

## Article

# Mesoporous Silica Nanocatalyst-Based Pyrolysis of a By-Product of Paper Manufacturing, Black Liquor

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**Abstract:** The valorization of black liquor, a by-product produced in considerable quantities from the paper manufacturing processes, has demonstrated the effectiveness of thermal reconversion into pyrolysis gas, bio-oil, and bio-char, a sustainable approach placing the feedstock into a circular economy concept. The present study focused on developing disposal solutions through energy recovery via pyrolysis at 300 °C and 450 °C when lignite and nanomaterials (such as Cu-Zn-MCM-41, Ni-SBA-3, or Ni-SBA16) were used as catalysts. The results were compared to those of non-catalytic pyrolysis. The use of the Cu-Zn-MCM-41 catalyst proved to be efficient for pyrolysis gas production, reaching 55.22 vol% CH<sub>4</sub>. The increase in the calorific value of the pyrolysis gas was associated with the use of the Cu-Zn-MCM-41, showing a value of 42.23 MJ/m<sup>3</sup> compared to that of the non-catalytic process, which yielded 39.56 MJ/m<sup>3</sup>. The bio-oil resulting from the pyrolysis with Cu-Zn-MCM-41 showed the highest energy value at 6457 kcal/kg compared to that obtained with the other two nanocatalysts, Ni-SBA-3 and Ni-SBA-16, as well as that of the raw material, which had a value of 3769 kcal/kg. The analysis of bio-char revealed no statistically significant differences when comparing the outcomes from using the various nanocatalysts, suggesting their minimal impact on the energy content.

**Keywords:** pyrolysis; black liquor; pyrolysis gas; bio-oil; bio-char



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## 1. Introduction

Carbon dioxide has been identified as a principal factor driving the onset and acceleration of the global climate change process, leading to rising global temperatures and sea levels and increased occurrences of floods, wildfires, and droughts. As part of the natural photosynthesis process, CO<sub>2</sub> is absorbed by plants through the carbon circuit into biomass, releasing O<sub>2</sub>. However, the atmosphere’s substantial CO<sub>2</sub> levels are primarily attributed to anthropogenic activities, especially the combustion of fossil fuels, coal, oil, and natural gas [1–4]. This underscores the urgent need for developing alternative fuels based on waste and/or biomass that offer similar energy–thermal characteristics but with a mitigated environmental impact and carbon footprint. Utilizing waste as feedstock for energy generation opens pathways to new alternative fuels, promoting better management of natural resources and sustainability. Consequently, numerous scientific studies have documented the energetic qualities of products resulting from the pyrolysis of various types of waste, including sewage sludge [5], agricultural waste [6], plastic waste [7], bone meal [8], and black liquor (BL) from the paper manufacturing process [9].

Climate change mitigation and energy security is one of the driving forces for an increase in the use of biomass energy. Different initiatives and methods were developed to

reduce dependence on fossil fuels that produce GHGs. Forest biomass plays an important role as a raw material for wood-based products and as a renewable material for energy consumption [10]. The EU's goal is to achieve climate neutrality by 2050, leaving a transition period in which the focus is on placing alternative fuels in the context of energy generation at the expense of fossil fuels. Biomass is considered CO<sub>2</sub> neutral if managed sustainably, thus using this type of waste for energy generation is a promising solution. Improving the efficiency of current bioenergy systems is important [11,12]. In the pulp and paper industry, large amounts of forest biomass have been used and the by-products or residues/wastes resulting from the industry, including bark, forest residues, and BL, are one of the major biomass resources that can be further used for the energy purpose of producing electricity, heat, and biofuels [13].

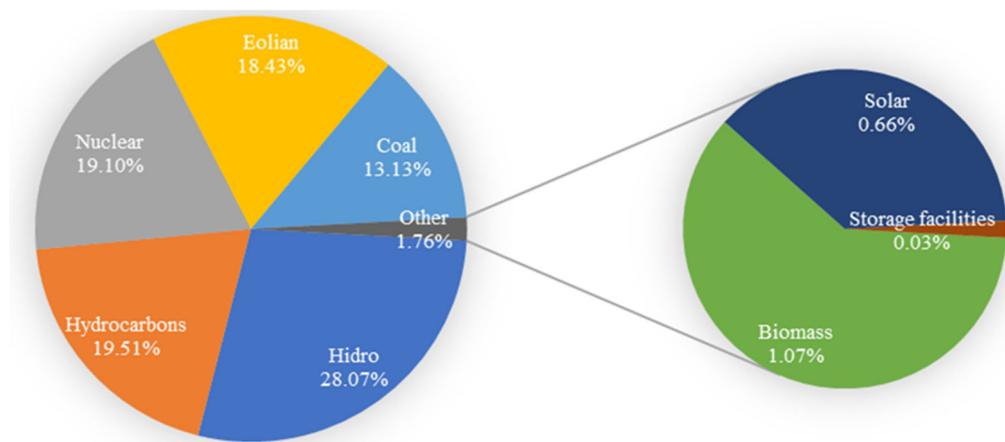
Black liquor (BL), a lignocellulosic by-product generated in significant volumes during the wood pulping process, is subjected to regulatory restrictions that prohibit its application as an agricultural soil amendment due to concerns over soil structure disruption [14]. The primary method for BL management involves combustion or incineration in recovery boilers, operating at temperatures around 1000 °C. This process, while effective for energy recovery, raises environmental concerns related to the emission of ash and the potential formation of furans, dioxins, and greenhouse gases (GHGs), thereby necessitating the exploration of alternative disposal strategies. BL is characterized by its composition of lignin residues, hemicelluloses, and various inorganic chemicals employed during the pulping process [4,15]. An emerging alternative for BL management is the pyrolysis process, conducted at elevated temperatures in an inert atmosphere, facilitating the production of pyrolysis gas (BL<sub>PYGAS</sub>), bio-oil (BL<sub>PYOIL</sub>), and bio-char (BL<sub>PYCHAR</sub>). The latter, a carbonaceous material, holds the potential for chemical and thermal activation, offering utility in soil amendment through CO<sub>2</sub> sequestration and carbon stabilization, alongside avenues for generating fuels and chemical products [4]. In addition, this thermochemical process facilitates the formation of valuable chemical compounds, such as phenols, organic acids, and tars, which can later be separated and used as products with added commercial value in various industrial applications [15].

Due to its high carbon content, BL utilization through the pyrolysis process is an efficient way of producing biofuels. The scientific literature describes different temperatures at which the pyrolysis process can be carried out, in the range of 500–1000 °C, under an inert nitrogen atmosphere [16]. Following the BL pyrolysis process, in addition to bio-oil and pyrolysis gas products, a black solid fraction is obtained, bio-char, with a specific smell of H<sub>2</sub>S.

In the clarifications described above, BL is considered a waste of the contemporary world, requiring a viable recovery solution. BL has an organic nature, with a high content of combustible elements, carbon (C), hydrogen (H), and oxygen (O) [15]. Therefore, it is appropriate to be used for thermal and electrical energy through thermochemical procedures and other specific techniques, such as pyrolysis, gasification, and rotary kiln incineration. BL is produced annually in the amount of 130 million tons globally. The effective use of BL could have an obvious effect on environmental protection and energy shortage mitigation from sustainable sources [17].

The data provided by the National Energy Regulatory Authority (ANRE), as shown in Figure 1, reveal that Romania presents an energy basket in which the share of biomass and/or waste is constantly increasing among other energy sources, whether conventional or renewable, which leads to a balanced, sustainable, resilient, and secure energy system.

The present work aimed to evaluate the energy potential of the products developed from the BL pyrolysis (in the presence or absence of catalysts), investigating the physical-chemical and energetic characteristics of both the raw material (BL) and the resulting products. Additionally, the heavy metal content of the BL<sub>PYOIL</sub> was examined and compared to other types of fuels, encompassing both conventional and alternative energy sources.



**Figure 1.** Energy sources in the Romanian National Energy System.

## 2. Materials and Methods

### 2.1. Materials

BL was selected for the present investigation due to the high interest shown by the paper processing industry. Samples of BL were purchased from the Pulp and Paper factory, Drobeta-Turnu Severin, Romania, a facility that primarily processes hardwoods. The BL used in the pyrolysis processes was in a viscous liquid state, with a coloration ranging from dark brown to black, and was not subjected to any other treatment, as shown in Figure 2.



**Figure 2.** Sample of the investigated black liquor.

Within the framework of this study, three types of catalysts (Ni-SBA-16, Ni-SBA-3, and Cu-Zn-MCM-41) were previously developed [8,18]. Briefly, for the Ni-SBA-16 catalyst, Pluronic P127 (Sigma Aldrich, Darmstadt, Germany) was solvated in ultrapure water and 37% hydrochloric acid (Sigma Aldrich, Darmstadt, Germany). Then, n-butanol was used as co-surfactant (Sigma Aldrich, Darmstadt, Germany), together with tetraethyl orthosilicate (Sigma Aldrich, Darmstadt, Germany) as silica source, under vigorous mixing for 24 h at 45 °C. The mixture was then subjected to hydrothermal treatment (100 °C) for 24 h, and the resulting solid was filtered, dried, and calcined at 550 °C (6 h) to eliminate the residual surfactant. The resulting material, denoted as SBA-16 was used as a support to impregnate the nickel acetate solution (1.34% Ni concentration) (Sigma Aldrich, Darmstadt, Germany), and the resulting product was dried for 24 h in air and then calcined at 550 °C (6 h) [8,18].

The SBA-3 support was synthesized according to the method described in previous studies [8,18], under magnetic stirring at 30 °C, using tetraethyl orthosilicate (Sigma Aldrich, Darmstadt, Germany) and cetyltrimethylammonium bromide (Sigma Aldrich, Darmstadt, Germany) as Si source and template, respectively. An aqueous solution of hydrochloric acid (37%—(Sigma Aldrich, Darmstadt, Germany) was used to adjust the pH; the white SBA-3 precursor was aged at ambient temperature for 12 h and then filtered and dried at

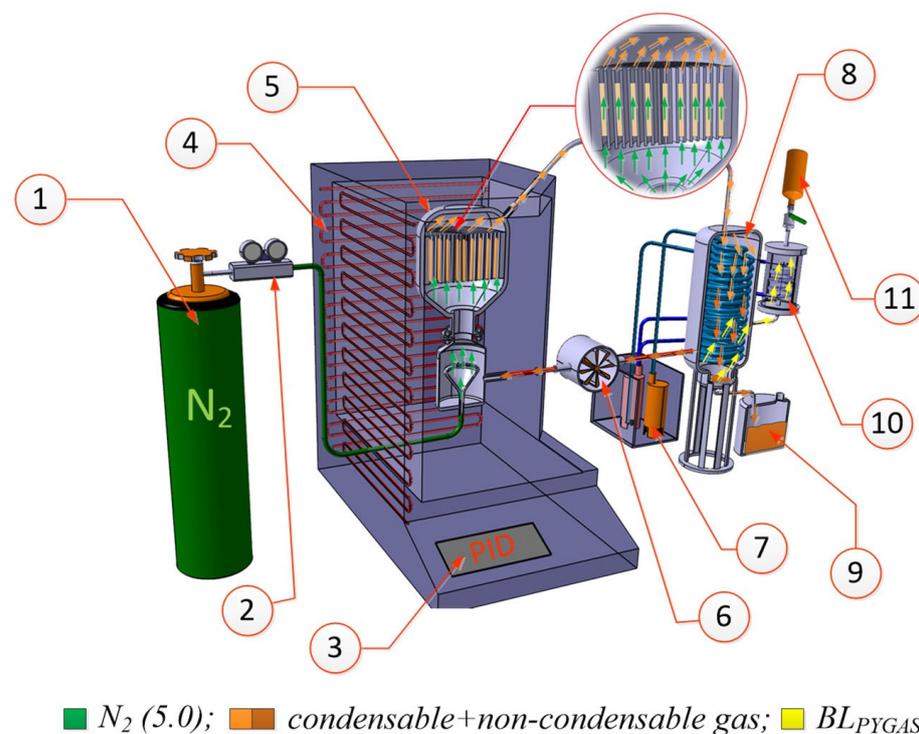
100 °C. To remove the residual surfactant, SBA-3 was refluxed in ethylic alcohol for 6 h and then filtered and washed with ultrapure water. The Ni-SBA-3 nanocatalyst was prepared according to the previously described method for Ni-SBA-16 [8,18].

MCM-41 catalytic support was obtained following the previously developed method [8] by pouring cetyltrimethylammonium bromide (CTAB) ultrapure water and stirring for 2 h at an ambient temperature [8]. Then, sodium silicate was added, and mixing continued for 2 h, after which tetramethylammonium hydroxide was used, with continuous stirring for 30 min. The pH was balanced to 10.5 and the mixture was kept under stirring overnight, after which it was hydrothermally treated at 100 °C for 5 days. The precipitate was filtered, washed, dried, and then calcined at 550 °C (6 h). The resulting MCM-41 silica was impregnated with  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , and the precursor was dried for 24 h and then calcined to 550 °C (6 h). To obtain the bimetallic system, the obtained grey solid was re-impregnated with  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , followed by drying and calcination in the same conditions [8].

For the accuracy of the results, reference materials were used in this study, such as the following: (i) BBOT—2.5-Bis-5-tert-butyl-2-benzo-oxazol-2-yl (Thermo Fisher Scientific Inc., Loughborough, UK), with the composition C—72.56 wt%, H—6.11 wt%, S—7.40 wt%, O—7.41 wt%, and N—6.49 wt%; (ii) Cystine (Thermo Fisher Scientific Inc., Loughborough, UK), with the composition O—26.67 wt%. To validate the results, the following certified reference materials were used: (i) Methionine (Thermo Fisher Scientific Inc., Loughborough, UK), with the composition C—40.26 wt%, H—7.37 wt%, S—21.46 wt%, O—21.55 wt%, and N—9.35 wt%; (ii) Acetanelide (Thermo Fisher Scientific Inc., Loughborough, UK), with the composition O—11.81 wt%; (iii) Benzoic acid (Sigma Aldrich, Darmstadt, Germany), with a calorific value (Qs) of 26,461 J/g.

## 2.2. Pyrolysis Experimental Setup

The catalytic and/or non-catalytic pyrolysis processes were carried out using an experimental laboratory setup as shown in Figure 3.



**Figure 3.** Simplified scheme of black liquor pyrolysis technological assembly.

The pyrolysis technological assembly consisted of the following components: 1. inert gas supply pyrolysis technological assembly ( $\text{N}_2/5.0$ ); 2. inert gas flow/pressure regulator;

3. temperature control panel; 4. electric heating element from PID-controlled temperature oven; 5. refractory steel fixed-bed reactor, insulated with basalt wool; 6. hot gas circulation fan unit; 7. water pump unit for heat exchanger unit cooling; 8. metallic capacitor (primary heat exchanger); 9. BL<sub>PYOIL</sub> collecting tank; 10. condensable gas collector (secondary heat exchanger); 11. BL<sub>PYGAS</sub> collecting tank/bag. The pyrolysis processes carried out in an inert atmosphere were performed with ~50 g of sample delivered inside the fixed-bed reactor in a ceramic crucible. The fixed-bed reactor was equipped with an automatic PID controller, ensuring a thermal range (300–450 °C) and a reactor heating gradient rate (5 °C/min). The inert gas flow was kept constant (Q: 100 mL/min), and the variations were low at ±5%. The products generated via pyrolysis reactions were liquid/BL<sub>PYOIL</sub>, gaseous/BL<sub>PYGAS</sub>, and a solid residue/BL<sub>PYCHAR</sub>. Water, at 10–12 °C, was used responsibly to condense the gases developed by the processes, without being affected by the generated chemical compounds.

### 2.3. Physical–Chemical and Morpho-Structural Investigation Techniques

The characterization of the BL sample, alongside its pyrolysis derivatives BL<sub>PYOIL</sub>, BL<sub>PYGAS</sub>, and BL<sub>PYCHAR</sub>, was carried out in the ISO 17025:2018 [19] accredited facilities of the National Research and Development Institute for Cryogenic and Isotopic Technologies—ICSI Ramnicu Valcea. These investigations provided both qualitative and quantitative information regarding the studied materials. Ash content(A) was assessed in accordance with ISO standards 1171:2010 [20] and 18122:2022 [21], using a calcination furnace (SNOL 8 - Snoltherm, UAB, Utena, Lithuania) at 550 °C for 2 h until a constant mass was achieved. The volatile matter content (V) was determined to gain information into the specific constituents of the solid fuels, utilizing a muffle calcination furnace (SNOL 3/11- Snoltherm, UAB, Utena, Lithuania) at a working temperature of 850 °C for a residence time of 7 min. For elemental analysis, the EA2000 elemental analyzer (Thermo Fisher Scientific Inc., Loughborough, UK) was employed, combining combustion or pyrolysis with gas chromatography in an innovative way to quantify chemical elements with significant environmental impacts. The samples subjected to the combustion process, solid or liquid, were determined in the form of oxides, namely CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>2</sub>, CO, and H<sub>2</sub>O, but expressed as elements, namely N, C, H, S, and O. Calorific values were determined using a calorimeter (C5000 - IKA-Werke GmbH & Co. KG, Staufen, Germany), and the combustion adiabatic method was used, providing information on the energy content of both the raw material and the resultant solid and liquid pyrolysis products developed in the present study.

The qualitative and quantitative composition of BL<sub>PYGAS</sub> was determined by using the gas chromatography technique (CP3800 Varian Inc., Palo Alto, CA, USA) for the permanent gases O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>, as well as for hydrocarbons, from C<sub>1</sub> to C<sub>6+</sub>.

To determine the content of heavy metals in the BL<sub>PYOIL</sub>, the samples were digested in a TOP wave microwave sample preparation system (Analytik Jena GmbH+Co. KG, Jena, Germany) equipped with closed Teflon vessels, and then analyzed using the Atomic Absorption Spectrophotometer (Analytik Jena, Germany).

The thermogravimetric analysis (TGA) was performed using GA-DSC–NETZCH STA 449 F5 Jupiter (NETZCH, Selb, Germany) to evaluate the thermal behavior of BL by measuring the mass variation as a function of temperature and its influence on BL composition. The temperature domain used for the TGA and the derivative thermogravimetric (DTG) was 25–500 °C, with a heating rate of 10 °C/min, under an inert atmosphere. The thermal decomposition behavior of the sample provides valuable information regarding the choice of the functioning temperature range for the pyrolysis process. For a correct assessment of the distribution of functional organic groups in BL and/or BL<sub>PYOIL</sub> samples, the FT-IR technique was applied using a CARY630 FTIR spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) to generate spectra in which bands were identified by screening the libraries available in the software (Microlab Expert - Agilent Technologies, Inc., Santa Clara, CA, USA) of the instrument equipped with an ATR detector. Also, the surface functional groups of the solid residues were characterized using the same technique.

### 3. Results

#### 3.1. Black Liquor Characterization

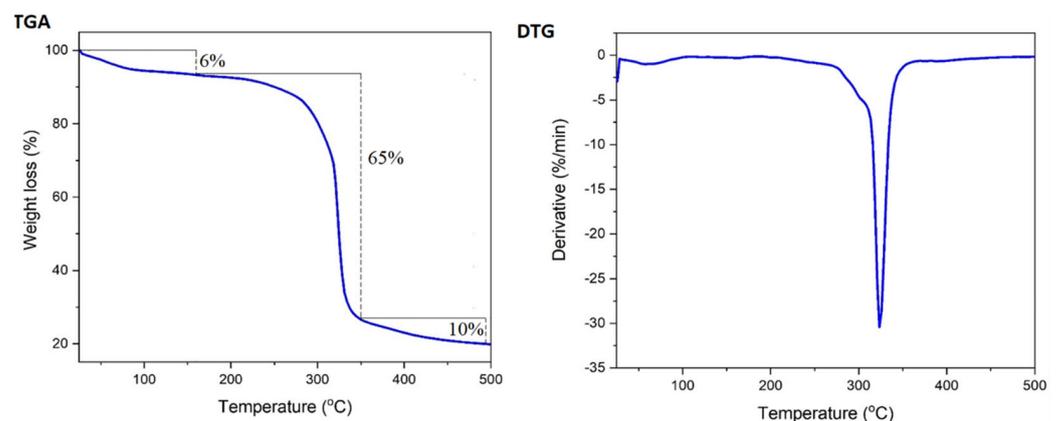
BL is a digestion product obtained from the Kraft processing of wood in the pulp and paper industry. As reported by other authors, BL represents an aqueous mixture of lignin residues, hemicellulose, and the inorganic chemicals used in the process. The BL comprises 15 wt% solids of which two-thirds are organic chemicals and the remainder are inorganic. Normally, the organics in BL are 40–45 wt% soaps, 35–45 wt% lignin, and 10–15 wt% other organics [4,22]. During the wood pulping process, through a series of evaporation procedures, the BL is recovered as a material that can be subjected to combustion for energy production [3]. BL may be a toxic mixture of pollutants such as phenols, chlorinated compounds, dioxins, furans, and diphenyls, which are organically adsorbable and extractable halogens [23]. Usually, BL is concentrated and burned in alkali recovery boilers that produce energy and recover chemicals. BL shows immense potential as an organic alkaline waste stream that can also be integrated through the biomethane recovery process. Therefore, BL is energetically and economically feasible. As a waste resource, lignin from BL can be converted into biofuels and chemicals, mainly phenolic chemicals and coal.

The contents of C, N, H, S, and O indicate the presence of a high superior calorific value ( $Q_{sup}$ ), 16 MJ/kg, which is almost similar to that of lignite coal, ~18 MJ/kg (Table 1) [24].

**Table 1.** Physical–chemical characterization of investigated BL.

A wt%		N wt%		C wt%		H wt%		S wt%		O wt%		$Q_{sup}$ MJ/kg
38.17 ± 1.15		0.34 ± 0.01		18.11 ± 0.26		6.51 ± 0.15		1.78 ± 0.09		73.26 ± 3.28		16 ± 0.12
Cd µg/L	Pb µg/L	Cr µg/L	Mn µg/L	Co µg/L	Ni µg/L	Cu µg/L	As µg/L	Se µg/L	Hg µg/L	Rb µg/L	Sr µg/L	
10	52	891	-	16	-	256	339	70	-	-	24	

The results of the TGA and the derivative thermogravimetric (DTG) investigations of BL are detailed in Figure 4. Three distinct weight loss sections were identified in the curves: the first one in the thermal range of 25–158 °C due to the dehydration process (~6%); a second one occurring at higher temperatures, credited to the specific pyrolysis reactions (~65%); and the third one with a weight loss of ~10% due to carbonization [25].



**Figure 4.** TGA/DTG curves of the investigated BL sample.

A sharp decrease in the curve's slope in the temperature range of 300–350 °C indicated the volatilization of organic compounds; in this segment, the most drastic weight loss compared to that registered after 350 °C was noticed. This specific decomposition event corresponded to the strong peak occurring in the middle of the range described above

the DTG curve. The response of chemical components of BL under thermal range was different, with hemicelluloses and cellulose being decomposed at 250–350 °C, and lignin at 280–500 °C [26]. Lignin decomposition continued and intensified during the third stage at 350–500 °C, with pyrolytic degradation involving chemicals structured on aromatic rings [27]. DTG<sub>max</sub> occurs at ~325 °C, and the degradation corresponds to the fragmentation of the interlinkages of hemicellulose, cellulose, and lignin of BL, with the consequent release of monomeric phenols [28]. The TGA curve confirmed that the thermal range of 300–450 °C was sufficient for the efficient thermochemical conversion of biomass compounds into products of interest. Carrying out pyrolysis processes at temperatures higher than 450 °C was not considered viable from the point of view of profitability.

The ATR FT-IR spectrum of BL (Figure 5) revealed the absorption band around 3340 cm<sup>-1</sup> corresponding to OH stretching vibrations, indicating the existence of phenols, alcohols, and water [29]. The sharp band from 2200 cm<sup>-1</sup> registered for BL was assigned to the C=C bond stretching, which was attributed to aromatic compounds, while the peak from 1643 cm<sup>-1</sup> indicated the aromatic structure vibrations, including the C=O stretching vibration [30–32]. The absorption band at 1420 cm<sup>-1</sup> indicated characteristic absorptions due to the metallic carbonates [33]. The C-H bonds from the methylene group were identified as a stretching vibration from the spectrum at 1250 cm<sup>-1</sup>. The sharp peak from 1000 cm<sup>-1</sup> can be associated with aromatic ethers, C-H polysaccharides, and C-O oxygenated compounds, followed by another one at 935 cm<sup>-1</sup>, assigned to the presence of cellulose. The large band from 2700 to 3700 cm<sup>-1</sup> can be attributed to a superposing of peaks, such as peaks characteristic of O-H stretching from phenols or aliphatic alcohols (typically from 3400 to 3500 cm<sup>-1</sup>) or physically adsorbed water molecules.

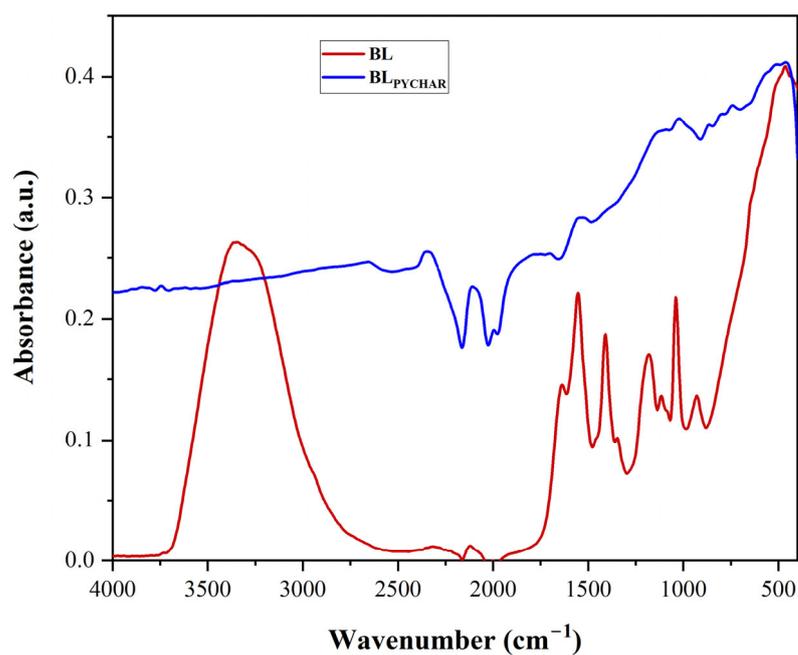


Figure 5. FT-IR spectra of the BL and BL<sub>PYCHAR</sub>.

BL<sub>PYCHAR</sub> presents distinct characteristics within the FT-IR spectrum, with the absorption peaks being more subtle due to the consumption of the organic compounds during the pyrolysis processes, as shown in Figure 5. A small band was identified at 3760 cm<sup>-1</sup>, which was correlated with the stretching of the -OH bonds. Also, the presence of a sharp band at 2329 cm<sup>-1</sup> was associated with stretching vibrations corresponding to C-H bonds within methyl and methylene species. An intensification of the C=C bond stretching vibrations was observed within the wavelength range of 2200–2000 cm<sup>-1</sup>, compared to the initial BL spectrum, which can indicate that some of the aromatic compounds remained within the char. The evolution of the peak at 1576 cm<sup>-1</sup> clearly indicated that the carbonyl and/or

carboxyl groups were removed via pyrolysis. The pyrolysis process altered the structure of the initial feedstock, substantially decreasing the level of lignin, cellulose, and oxygenated compounds in the  $BL_{PYCHAR}$ , confirmed by the drastic attenuation of the bands.

### 3.2. Effect of Process Parameters (Temperature and Catalyst) on $BL_{PYGAS}$ Production

Pyrolysis of BL is an extremely complex process, involving thermal degradation of the chemical compounds.

The most significant physical phenomenon that occurs during devolatilization is BL swelling. Fewer studies have been conducted on the actual loss of volatile material from BL during pyrolysis than on other aspects of pyrolysis, such as its swelling. Most of the work on the devolatilization process has been carried out either to investigate the feasibility of BL as a source for producing alternative fuels or to characterize the composition of BL.

In the gas and fuel research laboratory of the National Research and Development Institute for Cryogenic and Isotopic Technologies (ICSI Ramnicu Valcea), the initial product derived from complex pyrolysis processes was identified as a gaseous mixture, denoted as  $BL_{PYGAS}$ . This mixture was produced via both catalytic and non-catalytic pyrolysis methods. The generated gaseous fraction was collected and investigated for the qualitative and quantitative compositions of the permanent gases,  $O_2$ ,  $N_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$ , and  $H_2S$ , and also of hydrocarbons,  $C_1$ – $C_{6+}$  isomers.

In total, 99% of the gases generated either by catalytic or non-catalytic pyrolytic processes presented the same physical properties: high density, white/grey color (visualized in the interval 225–230 °C), bad smell, and significant proportion of  $H_2S$ . Even though the process benefited from two condensation columns, one of metal and one of glass with serpentine, traces of condensate/oily liquid were identified on the inner walls of the  $BL_{PYGAS}$  sampling bag, confirming the requirement for an increased condensation capacity. From the GC-TCD/Porapak investigations of  $BL_{PYGAS}$ , a moderate content in  $CO_2$  was noticed, less than 1 vol%. A high  $O_2$  content was observed, >40 vol% in the  $BL_{PYGAS}$ , probably due to the initial O elemental content of BL. Table 2 shows the physical and compositional characteristics of the  $BL_{PYGAS}$  produced under non-catalyzed and catalyzed pyrolysis. Comparing the energy value of  $BL_{PYGAS}$ , at  $\sim 40$  MJ/m<sup>3</sup>, with one of the gases obtained from the pyrolysis of plastic waste material, the value was found to be much lower than that of PPG (plastic waste pyrolysis gas), at  $\sim 99.83$  MJ/m<sup>3</sup> [34,35]. This fact was probably due to the feedstock initial composition, which showed lower levels of the energy components, C and H, in BL, while 99% of plastic waste composition was based on C and H. The cracking reaction produces free radicals reacting with S, naturally contained in BL, causing the formation of  $H_2S$ ,  $\sim 100$ –600 vol ppm, a harmful and highly corrosive gas, specific to different biogases from so-called waste.

According to the data presented in Table 2, the evolution of the energy level of  $BL_{PYGAS}$  was influenced by its composition, following the developed pyrolysis processes. It can be observed that regardless of the resident temperature, 300 °C and 450 °C, or the use of the catalyst/lignite, the levels of most gaseous components remain constant. Also, these factors did not seem to influence the appearance/development of new gaseous compounds. The varied composition of the  $BL_{PYGAS}$  obtained at a temperature of 450 °C recommended these conditions for the BL pyrolysis process because the energy value of the non-catalyzed pyrolysis gas (39.56 MJ/m<sup>3</sup>) was comparable to that of the catalyzed one, with  $BL_{PYGAS}$  reaching a value of 40.23 MJ/m<sup>3</sup>. Also, the high heating value (HHV) of  $BL_{PYGAS}$ , whether catalytic and/or non-catalytic at 450 °C, was clearly superior compared to other gaseous mixtures obtained from the same type of processes in the temperature range of 425–850 °C, which had values of 16.53 MJ/m<sup>3</sup> [36] and 27.26 MJ/m<sup>3</sup>, respectively [37,38]. A low heating rate also resulted in a higher level of hydrocarbons, which is similar to those reported in other studies published in the literature [37,38], compared to a pyrolytic process conducted at a higher heating rate.

**Table 2.** The chemical composition and calorific value of BL<sub>PYGAS</sub> based on different pyrolysis parameters (temperature and catalysts).

	BL <sub>PYGAS</sub> 300 °C	BL <sub>PYGAS</sub> 450 °C	BL <sub>PYGAS</sub> Lignite 300 °C	BL <sub>PYGAS</sub> Lignite 450 °C
C <sub>1</sub> vol%	37.60 ± 0.56	37.00 ± 0.56	35.52 ± 0.53	36.00 ± 0.54
C <sub>2</sub> vol%	7.40 ± 0.56	7.77 ± 0.58	8.94 ± 0.13	9.37 ± 0.14
C <sub>3</sub> vol%	2.44 ± 0.07	2.58 ± 0.08	2.98 ± 0.09	2.65 ± 0.08
iC <sub>4</sub> vol%	0.55 ± 0.02	0.57 ± 0.02	0.66 ± 0.02	0.55 ± 0.02
nC <sub>4</sub> vol%	0.44 ± 0.02	0.46 ± 0.02	0.44 ± 0.02	0.44 ± 0.02
neoC <sub>5</sub> vol%	1.31 ± 0.09	1.38 ± 0.09	1.69 ± 0.11	1.32 ± 0.09
iC <sub>5</sub> vol%	0.11 ± 0.01	0.12 ± 0.01	0.11 ± 0.01	0.11 ± 0.01
nC <sub>5</sub> vol%	3.46 ± 0.14	3.53 ± 0.14	3.44 ± 0.14	3.48 ± 0.14
C <sub>6+</sub> vol%	3.11 ± 0.12	3.27 ± 0.13	3.09 ± 0.12	3.13 ± 0.12
O <sub>2</sub> vol%	41.66 ± 1.25	41.39 ± 1.24	41.40 ± 1.24	41.25 ± 1.24
CO vol%	0.41 ± 0.01	0.50 ± 0.01	0.32 ± 0.01	0.40 ± 0.01
H <sub>2</sub> vol%	0.69 ± 0.02	0.67 ± 0.02	0.90 ± 0.02	0.90 ± 0.02
CO <sub>2</sub> vol%	0.80 ± 0.01	0.75 ± 0.01	0.50 ± 0.01	0.39 ± 0.01
H <sub>2</sub> S vol%	0.01 *	0.01 *	0.06 ± 0.01	0.02 ± 0.01
HHV MJ/m <sup>3</sup>	38.97	39.56	40.74	40.23

Note: \* value below the quantification limit of the GC Varian CP 3800 (<L<sub>Q</sub>).

The pyrolysis conducted at 450 °C in the presence of three nanocatalysts revealed variations in the gas composition of HHVs, as shown in Table 3.

**Table 3.** The chemical content and calorific value of BL<sub>PYGAS</sub>, according to different types of catalysts investigated during the pyrolysis process at 450 °C.

	BL <sub>PYGAS</sub> Cu-Zn-MCM-41 450 °C	BL <sub>PYGAS</sub> Ni-SBA-16 450 °C	BL <sub>PYGAS</sub> Ni-SBA-3 450 °C
C <sub>1</sub> vol%	55.23 ± 0.83	21.50 ± 0.32	25.24 ± 0.38
C <sub>2</sub> vol%	7.76 ± 0.58	3.37 ± 0.25	4.55 ± 0.34
C <sub>3</sub> vol%	8.29 ± 0.25	0.86 ± 0.02	1.08 ± 0.05
iC <sub>4</sub> vol%	0.52 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
nC <sub>4</sub> vol%	2.57 ± 0.12	0.10 ± 0.01	0.12 ± 0.01
neoC <sub>5</sub> vol%	0.01 ± 0.01	0.05 ± 0.01	0.01 ± 0.01
iC <sub>5</sub> vol%	0.28 ± 0.02	0.07 ± 0.01	0.07 ± 0.01
nC <sub>5</sub> vol%	1.77 ± 0.07	0.04 ± 0.01	0.04 ± 0.01
C <sub>6+</sub> vol%	0.32 ± 0.01	0.23 ± 0.01	1.26 ± 0.05
O <sub>2</sub> vol%	2.79 ± 0.07	0.22 ± 0.01	6.49 ± 0.16
CO vol%	0.04 ± 0.01	0.90 ± 0.02	1.22 ± 0.02
H <sub>2</sub> vol%	15.76 ± 0.39	8.51 ± 0.21	32.34 ± 0.81
CO <sub>2</sub> vol%	4.64 ± 0.12	64.10 ± 1.60	27.49 ± 0.69
HHV MJ/m <sup>3</sup>	42.23	13.80	20.66

In the presence of the Cu-Zn-MCM-41 catalyst, considerable levels of C<sub>1</sub> were generated at ~55 vol% compared to the non-catalytic pyrolysis process at 37 vol%. Also, the cracking reactions were stimulated, as evidenced by the level of H<sub>2</sub> at ~16 vol%, compared to the hydrogen obtained by the non-catalytic pyrolysis, which yielded only 0.67 vol%. The highest energy value of the BL<sub>PYGAS</sub> among all the developed processes was obtained under the effect of Cu-Zn-MCM-41 at ~42 MJ/m<sup>3</sup>. The level of CO<sub>2</sub> at ~4.64 vol% was the lowest compared to the other catalytic pyrolysis gases in this study, with Cu-Zn-MCM-41 behaving as an inhibitor. The BL<sub>PYGAS</sub> obtained by using Cu-Zn-MCM-41 presented another particularity in relation to other pyrolytic gases, namely C<sub>2</sub> and C<sub>3</sub>, which were hydrocarbons with longer chains than C<sub>1</sub>, developed in higher concentrations at respectively 7.76 vol% and 8.29 vol%, which was directly correlated with HHV. The high concentrations of CO<sub>2</sub> were the effect of the Ni-based catalysis that facilitated the decarboxylation of the carboxyl groups from the hemicellulose [39]. It is also worth noting that the evolution trend of H<sub>2</sub> was similar to that of hydrocarbons, and the precipitation of bound and free water, as well as the degradation of light organic compounds, gradually contributed to the concentration [40]. BL<sub>PYGAS</sub> produced via non-catalyzed pyrolysis showed a lower CO<sub>2</sub> content compared to pyrolysis gases generated from sewage sludge (SS) and bone meal (MBM), for example, as shown in Table 4, under the catalytic effect promoted by the BL's initial Ni and Cu content. The catalyzed pyrolysis gas obtained at 450 °C recorded an energy value of 42.23 MJ/m<sup>3</sup>, which was higher compared to other gaseous mixtures obtained from different raw materials, respectively biogas from sewage sludge [41,42] and geothermal gas (Geogas) [42]. Although BL<sub>PYGAS</sub> composition was similar to other gases

reported in other studies, the energy values were lower than the pyrolysis gas obtained from other matrices, bone meal (MBM<sub>PYGAS</sub>), and plastic waste (PPG), as shown in Table 4. The superior energy value obtained for the pyrolysis gas is also a consequence of the low CO<sub>2</sub> and CO concentrations. Natural gas (NG) has CH<sub>4</sub> as the main component and a calorific value of ~41 MJ/m<sup>3</sup>, which is comparable to the pyrolysis gas developed from BL [43].

**Table 4.** Physical–chemical characteristics of pyrolysis gas produced from different raw materials and other types of combustible gases.

	SS <sub>PYGAS</sub> [41]	MBM <sub>PYGAS</sub> [41]	Geogas [42]	PPG [34]	NG [43]
C <sub>1</sub> vol%	33.41 ± 0.50	16.05 ± 0.24	80.79 ± 1.21	3.93 ± 0.06	94.38 ± 1.41
C <sub>2</sub> vol%	5.74 ± 0.43	18.91 ± 1.42	<0.01	5.17 ± 0.39	2.59 ± 0.19
C <sub>3</sub> vol%	3.35 ± 0.10	21.12 ± 0.63	0.14 ± 0.01	19.54 ± 0.59	0.80 ± 0.02
iC <sub>4</sub> vol%	0.32 ± 0.01	1.80 ± 0.06	0.02 ± 0.01	0.15 ± 0.01	0.18 ± 0.00
nC <sub>4</sub> vol%	0.41 ± 0.02	1.33 ± 0.07	0.02 ± 0.01	12.17 ± 0.61	0.24 ± 0.01
neoC <sub>5</sub> vol%	0.01 ± 0.01	2.48 ± 0.16	<0.01	10.94 ± 0.71	0.01 ± 0.00
iC <sub>5</sub> vol%	0.20 ± 0.01	0.01 ± 0.001	<0.01	0.24 ± 0.01	0.09 ± 0.00
nC <sub>5</sub> vol%	0.30 ± 0.01	0.84 ± 0.03	<0.01	3.74 ± 0.15	0.06 ± 0.00
C <sub>6+</sub> vol%	0.30 ± 0.01	3.53 ± 0.14	<0.01	1.42 ± 0.06	0.06 ± 0.00
O <sub>2</sub> vol%	0.18 ± 0.01	0.72 ± 0.02	0.61 ± 0.02	0.00	0.04 ± 0.00
CO vol%	21.06 ± 0.53	3.28 ± 0.08	15.66 ± 0.39	2.19 ± 0.05	0.54 ± 0.01
H <sub>2</sub> vol%	9.36 ± 0.19	3.71 ± 0.07	<0.01	0.65 ± 0.01	0.07 ± 0.00
CO <sub>2</sub> vol%	11.03 ± 0.28	16.76 ± 0.42	0.34 ± 0.01	1.25 ± 0.03	1.01 ± 0.02
HHV MJ/m <sup>3</sup>	33.81	69.09	33.55	99.83	41.19

An important component of the research was allocated to consider factors such as operating conditions, temperature, and catalyst type to optimize the pyrolysis process for maximum energy recovery. Our findings show that the temperature variation in the range of 300 °C and 450 °C does not impact the process performances in terms of gas composition and energy values. Of the tested catalysts, Cu-Zn-MCM-41 is the only one that showed improved capabilities, compared to the non-catalyzed pyrolysis. Ni-based catalysts were found to be not satisfactory for energy recovery from black liquor thermochemical processing.

### 3.3. Effect of Process Parameters (Temperature and Catalyst) on BL<sub>PYOIL</sub> Production

Another reaction product developed following the pyrolysis process was a liquid–solid mixture of BL<sub>PYOIL</sub> generated within the thermal range of 175–200 °C, as presented in Figure 6.



**Figure 6.** Bio-oil produced from black liquor pyrolysis–BL<sub>PYOIL</sub>.

After the decantation of the mixture, the elemental investigations highlighted the fact that the most important amount of sulfur (S) from the BL was transferred to this fraction, regardless of the process conditions. BL<sub>PYOIL</sub> content of S ~2.5 wt% represented a great disadvantage in case of further combustion or gasification. High S levels may affect the environment by generating SO<sub>x</sub>, H<sub>2</sub>S, or even H<sub>2</sub>SO<sub>4</sub>. The highest energy value was

obtained with the Cu-Zn-MCM-41 catalyst, and the lowest value was obtained under the Ni-SBA-16 effect. The high energy value, as shown in Table 5, was mainly due to the high C, H, and O contents, and the elemental values were much higher than the coal characteristics—Berbești lignite [44]. The content of the energetic elements, C and H, generated in this study, was in the middle of the ranges reported in the scientific literature: C, 39.70–61.33 wt% [14,15,45], and H, 4.30–7.70 wt% [14,15,45]. Also, BL<sub>PYOIL</sub> can raise environmental issues due to the high content of N at 15.6 wt%, which was much higher than those presented in the scientific literature, respectively between 0.01 and 0.14 wt% [14,15,45,46].

**Table 5.** Physical–chemical characteristics of BL<sub>PYOIL</sub> and conventional fuels.

	C wt%	H wt%	N wt%	S wt%	O wt%	Q <sub>sup</sub> kcal/kg
BL <sub>PYOIL</sub> 450 °C	45.2 ± 0.7	5.8 ± 0.3	16.7 ± 0.3	2.6 ± 0.1	29.8 ± 1.3	5324 ± 52
BL <sub>PYOIL</sub> Cu-Zn-MCM-41 450 °C	49.5 ± 0.8	6.8 ± 0.1	15.6 ± 0.3	2.4 ± 0.1	25.7 ± 0.7	6457 ± 63
BL <sub>PYOIL</sub> Ni-SBA-16 450 °C	32.6 ± 0.5	5.5 ± 0.1	24.0 ± 0.4	3.0 ± 0.2	34.9 ± 1.0	5100 ± 50
BL <sub>PYOIL</sub> Ni-SBA-3 450 °C	33.0 ± 0.5	5.0 ± 0.1	23.1 ± 0.4	2.7 ± 0.2	36.1 ± 1.0	5324 ± 52
BL <sub>PYOIL</sub> [45]	61.3	4.3	0.0	-	-	-
BL <sub>PYOIL</sub> [14]	39.7	7.7	0.1	0.0	52.5	3821
BL <sub>PYOIL</sub> [15]	55.4	6.6	0.1	-	37.9	5493
Diesel [34]	83.5	12.1	0.8	0.0	3.7	11,002

The high N content of BL<sub>PYOIL</sub> was mainly due to the pyrolysis process, which significantly reduced the level of O contained in the original BL sample, but also due to the reaction medium, with the pyrolysis process being conducted under an inert atmosphere. The use of catalysts did not show a direct correlation with the N evolution in BL<sub>PYOIL</sub>. Used without further processing, the nitrogen content from the BL<sub>PYOIL</sub> can have significant environmental implications as follows (i) the greenhouse effect generated by the NH<sub>3</sub> and N<sub>2</sub>O emissions; (ii) the formation of acid rain by NO<sub>x</sub> released during a hypothetical combustion process, which could affect soil, water, and the ecosystem; (iii) eutrophication, manifested through the multiplication of algae, oxygen depletion, and damage to aquatic life [47,48]. By exploring these aspects, a sustainable strategy to mitigate the impact on the environment may contain, among others, nitrogen disposal as follows: (i) via hydrodenitrogenation, a process that involves reaction with hydrogen over a suitable catalyst, converting nitrogen-containing compounds into nitrogen-free species; (ii) through the selective catalytic action of some zeolites; (iii) through the use of bimetallic catalysts; (iv) by turning BL<sub>PYOIL</sub>'s into biochar, which can trap nitrogen and prevent its release into the environment; (v) using selective catalytic reduction system to remove nitrogen compounds from exhaust gases [49].

Regarding the content of heavy metals in BL<sub>PYOIL</sub>, their levels were low in relation to conventional fossil fuels [49,50], as shown in Table 6, indicating that the initial metal levels from the BL most likely migrated to the BL<sub>PYCHAR</sub>.

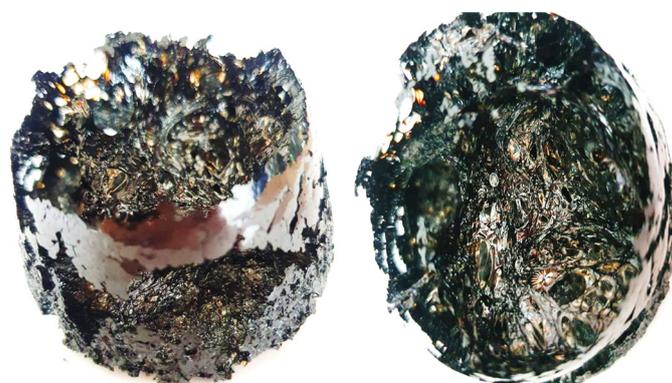
**Table 6.** Metal content (µg/l) of BL<sub>PYOIL</sub>, comparatively presented to that of alternative and conventional fuels.

	Cd	Pb	Cr	Mn	Co	Ni	Cu	As	Se	Hg	Rb	Sr
BL <sub>PYOIL</sub> 450 °C	0.001	0.01	0.45	0.13	0.29	0.87	0.45	0.35	-	-	-	-
SS <sub>PYOIL</sub> [41]	0.02	0.20	1.79	0.29	0.01	9.30	20.92	1.86	-	0.06	-	0.10
MBM <sub>PYOIL</sub> [41]	0.01	1.55	0.81	0.07	0.02	1.29	0.00	0.29	-	0.00	-	-
PPO <sub>PP</sub> [34]	0.12	0.09	1.97	0.29	0.21	0.56	0.06	0.37	1.61	<0.01	0.17	0.06
PPO <sub>HDPE</sub> [34]	0.34	0.53	2.49	8.11	1.39	3.83	2.31	0.17	1.72	<0.01	0.01	0.72
PPO <sub>LDPE</sub> [34]	0.05	0.06	3.11	0.01	0.07	4.56	1.75	0.35	2.40	<0.01	0.21	0.05
PPO <sub>PS</sub> [34]	0.07	0.07	10.03	0.37	0.16	0.02	0.27	0.30	2.12	<0.01	0.22	0.15
Gasoline [49]	16.80	2.40	5.40	-	-	-	17.40	-	-	0.77	-	-
Kerosene [51]	13.30	4.10	3.30	-	-	-	19.80	-	-	-	-	-
Diesel [51]	15.00	10.10	8.60	-	-	-	17.70	-	-	-	-	-

### 3.4. Effect of Process Parameters (Temperature and Catalyst) of Pyrolysis on BL<sub>PYCHAR</sub> Production

Following the BL pyrolysis process, a solid fraction was also generated, namely BL<sub>PYCHAR</sub>, a black product as shown in Figure 7, with a specific smell of H<sub>2</sub>S. This bio-char

product may find different valorization pathways such as combustion for the generation of heat and power, gasification for syngas production, activation for adsorption applications, or use as a soil amendment [52].



**Figure 7.** BL<sub>PYCHAR</sub> obtained from the BL pyrolysis.

The specific elemental analysis investigations indicated a high C content reflected in an energy value of ~3000 kcal/kg, as shown in Table 7. Regardless of the applied parameters of the pyrolysis process ( $T$  °C, flow rate, use of catalysts), the elemental concentrations of N, S, H, C, and O had a distribution/standard deviation of <0.5%. It should be noted that the lower content of S ~1 wt% was obtained during the catalyzed pyrolysis, regardless of the temperature used.

The solid pyrolysis residue, obtained under different technical conditions of the pyrolysis process, has a high energy value that falls within the ranges recorded in the scientific literature [37], which is close to the level of lignite exploited in the Berbesti Mine, Valcea, at 2100 kcal/kg [44].

However, the high content of Ash (A) does not make it attractive for the energy sector. These elements, associated with the inorganic content, remained in the matrix of the solid pyrolysis residue, with a distinct characteristic of the solid residue originating from lignocellulosic materials [49]. According to the results presented in Table 7, the elemental composition of the pyrolysis residue, depending on the temperature used during the pyrolysis process, did not vary to a great extent. The average N levels of <0.4 wt% make BL<sub>PYCHAR</sub> a candidate for a safe alternative fuel in terms of NO<sub>x</sub> emissions, but unlikely given considerable average levels of ash (A) ~55–60 wt%. It should be noted that within catalytic pyrolysis, BL<sub>PYCHAR</sub> resulted in a higher amount, ~59% vs. 53%, compared to the non-catalytic one, hence the lower energy content,  $Q_s$  ~2800 kcal/kg vs. 3000 kcal/kg.

**Table 7.** Physical–chemical characterization of BL<sub>PYCHAR</sub>, based on different pyrolysis parameters (temperature and catalysts—lignite).

	BL <sub>PYCHAR</sub> 300 °C	BL <sub>PYCHAR</sub> 450 °C	BL <sub>PYCHAR</sub> Lignite 300 °C	BL <sub>PYCHAR</sub> Lignite 450 °C
A wt%	52.96 ± 2.93	53.68 ± 2.97	57.88 ± 3.21	58.91 ± 3.26
C wt%	35.79 ± 0.56	35.47 ± 0.56	35.55 ± 0.56	35.39 ± 0.56
N wt%	0.39 ± 0.01	0.38 ± 0.01	0.35 ± 0.01	0.37 ± 0.01
H wt%	1.70 ± 0.03	1.68 ± 0.03	0.77 ± 0.01	0.75 ± 0.01
S wt%	1.67 ± 0.09	1.53 ± 0.08	1.21 ± 0.07	1.21 ± 0.07
O wt%	7.49 ± 0.21	7.30 ± 0.21	4.24 ± 0.12	3.37 ± 0.10
$Q_{sup}$ kcal/kg	3006 ± 29	2992 ± 29	2774 ± 27	2800 ± 27

#### 4. Conclusions

In this study, BL was used to explore the production of sustainable and environmentally friendly fuels via both catalytic and non-catalytic pyrolysis processes at 300 °C and

450 °C, respectively, under an inert N<sub>2</sub> atmosphere. The investigations employed three types of nanocatalysts based on porous silica supports (Ni-SBA-16, Ni-SBA-3, and Cu-Zn-MCM-41) to assess their effectiveness in facilitating the thermochemical conversion of BL into clean alternative fuels, as well as valuable precursors for the chemical or petrochemical industry. This approach highlighted a promising pathway for BL management. The results of the characterization of the BL pyrolysis products emphasize the following aspects:

- ❖ BL<sub>PYGAS</sub> obtained from the non-catalytic pyrolysis contained CH<sub>4</sub> ~37vol%, while the efficiency of the Cu-Zn-MCM-41 catalyst was demonstrated by a CH<sub>4</sub> level of ~55 vol%. The increase in the HHV of the pyrolysis gas was closely related to the use of the Cu-Zn-MCM-41 catalyst, showing a value of 42.23 MJ/m<sup>3</sup> compared to that of the non-catalytic process, which yielded 39.56 MJ/m<sup>3</sup>.
- ❖ For BL<sub>PYOIL</sub>, Cu-Zn-MCM-41-catalyzed pyrolysis proved a superior influence over the Q<sub>sup</sub> (6457 kcal/kg) than the non-catalyzed and other catalyzed (Ni-SBA-3 and Ni-SBA-16) processes. Consequently, BL<sub>PYOIL</sub> can be considered a low carbon footprint alternative to classic diesel fuel, keeping in mind that a prior refining and desulfurization process is essential.
- ❖ BL<sub>PYCHAR</sub> chemical properties make its use in the energy sector unfeasible due to the possible environmental issues that could be generated through high levels of greenhouse gases and particle matter. Therefore, alternative strategies, such as adsorbent-selective material synthesis, are required for the elimination of this solid residue.

The BL pyrolysis process investigated in the present study as well as its products have several economic and environmental advantages. The main advantage is given by the disposal of BL waste by developing alternative and renewable fuels with high levels of carbon. An advantage of the BL pyrolysis process is the absence of some oxides with high toxic potential, such as NO<sub>x</sub> and SO<sub>x</sub> in the resulting gaseous mixture, due to the pyrolytic process conducted in the absence of O<sub>2</sub>.

By scaling up the proposed pyrolysis process for black liquor, potential economic benefits could be reached through various channels: (i) the use of the final value-added products, therefore generating fresh sources of income; (ii) reduction in current management practices high costs; (iii) in-house energy generation, lowering energy costs and reducing the reliance of paper factories on fossil fuels; and (iv) job creation.

Along with the economic benefits, this process can have a positive environmental impact by mitigating GHG emissions and waste generation. The conduction of the process in the absence of O<sub>2</sub> ensures the absence of the resulting gaseous mixture of some oxides with high toxic potential, such as NO<sub>x</sub> and SO<sub>x</sub>. Furthermore, BL<sub>PYCHAR</sub> is a product that can be used as a soil amendment, acting as a carbon sink.

This study also underscores the importance of adopting a circular approach to the thermochemical conversion process, emphasizing the field of waste-to-energy technologies. This strategy not only enhances the sustainability of the process but also contributes to economic efficiency by reducing the need for external inputs and minimizing waste. Furthermore, the implementation of advanced technologies, including artificial intelligence and dedicated mixing equipment for the optimization of gas mixtures (pyrolysis gas with natural gas) presents a novel approach to developing alternative fuels with a lowered carbon footprint. These mixtures hold great promise as sustainable alternatives to conventional fossil fuels, offering comparable energy profiles while significantly reducing the environmental impact.

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