Management of Lignocellulosic Waste towards Energy Recovery by Pyrolysis in the Framework of Circular Economy Strategy

Anna Poskart 1,*, Magdalena Skrzyniarz 2, Marcin Sajdak 3, Monika Zajemska 2 and Andrzej Skibiński 1

Citation: Poskart, A.; Skrzyniarz, M.; Sajdak, M.; Zajemska, M.; Skibiński, A. Management of Lignocellulosic Waste towards Energy Recovery by Pyrolysis in the Framework of Circular Economy Strategy. Energies 2021, 14, 5864. https://doi.org/10.3390/en14185864

Abstract: The article presents the possibilities of effective management of lignocellulosic waste by including it in the circular economy. The pyrolysis process was chosen as the thermal conversion method. This approach, due to a high flexibility of the obtained products, better quality of the solid residue (char), and the lower emission of pollutants into the atmosphere, e.g., SO₂ and NOₓ, is a competitive solution compared to combustion process. Wood waste from alder and pine were analyzed. As part of laboratory tests, the elementary composition was determined, i.e., C, H, N, S, and O. The pyrolysis process was carried out at a temperature of 600 ℃ on an experimental stand for the conversion of solid fuels in a stationary bed. For the obtained data, using the Ansys Chemkin-Pro calculation tool, the detailed chemical composition of gaseous products of the pyrolysis process was modeled for a varying temperature range and residence time in the reactor. The studies have shown that for certain process conditions it is possible to obtain a high calorific value of pyrolytic gas, up to 25 MJ/m³.

Keywords: waste management; circular economy; biomass; energy recovery; pyrolysis

1. Introduction

Progressive urbanization, digitization, and industrialization lead to a high demand for energy sources [1]. Today, the major source of energy are still fossil fuels such as coal, petroleum, and natural gas [2]. However, due to increasing awareness of resources depletion and environmental issues such as air pollution (mainly by CO₂, NOₓ, SOₓ, and particulate matter emissions) being responsible for global warming and climate change, acid rain, etc., more sustainable energy sources are sought after [3]. So, there is a need to modify the recent trends in energy management [4]. Thus, a number of activities, policies, and legislation were implemented to replace conventional fuels and improve energy generation technologies in accordance to the principles of the sustainable development of society [5–7]. Due to the above, more and more attention is paid to the production of energy from biomass which is regarded as a promising, clean and renewable fuel [8].

However, converting raw biomass directly into energy is not very profitable due to the fact that it is characterized by a high moisture and oxygen content, low calorific value and highly variable composition and properties [9]. Worth noting is the fact that biomass can be thermochemically transformed into different types of fuels, such as biochar, bio-oil, and gas, during such processes as torrefaction [10], pyrolysis [11], gasification [12] and hydrothermal liquefaction (Figure 1) [13,14]. Furthermore, pyrolysis and gasification seem to be, at the moment, the most reasonable and cost-effective methods for converting biomass
to energy [15,16]. In recent decades, increasing interest in the development of pyrolysis pathways for the production of biofuels from lignocellulosic biomass is observed [17,18]. Lignocellulosic biomass is a plant material that is not used for food or feed. It mainly consists of agricultural residues, energy crops, forestry residues, and yard trimming [19]. Lignocellulosic biomass is considered to be the third largest energy source after coal and petroleum products and one of the main sources of renewable carbon [20]. Its wide availability worldwide, low cost, and low greenhouse gas emission make it one of the most suitable candidates for the production of chemicals and fuel intermediates [21]. It was estimated that the annual production of lignocellulosic biomass on Earth is greater than 200 billion tons [22]. It has a huge potential for the production of liquid biofuels [23]. It consists mainly of cellulose (30–50 wt%), hemicellulose (20–40 wt%) and lignin (15–25 wt%) [24,25]. The remaining fraction of lignocellulosic biomass includes proteins, oils, and ash [26,27]. Lignocellulosic biomass can be converted into liquid fuels in three primary ways, i.e., synthesis gas production by gasification, bio-oil production by pyrolysis or liquefaction, and hydrolysis of lignocellulosic biomass to produce sugar monomer units [22]. The elemental and chemical compositions of lignocellulosic biomass can vary depending on the species [23,28–31]. The carbon content is the main contributor to the total calorific value and its share ranges between 34.1–53.5 wt% of the biomass. In general, the content of nitrogen (<1.8 wt%) and sulfur (0.1–0.6 wt%) in the biomass is relatively low compared to fossil fuels. The relative content of the biomass component is a significant factor affecting the bio-oil yield as well as its chemical composition, as each fraction undergoes different degradation pathways under different reaction conditions [23].

The pyrolysis can be considered as the first stage of many thermal processes as well as one of the most commonly used methods of obtaining renewable energy from biomass [32]. Various types of lignocellulosic biomass or contaminated biomass can be used as a feedstock to produce bio-oil, bio-char, and pyrolytic gases during the pyrolytic process [26,33]. Pyrolysis is a thermochemical process in which organic substances are transformed into gaseous (pyrolytic gas), liquid (pyrolysis oil), and solid products (charcoal) [34,35]. The bio-oil can be further upgraded to transportation fuels and value-added chemicals, in turn the solid and gaseous products might be combusted to supply energy for the pyrolysis reaction or heat/power generation [36]. The process is performed under temperature range between 300 and 600 °C and in the absence of oxygen, which converts biomass into high-value biofuels and biofuel precursors [37]. Many factors influence the composition and yield of waste pyrolytic products. The properties of such products are determined among others by the type of waste to be pyrolyzed, as well as the reactor type, heating method, pyrolysis temperature, feedstock particle size, fuel residence time in the reactor, or the residence time of primary decomposition products in a high temperature zone [38–40]. Depending on the residence time and heating rate, there are three main categories of biomass pyrolysis: slow (conventional), fast and flash pyrolysis mainly aiming at maximizing either the bio-oil or biochar yields [33,37]. Slow pyrolysis leads mainly to the production of biochar and requires a lower heating rate and temperature with a longer residence time [41,42]. In turn, in fast pyrolysis, bio-oil is the main product, and it is performed under a high heating rate and short residence time. For example, the research presented in the work [36] has shown that fast pyrolysis of biomass performed at rapid heating rates and short hot vapor residence times (<1 s) produces liquid with yield up to 75 wt%. The quality of obtained pyrolytic products determines their further application. For example, it is widely confirmed that a low heating rate favors the production of char while a high one promotes the formation of volatile compounds [43].
The rational utilization of these products makes the pyrolysis process a serious candidate to be included in the chain of waste management activities consistent with the idea of a circular economy [44,45]. The definitions of circular economy presented in the world literature take into account the evolution of its creation and implementation. This idea appeared in the 1960s, which partly refers to the concept presented in the publication by Barry Commoner, The Closing Circle, from the early 1970s, which details the relationship between the level of technological development, the ecosystem, and the economy. The role of circularity in six important areas was also indicated: energy resources (including electrochemical and water), metals (including coking coal), non-metallic raw materials, forest biomass, agricultural resources, and flora and fauna resources [46]. Many research works appeared in the late 1970s after the publication of the Club of Rome Reports. They emphasized the need for changes in the world economy due to the depletion of natural resources. It is worth noting that already in the 1980s, the circular economy concept was described as a closed-loop economy by Stahel and Reday, who emphasized not only the necessity of recycling in the economy, but also the reuse and regeneration of products. Circular economy was defined as a development strategy in 2011, which maximizes resource efficiency and minimizes waste production in the context of sustainable economic and social development. The idea behind the circular economy is that the used product does not become a waste, but a raw material for further production. It is a move from the current approach “take-produce-consume-dispose” to a material re-use model that ultimately aims to eliminate the end-of-life stage of a product. The circular economy is, therefore, an economy model in which all products, materials, and raw materials should be used for as long as possible. As a result, many countries started to treat circular economy not as a concept, but as a model, strategy, and even economic system, adjusting legislation and economic instruments to facilitate its implementation [46,47]. The definitions of this concept emphasize the distinction between the specificity of circular economy and sustainable development, and at the same time indicate that in this strategy it is important to search for economic solutions that are profitable and beneficial for the natural environment, which create not only new business models, but most of all innovative technological solutions and new materials. In this context, it is worth noting that the new circular economy action plan for a cleaner and more competitive Europe, and the European Commission (2020) encourages the stimulation of the circular economy by implementing several economic instruments such as landfill and waste incineration taxes. This attracts the attention for other available waste-to-energy technologies, such as gasification or pyrolysis [48]. The approach of the lignocellulosic waste management proposed in the present article may be helpful in the initial assessment of the profitability and direction of their energy use.
Figure 1. Scheme of the possibilities of biomass waste treatment [19,49–52].

A type of biomass also determines the characteristics of the pyrolysis end products [53]. The research performed by Pang et al. [32] showed that depending on the biomass composition, different percentage proportions of products can be obtained. Biomass with high proportion of hemicellulose would result in products being rich in bio-gas, while cellulose-dominant biomass would yield products rich in bio-oil. In turn, biomass with high lignin content would lead to products rich in bio-char. Moreover, the economic evaluation and the sensitivity analysis showed that lignocellulosic components influence the economic efficiency of biomass pyrolysis [32].

The article presents a comprehensive approach to biomass pyrolysis, including not only laboratory experiments, but also computer simulations. Taking into account the complexity of the chemical phenomena occurring during the thermal conversion of lignocellulosic waste, conducting the laboratory tests alone does not allow for a thorough analysis and optimization of the process. Due to the use of computer simulations in the article, the presented research results not only supplement the knowledge obtained so far in the above-mentioned subject, but also provide a new knowledge in the field of detailed
chemical analysis of gaseous pyrolysis products. The complexity of the pyrolysis process, which hinders its mathematical description, makes it difficult to understand and predict the ecological effects of this process, which is the basis for the development of competitive technological solutions aimed not only at minimizing the negative environmental effects, but above all at reducing the financial outlays. Moreover, the literature on the subject repeatedly emphasizes that modeling of chemical kinetics makes a significant contribution to the chemical analysis of complex phenomena occurring during the process of thermal biomass conversion. Due to the above, the results of the computer simulations presented in the article are the starting point for deliberations on the detailed chemical composition of the pyrolytic gas formed, and thus its quality, decisive for energy use. The high calorific value of pyrolysis gas may contribute to lower consumption of conventional gaseous fuels, e.g., natural gas, which will bring tangible economic benefits.

2. Materials and Methods

2.1. Materials

The material selected for the purpose of the present research was lignocellulosic biomass in the form of alder and pine chips, for which the content of carbon, hydrogen, nitrogen, and sulfur was determined using the Vario Macro Cube CHNS analyzer. The oxygen content, being present in small amounts during the pyrolysis process, was determined by the direct method in a reducing atmosphere (N$_2$/H$_2$ 95%/5%) at the temperature of 1120 °C. Oxygen was determined using the automatic elemental analyzer by alementar analysensysteme GmbH. Determination of the calorific value for the analyzed biomass was performed using the calorimetric method in the calorimetric bomb under constant volume conditions. The calorific value of the tested materials was determined based on the rate of the temperature rise, the calorimeter heat capacity, and the mass of the samples. The obtained value was corrected by the heat value resulting from the combustion of auxiliary substances, i.e., the ignition wire. The results of the tests performed are summarized in Table 1.

Table 1. Proximate and ultimate analysis of pine and alder wood.

| Parameter                        | Pine Wood | Alder Wood |
|----------------------------------|-----------|------------|
| Sample’s view                    | unit      |            |
| Moisture content—W$^a$           | 3.13 ± 0.1| 4.5 ± 0.1  |
| Ash content—A$^a$                | 1.58 ± 0.2| 1.3 ± 0.2  |
| Volatile matter content—V$^a$   | 81.5 ± 0.45| 87.55 ± 0.45 |
| Carbon content—C$_t$ $^a$       | 49.5 ± 0.6| 47.5 ± 0.6 |
| Hydrogen content—H$_t$ $^a$     | Wt%       |            |
| Nitrogen content—N$_t$ $^a$     | 0.07 ± 0.01| 0.29 ± 0.01 |
| Sulfur content—S$_t$ $^a$       | 0.06 ± 0.01| 0.15 ± 0.01 |
| Oxygen content—O$_t$ $^a$       | 42.99 ± 0.82| 40.85 ± 0.82 |
| Heat of combustion—HHV          | MJ/kg     |            |
| Cellulose                        | 20.22 ± 0.20| 19.62 ± 0.20 |
| Hemicellulose                    | Wt%       |            |
| Lignin                           | 25.29 ± 0.6| 28.30 ± 0.6 |
|                                  | 22.79 ± 0.4| 26.45 ± 0.4 |

$^a$total, $^a$—analytical state (dry in 105 °C and milled to less than 1 mm).
2.2. Experimenatal Stand

The lignocellulosic biomass pyrolysis process was carried out on the experimental stand for solid fuel conversion in a stationary bed, described in detail in [54]. The main element of the stand was an electric furnace with a steel retort, in which the biomass conversion process took place together with the liquid and gas phase collection system. The diagram of the stand is shown in Figure 2.

![Figure 2](image_url)

Figure 2. Test stand for pyrolysis of lignocellulosic waste, where: 1-retort-conversion section, 2-retort-pyrolysis section, 3-two section heating unit, 4-cooler 5-gas washers, 6-adsorbtion filter, 7-gas storage system, 8-pressure control valve.

In each pyrolysis run, the analyzed waste (100 g) was placed in a steel retort and closed tightly. Nitrogen was supplied at the bottom of the retort for about 15 min at a constant flow of 500 cm$^3$/h, which allowed obtaining chemically neutral conditions of the process. After 15 min, the nitrogen flow was reduced to 100 cm$^3$/h and the heating of the retort was started. The pyrolysis process was performed at a temperature of 600 °C. In all the experiments conducted, the heating rate was kept constant at 10 °C/min. After reaching the set temperature, the retort with the sample was kept at the final temperature for 5 min, then immediately removed from the furnace, and then cooled to an ambient temperature. Keeping the sample in the given temperature conditions was related to the time of heat penetration and its normalization inside the retort.

2.3. Computer Calculations

The purpose of employing the computer calculations was to determine the detailed chemical composition of pyrolytic gas for variable process conditions, i.e., temperature and residence time, and then to calculate its calorific value. The proposed approach showed the energy potential of gaseous pyrolysis products and, as a consequence, made it possible to indicate an effective direction for the management of lignocellulosic waste.

The pyrolysis process of waste was modeled using the widely distributed ANSYS CHEMKIN-PRO software [55-58]. A detailed chemical mechanism dedicated to biomass conversion, developed by the CRECK Modeling Group, was implemented for the calculations. The mechanism involved 137 compounds and 4533 chemical reactions. The calculations were made for the process temperature variable in the range of 600–900 °C and the residence time from 1–15 min. The process was carried out under the assumption that the reactants were perfectly mixed with the PSR Reactor (perfectly stirred reactor). Based on the determined gas composition, the calorific value was calculated, indicating the most favorable variant. The diagram of the performed calculations is shown in Figure 3.
reactants were perfectly mixed with the PSR Reactor (perfectly stirred reactor). Based on the determined gas composition, the calorific value was calculated, indicating the most favorable variant. The diagram of the performed calculations is shown in Figure 3.

![Figure 3. Scheme of calculation procedure.](image)

3. Results

3.1. Experimental Results

The Table 2 summarizes the properties of the pyrolysis products obtained from the tested lignocellulosic wastes.

| Product                  | Yield [wt%] | Char 20.5 ± 0.2 | Bio-oil 60.3 ± 0.2 | Pyrolytic gas 19.0 ± 0.5 |
|--------------------------|-------------|-----------------|--------------------|--------------------------|
| Char                     |             |                 |                    |                          |
| Ultimate and Proximate Analysis [wt%] |
| C                        | 88.1 ± 0.60 | 90.8 ± 0.60     |                    |                          |
| H                        | 2.7 ± 0.32  | 2.2 ± 0.32      |                    |                          |
| N                        | 1.1 ± 0.01  | 0.3 ± 0.01      |                    |                          |
| S                        | 0.5 ± 0.01  | 0.1 ± 0.01      |                    |                          |
| O                        | 6.3 ± 0.82  | 3.3 ± 0.82      |                    |                          |
| HHV [MJ/kg]              | 33.5 ± 0.20 | 33.7 ± 0.20     |                    |                          |
| Moisture [wt%]           | 1.1 ± 0.10  | 3.1 ± 0.10      |                    |                          |
| Ash                      | 1.5 ± 0.20  | 1.5 ± 0.20      |                    |                          |
| Volatile matter [wt%]   | 8.6 ± 0.45  | 5.5 ± 0.45      |                    |                          |

3.2. Calculation Results

The results of the computer simulations are presented in Figures 4 and 5.

![Figure 4. Cont.](image)
Figure 4. Concentration of selected pyrolysis gas products as a function of temperature.

Figure 5. Cont.
An important part of the study was to verify the correctness of the model adopted for calculations by comparing the results obtained during the calculations with the results of the experiment (Figures 6 and 7).

Figure 5. Concentration of selected pyrolysis gas products as a function of residence time.

Figure 6. Comparison of pyrolysis gas composition for alder wood (600 °C/5 min).

Figure 7. Comparison of pyrolysis gas composition for pine wood (600 °C/5 min).
### Table 2. Products of biomass pyrolysis.

|                     | Alder Wood       | Pine Wood       |
|---------------------|------------------|-----------------|
| **Product Yield [wt%]** |                  |                 |
| Char                | 20.56 ± 0.2      | 23.6 ± 0.2      |
| Bio-oil             | 60.38 ± 0.2      | 56.2 ± 0.2      |
| Pyrolytic gas       | 19.06 ± 0.5      | 20.2 ± 0.5      |
| **Char Ultimate and Proximate Analysis [wt%]** |                  |                 |
| C                   | 88.13 ± 0.60     | 90.86 ± 0.60    |
| H                   | 2.71 ± 0.32      | 2.27 ± 0.32     |
| N                   | 1.16 ± 0.01      | 0.34 ± 0.01     |
| S                   | 0.51 ± 0.01      | 0.11 ± 0.01     |
| O                   | 6.34 ± 0.82      | 3.31 ± 0.82     |
| HHV [MJ/kg]         | 33.56 ± 0.20     | 33.71 ± 0.20    |
| Moisture            | 1.15 ± 0.10      | 3.11 ± 0.10     |
| Ash                 | 1.53 ± 0.20      | 1.53 ± 0.20     |
| Volatile matter     | 8.67 ± 0.45      | 5.57 ± 0.45     |
| **Elemental Analysis of Pyrolysis Gas [mol%] in Airless State** |                  |                 |
| H2                  | 7.86 ± 0.43      | 8.71 ± 0.43     |
| CO2                 | 41.52 ± 0.30     | 34.75 ± 0.30    |
| CO                  | 33.41 ± 0.15     | 31.25 ± 0.15    |
| CH4                 | 14.9 ± 0.4       | 22.48 ± 0.4     |
| C2H4                | 0.6 ± 0.1        | 0.63 ± 0.1      |
| C2H6                | 1.05 ± 0.2       | 1.34 ± 0.2      |
| C3H6                | 0.33 ± 0.03      | 0.43 ± 0.03     |
| C3H8                | 0.25 ± 0.02      | 0.31 ± 0.02     |
| C4H10               | 0.04 ± 0.01      | 0.04 ± 0.01     |
| C5H12               | 0.04 ± 0.01      | 0.06 ± 0.01     |
| HHV [MJ/m^3]        | 16.18 ± 0.40     | 12.94 ± 0.40    |
| **Elemental Analysis of Bio-Oil [wt%]** |                  |                 |
| C                   | 54.33 ± 0.60     | 57.95 ± 0.60    |
| H                   | 10.45 ± 0.32     | 6.98 ± 0.32     |
| N                   | 0.41 ± 0.01      | 0.12 ± 0.01     |
| S                   | 0.08 ± 0.01      | 0.08 ± 0.01     |
| O                   | 34.73 ± 0.20     | 34.87 ± 0.20    |
| HHV [MJ/kg]         | 26.51 ± 0.20     | 24.81 ± 0.20    |
| Moisture [wt%]      | 48.44 ± 0.10     | 38.78 ± 0.10    |

In a further step, four main components of the pyrolysis gas, namely: H2, CO, CO2, and CH4 obtained in laboratory conditions, were compared with the ones obtained from the computer simulations (Figure 8).
Figure 9. Comparison of selected pyrolysis gas components for all analyzed variants.

Subsequently, the calorific value of pyrolysis gas was calculated for all variants of the performed calculations and compared with the calorific value obtained in the experimental conditions (Figure 9).

Figure 9. Comparison of the calorific value for the analyzed variants.

4. Discussion and Future Work

The main product in the pyrolysis process was the liquid fraction—bio-oil, and its share was 56.2% for pine wood and 60.38% for alder wood. The solid (char) and gaseous (pyrolysis gas) fractions were comparable and amounted to approx. 20%. The calorific values of the obtained pyrolysis products were, respectively, char—approx. 33%, bio-oil from 24.81–26.51% and pyrolysis gas from 5.41–7.86%. Similar results were obtained by Manzano et al. [30], who carried out the pyrolysis process for pine and poplar waste. As indicated by numerous studies [59,60], the process temperature and residence time have a significant impact on the yield of pyrolysis products. As demonstrated in their works by Garcia-Perez et al. [61], Fan et al. [62], as well as Özbay et al. [63], with increasing temperature, in the range from 350 °C to 600 °C, the share of the gaseous fraction increases (pyrolysis gas) from 22% to 32% and liquid (bio-oil) from 36% to 40%, while the solid fraction (char) significantly decreases from 42.5% to 28.5%. Yan et al. [64] explained that the increase in pyrolysis gas efficiency and the decrease in oil yield with increasing temperature, is the effect of stronger cracking of carbon bonds at higher temperatures and obtaining lighter hydrocarbons with shorter carbon chains. Moreover, they indicated that with the increase in residence time in the range of 0–15 min, a significant decrease in carbonizate yield is observed in favor of the increase in both the yields of oil and pyrolysis gas [64]. The quality of the obtained products was determined primarily by the elemental composition of the analyzed biomass. As indicated by the obtained test results, the pyrolysis gas contained mainly CO₂ (28.54% for the alder wood and 31.4% for the pine wood), CO (22.97% for the alder wood and 28.24% for the pine wood), H₂ (5.14% for the alder wood and 7.88% for the pine wood) and lighter hydrocarbons, in particular methane (10.25% for the alder wood and
20.32% for the pine wood) and in small amounts (less than 1%) ethane, ethene, propane, propene, and butane. As indicated by the results, for other types of waste, including municipal waste [65–70], the temperature and residence time also have a significant impact on the quality of the obtained products, in particular on the pyrolysis gas as its calorific value increases with increasing process temperature [71].

Taking into account the fact that pyrolysis oil obtained from waste, including lignocellulosic ones, are often a mixture of oxidized and unoxidized hydrocarbons [72–77], which makes their a direct application difficult [77–79]. Hence, the conversion of waste analyzed in the article for parameters that ensure obtaining high calorific pyrolysis gas is fully justified. The chemical composition of bio-oils is determined by many factors, namely [80]:

- The type of biomass (elemental composition, properties);
- The initial preparation of the raw material (fragmentation, particle size and shape, moisture and ash content);
- The conditions for the pyrolysis process (temperature, heating rate, residence time, pressure, and gas environment);
- Filtration and steam condensation (filter type, condensation method and medium, cooling rate).

An additional argument for a more effective use of pyrolysis gas is the fact that the technologies for storage and use of hydrocarbon gases are well researched and highly developed [81]. Due to the above, in the article, apart from experimental tests, computer simulations were carried out, which allowed the prediction of the composition of pyrolysis gas for a wide range of temperature and residence time in the reactor.

The computer simulations carried out have shown, for both pine wood and alder wood, that with appropriate process conditions it is possible to obtain gaseous products that are valuable in terms of energy (Figures 4 and 5). As the temperature increases, the concentration of CO (from 16% to 32% at 900 °C) and H₂ (from 7% at 600 °C to 20% at 900 °C) increases significantly, and C₂H₄ and C₆H₁₂ rises several times, but only up to the temperature of 700–750 °C, and after exceeding it, it rapidly decreases. The share of carbon dioxide diminishes twice, which has a positive effect on the calorific value of the pyrolysis gas. The opposite situation is observed in Figure 5. With the increase in residence time, the concentration of hydrogen and carbon monoxide decreases several times, while for the remaining compounds it increases over the entire range of the analyzed residence time.

The comparative analysis (Figures 6 and 7) showed a high agreement of the obtained results. The observed differences, in particular for the concentration of CH₄ and CO in the gas obtained from the alder wood pyrolysis, should be explained by the assumption of perfect mixing adopted for calculations and the approximate residence time in the zone of the highest temperatures. Moreover, the calculated composition of the pyrolysis gas relates to the gaseous products at the temperature prevailing in the reactor and not, as in the experiment, to already partially cooled gases. From the point of view of the calculations performed, it was important to estimate the share of higher hydrocarbons, such as C₂H₄, C₃H₆, and C₃H₈, as their content in the calculated gas composition was definitely higher than in the measured one. These compounds, due to the higher boiling point, are much easier to liquefy, which explains their smaller share in the composition of the gas obtained under the conditions of the experiment.

Figure 8 shows that the best compatibility, both for pine and alder wood, was obtained at 600 °C and for the residence time of 5 min, i.e., the conditions under which the experiment was conducted, which confirms the correctness of the model adopted for calculations.

The calculations show that the gas obtained from the pine wood pyrolysis carried out at the temperature of 600 °C and during 15 min had the highest calorific value. This is due to the fact that the gas composition has a much higher content of higher hydrocarbons than in other variants. For the remaining modeling cases, comparable values were obtained in the range of 20.61–23.94%. Comparing the modeling results with the calorific value obtained in the experimental conditions, a large disproportion is visible, resulting from
the aforementioned differences, in particular the temperature of the analyzed gases. The results obtained as a part of the calculations encourage the energetic use of hot pyrolysis gas for firing e.g., industrial heating chambers [82,83].

As indicated in the article, pyrolysis is one of the most promising technologies for the treatment of various types of waste, including lignocellulosic waste. The conducted experimental studies showed a high yield of pyrolysis liquid, which can be a substitute for petroleum-derived fuels. However, the effective use of bio-oils in the field of liquid fuels requires the knowledge of highly differentiated properties of biomass. Moreover, due to the properties of pyrolysis oils, including the presence of impurities, their direct application is very difficult. On the other hand, technologies for the use and storage of hydrocarbon gases are the opposite, which are now well researched and further improved. Due to the above, the article focuses on the conversion of biomass towards the yield of pyrolysis gas. The computer simulations have shown that it is possible to obtain high-calorific pyrolysis gas.

The authors of the article, based on their own experience and current research in this field, proposed an effective direction for the energy management of pyrolysis gas, namely for firing industrial heating chambers, in particular heating furnaces in the steel industry. In the face of intensive optimization of the production processes and the reduction of incurred financial outlays, an opportunity is perceived to increase the competitiveness of steel plants thanks to the use of pyrolysis gas. At the same time, this method of the energetic use of pyrolysis gas may contribute to lower consumption of natural gas, which will allow for the diversification of fuel and energy sources, and will also bring tangible economic benefits. Thus, such an approach is in full compliance with the idea of a circular economy. Furthermore, the vision of a circular economy has recently gained more and more interest from both governments and business leaders who see it as an attractive alternative to the linear “take, make, throw away” model of the economy. The possibilities of independence of economic development from the supply of primary materials, stimulating innovation, accelerating growth and creating a more stable labor market are particularly important here. The world economy is ready for change and its trend is set, in particular by such countries as the Netherlands, Finland, and Scotland.

5. Conclusions

The conducted experiments and computer simulations have shown that:

- The pyrolysis process is one of the most promising technologies for the treatment of various types of waste, including lignocellulosic.
- The yield and quality of individual fractions depend on the properties of the lignocellulosic waste and the operating conditions of the process, in particular the temperature and residence time.
- Taking into account the complexity of chemical phenomena occurring during a thermal conversion of waste, including lignocellulosic waste, conducting laboratory tests alone does not allow for a thorough analysis and optimization of the process. Other problems include high costs, technical difficulties related to the collection of samples for testing, limited possibilities of control and measurement equipment, and time-consuming experimental research.
- Understanding and anticipating the above-mentioned processes are the key for further development of competitive technological solutions, aimed not only at minimizing negative environmental effects, but above all at reducing financial outlays.
- The use of the computational tool, which is ANSYS CHEMKIN-PRO software, made it possible to determine the detailed chemical composition of the pyrolysis gas for diversified process conditions, i.e., temperature and residence time.
- The results obtained during computer simulations made it possible to calculate the approximate calorific value of the pyrolysis gas, ranging from 20.61 to 25.19 MJ/m$^3$. The high calorific value of gas encourages its wider use in both the heating and steel industries.
• The computer simulations carried out have shown, for both pine wood and alder wood, that with appropriate process conditions it is possible to obtain gaseous products that are valuable in terms of energy.
• The main product in the pyrolysis process was the liquid fraction—bio-oil, and its share was 56.2% for the pine wood and 60.38% for the alder wood. In turn, the solid (char) and gaseous (pyrolysis gas) fractions were comparable and amounted to approx. 20%.
• The conducted experimental studies showed a high yield of pyrolysis liquid, which can be a substitute for petroleum-derived fuels; however, the effective use of bio-oils in the field of liquid fuels requires the knowledge of highly differentiated properties of biomass.
• The gas from the pyrolysis of the lignocellulosic waste can be co-combusted with the natural gas, which will contribute to its lower consumption. The aforementioned facts show that the pyrolysis gas can be an excellent alternative to conventional fuels, while at the same time contributing to the increasing level of environmental protection and can play an important role of biomass in the circular economy.

Author Contributions: Conceptualization, M.Z., A.P., A.S. and M.S. (Marcin Sajdak); methodology, M.S. (Marcin Sajdak) and M.Z.; software, M.Z.; validation, M.S. (Marcin Sajdak) and M.Z.; formal analysis, M.S. (Marcin Sajdak) and M.Z.; investigation, M.S. (Marcin Sajdak) and M.Z.; resources, A.P. and A.S.; data curation, A.P. and A.S.; writing—original draft preparation, A.P., M.S. (Marcin Sajdak) and M.Z.; writing—review and editing, A.P. and M.S. (Marcin Sajdak); visualization, M.S. (Magdalena Skrzyniarz); graphic design of the results, M.S. (Magdalena Skrzyniarz); supervision, M.Z., A.P., A.S. and M.S. (Marcin Sajdak) All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Kowalczyk, Ł.; Elsner, W.; Niegodajew, P.; Marek, M. Gradient-free methods applied to optimisation of advanced ultra-supercritical power plant. Appl. Therm. Eng. 2016, 96, 200–208. [CrossRef]
2. Hruška, M.; Variny, M.; Haydary, J.; Janošovský, J. Sulfur recovery from syngas in pulp mills with integrated black liquor gasification. Forests 2020, 11, 1173. [CrossRef]
3. Dyrstad, J.M.; Skonhoft, A.; Christensen, M.Q.; Ødegaard, E.T. Does economic growth eat up environmental improvements? Electricity production and fossil fuel emission in OECD countries 1980–2014. Energy Policy 2019, 125, 103–109. [CrossRef]
4. Thakur, A.; Kumari, S.; Sinai Borker, S.; Prashant, S.P.; Kumar, A.; Kumar, R. Solid Waste Management in Indian Himalayan Region: Current Scenario, Resource Recovery, and Way Forward for Sustainable Development. Front. Energy Res. 2021, 9, 1–18. [CrossRef]
5. Sharma, H.B.; Panigrahi, S.; Sarmah, A.K.; Dubey, B.K. Downstream augmentation of hydrothermal carbonization with anaerobic digestion for integrated biogas and hydrochar production from the organic fraction of municipal solid waste: A circular economy concept. Sci. Total Environ. 2020, 706, 135907. [CrossRef]
6. Variny, M. A study on black liquor gasification technology efficiency compared to the traditional kraft boilers technology. In Proceedings of the 18th International Scientific Conference, Kouty nad Desnou, Czech Republic, 17–19 May 2017; pp. 1–6.
7. Lukáč, L.; Rimár, M.; Variny, M.; Kizek, J.; Lukáč, P.; Jablonský, G.; Janošovský, J.; Fedák, M. Experimental investigation of primary de-NOx methods application effects on NOx and CO emissions from a small-scale furnace. Processes 2020, 8, 940. [CrossRef]
8. Lukáč, L.; Kizek, J.; Jablonský, G.; Karakash, Y. Defining the Mathematical Dependencies of NOx and CO Emission Generation after Biomass Combustion in Low-Power Boiler. Civ. Environ. Eng. Rep. 2019, 29, 153–163. [CrossRef]
9. Mlonka-Mędrala, A.; Evangelopoulos, P.; Sieradzka, M.; Zajemska, M.; Magdziarz, A. Pyrolysis of agricultural waste biomass towards production of gas fuel and high-quality char: Experimental and numerical investigations. Fuel 2021, 296, 120611. [CrossRef]
10. Iwaszko, J.; Zajemska, M.; Zawada, A.; Szwaja, S.; Poskart, A. Vitrification of environmentally harmful by-products from biomass torrefaction process. J. Clean. Prod. 2020, 249, 119427. [CrossRef]
11. Sieradzka, M.; Rajca, P.; Zajemska, M.; Mlonka-Mędrala, A.; Magdziarz, A. Prediction of gaseous products from refuse derived fuel pyrolysis using chemical modelling software-Ansys Chemkin-Pro. J. Clean. Prod. 2020, 248, 119277. [CrossRef]
12. Szwaja, S.; Poskard, A.; Zajemka, M.; Szwaja, M. Theoretical and experimental analysis on co-gasification of sewage sludge with energetic crops. Energies 2019, 12, 1750. [CrossRef]

13. Ng, K.S.; Phan, A.N. Evaluating the Techno-economic Potential of an Integrated Material Recovery and Waste-to-Hydrogen System. Resour. Conserv. Recycl. 2021, 167, 105932. [CrossRef]

14. Szwaja, S.; Poskard, A.; Zajemka, M. A new approach for evaluating biochar quality from Virginia Mallow biomass thermal processing. J. Clean. Prod. 2019, 214, 356–364. [CrossRef]

15. Gao, N.; Chen, C.; Magdziarz, A.; Zhang, L.; Quan, C. Modeling and simulation of pine sawdust gasification considering gas mixture reflux. J. Anal. Appl. Pyrolysis 2021, 155, 105984. [CrossRef]

16. Thamizhvel, R.; Suryavarman, K.; Velumurugan, V.; Sethuraman, N. Comparative study of gasification and pyrolysis derived from coconut shell on the performance and emission of CI engine. Mater. Today Proc. 2021. [CrossRef]

17. Ślefarski, R.; Jójka, J.; Czyżewski, P.; Gołubiewski, M.; Jankowski, R.; Markowski, J.; Magdziarz, A. Experimental and Numerical-Driven Prediction of Automotive Shredder Residue Pyrolysis Pathways toward Gaseous Products. Energies 2021, 14, 1779. [CrossRef]

18. Wang, S.; Dai, G.; Yang, H.; Luo, Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. Prog. Energy Combust. Sci. 2017, 62, 33–86. [CrossRef]

19. Rajesh Banu, J.; Preethi; Kavitha, S.; Tyagi, V.K.; Gunasekaran, M.; Karthikeyan, O.P.; Kumar, G. Lignocellulosic biomass based biorefinery: A successful platform towards circular bioeconomy. Fuel 2021, 302, 121806. [CrossRef]

20. Elsner, W.; Wysocki, M.; Niegodajew, P.; Borecki, R. Experimental and economic study of small-scale CHP installation equipped with downdraft gasifier and internal combustion engine. Appl. Energy 2017, 202, 213–227. [CrossRef]

21. Ojha, D.K.; Viju, D.; Vinu, R. Fast pyrolysis kinetics of lignocellulosic biomass of varying compositions. Energy Convers. Manag. X 2021, 10, 100071. [CrossRef]

22. Qian, E.W. Pretreatment and Saccharification of Lignocellulosic Biomass. In Research Approaches to Sustainable Biomass Systems; Elsevier: Amsterdam, The Netherlands, 2013; pp. 181–204. ISBN 9780124046092.

23. Kim, J.Y.; Lee, H.W.; Lee, S.M.; Jae, J.; Park, Y.K. Overview of the recent advances in lignocellulose liquefaction for producing biofuels, bio-based materials and chemicals. Bioresour. Technol. 2019, 279, 373–384. [CrossRef]

24. Zhang, L.; Yang, Z.; Li, S.; Wang, X.; Lin, R. Comparative study on the two-step pyrolysis of different lignocellulosic biomass: Effects of components. J. Anal. Appl. Pyrolysis 2020, 152, 104966. [CrossRef]

25. Liang, J.; Shan, G.; Sun, Y. Catalytic fast pyrolysis of lignocellulosic biomass: Critical role of zeolite catalysts. Renew. Sustain. Energy Rev. 2021, 139, 110707. [CrossRef]

26. Jerzak, W.; Bieniek, A.; Magdziarz, A. Multifaceted analysis of products from the intermediate co-pyrolysis of biomass with Tetra Pak waste. Int. J. Hydrogen Energy 2021. [CrossRef]

27. Kapoor, R.; Ghosh, P.; Kumar, M.; Sengupta, S.; Gupta, A.; Kumar, S.S.; Vijay, V.; Kumar, V.; Kumar Vijay, V.; Pant, D. Valorization of agricultural waste for biogas based circular economy in India: A research outlook. Bioresour. Technol. 2020, 304, 123036. [CrossRef]

28. Cai, W.; Luo, Z.; Zhou, J.; Wang, Q. A review on the selection of raw materials and reactors for biomass fast pyrolysis in China. Fuel Process. Technol. 2021, 221, 106919. [CrossRef]

29. Jagwe, J.; Olupot, P.W.; Menya, E.; Kalibbala, H.M. Synthesis and application of Granular activated carbon from biomass waste materials for water treatment: A review. J. Bioreour. Bioprod. 2021. [CrossRef]

30. Nunez Manzano, M.; Gonzalez Quiroga, A.; Magdziarz, A.; Pang, Y.X.; Yan, Y.; Foo, D.C.Y.; Sharmin, N.; Madanikashani, S.; Van der Wolde, L.A.; Marin, G.B.; Heynderickx, G.J.; Van Geem, K.M. Biomass fast pyrolysis in an innovative gas-solid hot vortex reactor: Experimental proof of concept. J. Anal. Appl. Pyrolysis 2021, 156, 101655. [CrossRef]

31. Lin, C.Y.; Lu, C. Development perspectives of promising lignocellulose feedstocks for production of advanced generation biofuels: A review. Renew. Sustain. Energy Rev. 2021, 136, 110445. [CrossRef]

32. Pang, Y.X.; Yan, Y.; Foo, D.C.Y.; Sharmin, N.; Zhao, H.; Lester, E.; Wu, T.; Pang, C.H. The Influence of Lignocellulose on Biomass Pyrolysis Product Distribution and Economics via Steady State Process Simulation. J. Anal. Appl. Pyrolysis 2020, 158, 104968. [CrossRef]

33. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renew. Sustain. Energy Rev. 2016, 57, 1126–1140. [CrossRef]

34. Sun, C.; Li, W.; Chen, X.; Li, C.; Tan, H.; Zhang, Y. Synergistic interactions for saving energy and promoting the pyrolysis of polylactic acid and wood flour. Renew. Energy 2021, 171, 254–265. [CrossRef]

35. Jagodziriska, K.; Zaini, I.; Svanberg, R.; Yang, W.; Jönsson, P.G. Pyrolysis of excavated waste from landfill mining: Characterization of the process products. J. Clean. Prod. 2021, 279, 123541. [CrossRef]

36. Bridgwater, A.V. Review of fast pyrolysis and product upgrading. Biomass Bioenergy 2012, 38, 68–94. [CrossRef]

37. Qureshi, K.M.; Kay Lup, A.N.; Khan, S.; Abrina, F.; Wan Daud, W.M.A. Optimization of palm shell pyrolysis parameters in helical screw fluidized bed reactor: Effect of particle size, pyrolysis time and vapor residence time. Clean. Eng. Technol. 2021, 4, 100174. [CrossRef]
67. Win, M.M.; Asari, M.; Hayakawa, R.; Hosoda, H.; Yano, J.; Sakai, S.I. Gas and tar generation behavior during flash pyrolysis of wood pellet and plastic. J. Mater. Cycles Waste Manag. 2020, 22, 547–555. [CrossRef]
68. Singh, R.K.; Ruj, B. Time and temperature depended fuel gas generation from pyrolysis of real world municipal plastic waste. Fuel 2016, 174, 164–171. [CrossRef]
69. Jun, Z.; Shuzhong, W.; Zhiqiang, W.; Haiyu, M.; Lin, C. Hydrogen-rich syngas produced from the co-pyrolysis of municipal solid waste and wheat straw. Int. J. Hydrogen Energy 2017, 42, 19701–19708. [CrossRef]
70. Daouk, E.; Sani, R.; Pham Minh, D.; Nziouh, A. Thermo-conversion of Solid Recovered Fuels under inert and oxidative atmospheres: Gas composition and chlorine distribution. Fuel 2016, 174, 164–171. [CrossRef]
71. Jun, Z.; Shuzhong, W.; Zhiqiang, W.; Haiyu, M.; Lin, C. Hydrogen-rich syngas produced from the co-pyrolysis of municipal solid waste and wheat straw. Int. J. Hydrogen Energy 2017, 42, 19701–19708. [CrossRef]
72. Bosmans, A.; Vanderreydt, I.; Geysen, D.; Helsen, L. The crucial role of Waste-to-Energy technologies in enhanced land fill mining: A technology review. J. Clean. Prod. 2013, 55, 10–23. [CrossRef]
73. Kataki, R.; Bordoloi, N.J.; Saikia, R.; Sut, D.; Narzari, R.; Gogoi, L.; Bhuyan, N. Waste Valorization to Fuel and Chemicals Through Pyrolysis: Technology, Feedstock, Products, and Economic Analysis. In Waste to Wealth; Springer: Berlin/Heidelberg, Germany, 2018; pp. 477–514. ISBN 9789811074318.
74. Ouadi, M.; Jaeger, N.; Greenhalf, C.; Santos, J.; Conti, R.; Hornung, A. Thermo-Catalytic Reforming of municipal solid waste. Waste Manag. 2017, 68, 198–206. [CrossRef]
75. Miskolczi, N.; Borsodi, N.; Buyong, F.; Angyal, A.; Williams, P.T. Production of pyrolytic oils by catalytic pyrolysis of Malaysian refuse-derived fuels in continuously stirred batch reactor. Fuel Process. Technol. 2011, 92, 925–932. [CrossRef]
76. Miskolczi, N.; Atas, F.; Borsodi, N. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: Contaminants, char and pyrolysis oil properties. Bioresour. Technol. 2013, 144, 370–379. [CrossRef]
77. Wang, N.; Chen, D.; Arena, U.; He, P. Hot char-catalytic reforming of volatiles from MSW pyrolysis. Appl. Energy 2017, 191, 111–124. [CrossRef]
78. Efika, E.C.; Onwudili, J.A.; Williams, P.T. Products from the high temperature pyrolysis of RDF at slow and rapid heating rates. J. Anal. Appl. Pyrolysis 2015, 112, 14–22. [CrossRef]
79. Kumar, A.; Samadder, S.R. A review on technological options of waste to energy for effective management of municipal solid waste. Waste Manag. 2017, 69, 407–422. [CrossRef]
80. Sari, A.; Toklu, E. Investigation of the effect of municipal solid waste fragmentation to gaseous formation. J. Eng. Res. Appl. Sci. 2019, 8, 1238–1247. [CrossRef]
81. Qiang, L.; Wen-zhi, L.; Xi-feng, Z. Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers. Manag. 2009, 50, 1376–1383. [CrossRef]
82. Hu, M.; Guo, D.; Ma, C.; Hu, Z.; Zhang, B.; Xiao, B.; Luo, S.; Wang, J. Hydrogen-rich gas production by the gasification of wet MSW (municipal solid waste) coupled with carbon dioxide capture. Energy 2015, 90, 857–863. [CrossRef]
83. Zajemska, M.; Poskart, A. Prediction of the chemical composition of combustion products in metallurgical reheating furnaces by use of numerical methods. Metall. Ital. 2013, 105, 1–11.
84. Zajemska, M.; Poskart, A. Możliwości zastosowania metod numerycznych do przewidywania i ograniczania emisji zanieczyszczeń z instalacji spalania stosowanych w przemyśle chemicznym i rafinerijnym. Przem. Chem. 2013, 92, 357–361.