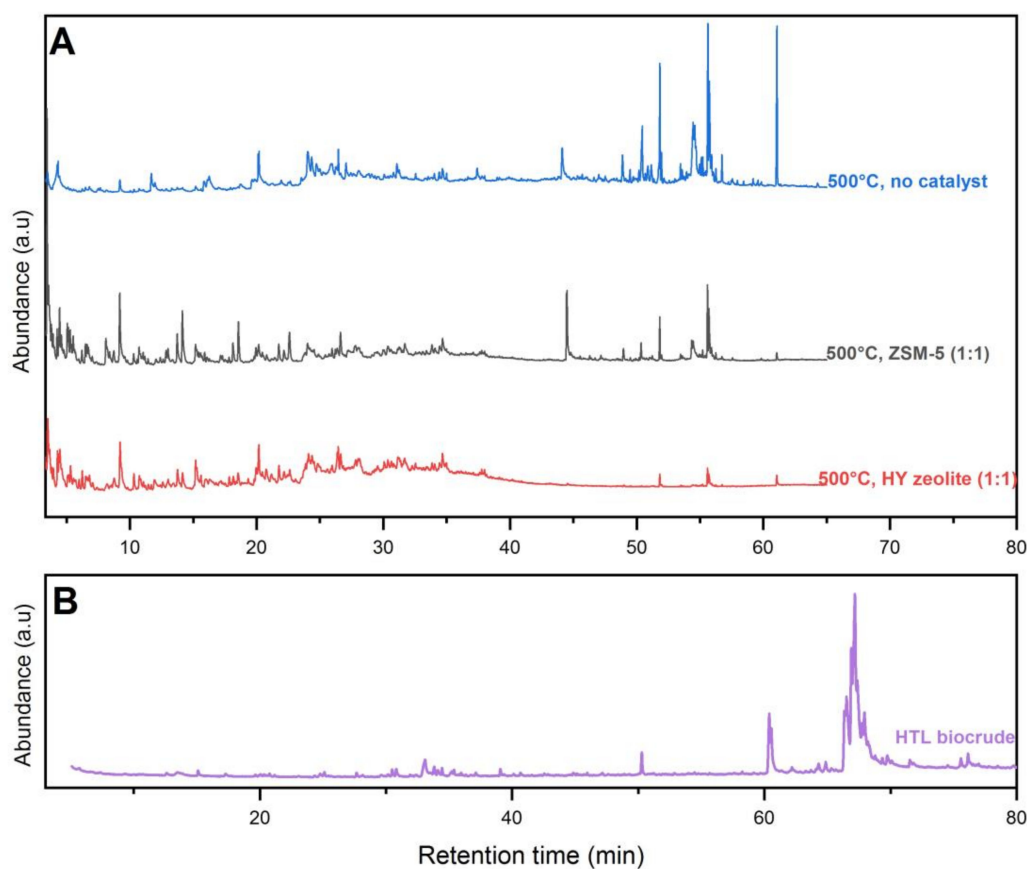

Figure 4. Comparison of total ion chromatograms (TIC) for the products of the thermal and catalytic pyrolysis of HTL biocrude (over ZSM-5 and HY zeolite) investigated through Py-GC-MS analysis (**A**), and TIC for biocrude (**B**).

The compounds evolved during the thermal and catalytic pyrolysis of biocrude were identified and classified into four main groups: (A) hydrocarbons, (B) oxygen compounds, (C) nitrogen compounds, and (D) carbon dioxide. The hydrocarbon group was further divided into: (A1) aliphatic unsaturated hydrocarbons, (A2) aliphatic saturated hydrocarbons, (A3) cyclic hydrocarbons, and (A4) aromatic hydrocarbons. The oxygen compounds were divided into: (B1) carboxylic acids, (B2) esters, (B3) alcohols, ketones, and aldehydes, and (B4) phenol derivatives. It is worth noting here that we also checked the mass of solid residue left after the process in the pyrolyzer unit. The average mass left over after the process ranged between 23.5–27.8 wt%, while the highest one was noted for purely thermal processing. Thus, *circa* three-quarters of the sample was theoretically amenable for conversion (Table S1 in Supplementary Materials). The identified peaks accounted for ca. 90% of the total peak area in the resultant chromatograms. The contributions of the respective groups' compounds for the different modes of pyrolysis was depicted in Figure 5. As seen, the analytes that evolved during catalytic pyrolysis were mainly composed of hydrocarbons. The total share of hydrocarbons in the case of ZSM-5 and HY zeolites reached 69.2% and 74.2%, respectively (in relation to identified compounds). These values were much higher compared to the thermal process (29.1%), at which the pyrolysis released vapors were composed mainly of oxygen compounds with the highest share of carboxylic acids (19.3%) and esters (22.6%). There was also a significant total share of alcohols, ketones, and aldehydes (12.2%), and phenol derivatives (6.5%). In the case of the non-catalytic process, the share of aromatic hydrocarbons reached 12.6%, while the contributions of unsaturated aliphatic hydrocarbons was 10.7%. The pyrolytic conversion over ZSM-5 and HY zeolites resulted in a significant decrease in oxygen compounds, which equalled cumulatively for 28.2% and 20.4%, respectively. It can clearly be seen that these compounds underwent deoxygenation, mainly toward unsaturated aliphatic hydrocarbons (32.8% and 33.4%). In addition, the contribution of aromatics increased noticeably and was around twice as high compared to no catalytic processes (i.e., 23.2% for ZSM-5 and 25.8% for HY zeolite). The share of cyclic hydrocarbons was also more than doubled for both catalysts. It is known that zeolite catalysts increased the aromatic production. However, it can be emphasized here that tests in the presented contribution were in fact the fast pyrolysis (heating time 50 °C/s) with really short contact time, which could result in the production of intermediate aromatization products such as aliphatic and cyclic compounds. This can be a valuable observation because these compounds are desirable as fuel components. The aliphatic components can most probably be formed through the transformation of lipid derivatives (esters and carboxylic acids). It is worth mentioning that in the raw biocrude, we did not detect hydrocarbons. The share of nitrogen compound groups was also the highest for thermal decomposition (9.5%), while the share of saturated hydrocarbons was negligible, which we noted as only 2.1% in the case of the HY zeolite. It can be underlined here that the identified nitrogen compounds mostly contained heterocyclic systems with nitrogen atoms, which can prove the occurrence of Maillard reactions during HTL. These compounds could undergo some denitrogenation processes in the case of the catalytic process. The deoxygenation could partially occur via decarboxylation, which is supported by the increasing share of carbon dioxide. It is also worth noting that in the Supplementary Materials (Table S2), we compared the relative and estimated real share (in relation to the sample size amenable for de-volatilization) of each group of compounds as well as the factor of identified compounds.
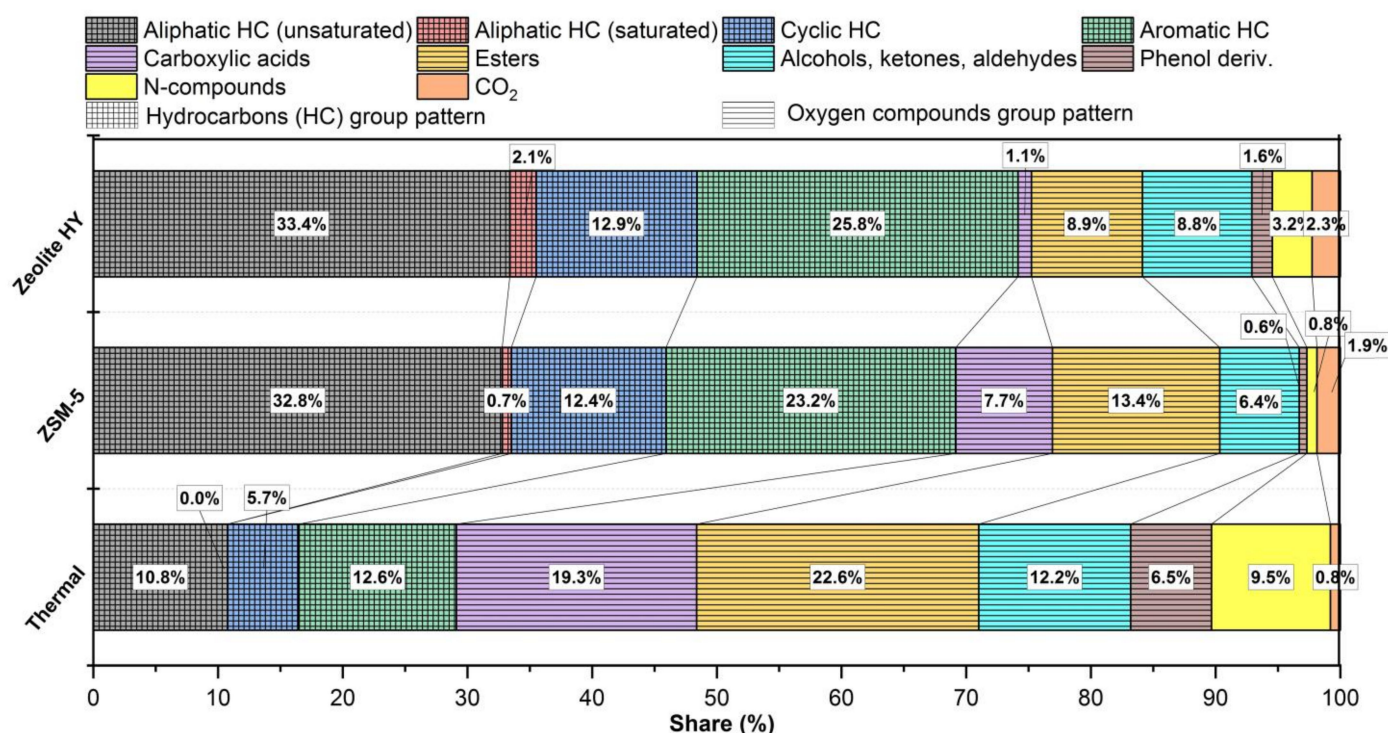
Figure 5. Comparison of group composition of the fractions evolved after thermal (500 °C) and catalytic pyrolysis over ZSM-5 and HY zeolites (500 °C) of the studied HTL biocrude.

In Table S3 (Supplementary Materials), a detailed list of the identified volatile products that evolved during the thermal and catalytic fast pyrolysis of biocrude within each group of compounds presented in Figure 5 were gathered. Among the aliphatic compounds, there were mostly alkenes with a single unsaturated bond containing from three to 13 C atoms. Aliphatic hydrocarbons can be produced from the transformation of fatty acids and esters contained in the biocrude. These compounds can comprise a valuable fraction with potential as biocomponents for SI engine fuels, chemicals, or bioplastics precursors. Cyclic compounds are also mainly a group of unsaturated compounds, with a lower share of saturated naphthenes. Aromatics are mainly structured with one ring substituted with various aliphatic side chains. The share of complex polycyclic aromatic hydrocarbons is negligible. We also calculated the C and H elemental balance among the identified compounds evolved during thermal and catalytic runs, which were depicted in Figure S1 (Supplementary Materials). The results were related to the fractions amenable to analysis, while the shares of C/H in solid residues and wastes were calculated by difference. The identified compounds after catalytic processing accounted for ca. 82.9–83.6 wt% and 85.0–85.5 wt% for the C and H elements, respectively. For thermal runs, the C/H elements' mass balance closure was lower and ranged between 63.5–65.9 wt%. This proves that the zeolite addition allows for more effective conversion via fast pyrolysis and the effects of other processing variables will be worth investigating in the future.

4. Conclusions

Poland is among the leading global and European countries in the production and processing of various fruits and vegetables (e.g., blackcurrant). As a result, there is an abundant amount of various available wet-type organic residuals having significant potential for bioproducts manufacturing. Herein, we proposed a novel, two-stage processing route consisting of hydrothermal liquefaction of blackcurrant pomace as an exemplary residual material toward biocrude, followed by further upgrading via catalytic fast pyrolysis toward obtaining a higher yield of lighter fractions. The produced HTL biocrude was formed in a relatively high yield (45 wt%) and exhibited quite high HHV (~33 MJ

kg^{-1}). The product was a complex mixture of organic compounds with a dominant share of oxygen compounds, especially carboxylic acids and esters. Its troublesome physiochemical characteristics influence its limited application potential and the need for upgrading. Therefore, we investigated the possibility of biocrude upgrading by thermal and catalytic fast pyrolysis to obtain more prospective lighter fractions of hydrocarbons and their derivatives. We found that the analytes that evolved after catalytic pyrolysis were composed of the majority of hydrocarbons, whose total share reached 69.2% and 74.2% for the ZSM-5 and HY zeolites, respectively. These values were much higher compared to the thermal (non-catalytic) process for which only 29.1% of the identified compounds accounted for hydrocarbons. In the case of thermal processing, the released pyrolysis vapors were composed mainly of oxygenates with the highest share of carboxylic acids, esters, alcohols, and phenol derivatives. In conclusion, it is worth emphasizing that the proposed innovative approach for the two-stage processing of waste fruit pomace is prospective as it allows for upgraded value-added final products to be obtained. To the best of our knowledge, herein we report on such a processing approach for the first time. However, further investigation regarding the effect of other process variables and different types of catalysts is necessary.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14217288/s1, Figure S1: C and H elements distribution in the products of thermal and catalytic cracking of HTL biocrude calculated based on the Py-GC-MS analyses, Table S1: The mass of solid residue and share of identified products evolved after thermal and catalytic decomposition of the studied HTL biocrude, Table S2: Comparison between the relative and estimated real share of group composition of the fractions evolved after thermal (500 °C) and catalytic pyrolysis of the studied HTL biocrude, Table S3: Identified volatile products evolved during thermal and catalytic pyrolysis of biocrude from blackcurrant pomace at 500 °C determined by Py-GC-MS.

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