



Article

Thermochemical Conversion of Biomass into 2nd Generation Biofuel

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Abstract: Bioenergy is considered the largest contributor to the renewable and sustainable energy sector worldwide, playing a significant role in various energy sectors such as heating, electricity supply, and even in replacing fossil fuels in the transportation sector. As part of renewable, low-carbon energy systems, bioenergy can also ensure atmospheric carbon sequestration, provide numerous environmental and socio-economic benefits, and thus contribute to achieving global climate change goals, as well as broader environmental, social, economic, and sustainable development objectives. The use of bioenergy can significantly reduce our carbon footprint and thus contribute to improving the environment. While bioenergy conversion of biomass produces some amount of carbon dioxide, similar to traditional fossil fuels, its impact can be minimized by replacing forest biomass with fast-growing trees and energy crops. Therefore, fast-growing trees and energy crops are the primary raw materials for bioenergy. The results of the research in this publication confirm the high efficiency of biomass depolymerization through thermochemical conversion. The principle of continuous biomass conversion was used at a process temperature of 520 °C. The experiments were carried out in the Biomass Gasification Laboratory at the AgroBioTech Research Center of the Slovak University of Agriculture in Nitra. The biomass used for the experiments was from energy-producing fast-growing willows, specifically the varieties Sven, Inger, and Express. The aim was to determine the amount of biochar produced from each of these tree species and subsequently to investigate its potential use for energy purposes. During the experiments, 0.106 kg of biochar was produced from 1 kg of Inger willow biomass, 0.252 kg from 1 kg of Express willow biomass, and 0.256 kg from 1 kg of Sven willow biomass. A subsequent goal was to determine the production of gas, which can also be used for energy purposes. The biofuel samples obtained were subsequently subjected to thermogravimetric analysis to determine moisture content, volatile matter, and ash content. The ash content in dry matter ranged from 6% to 7.28%, while the volatile matter in dry matter was between 92.72% and 94%. The moisture content in the samples ranged from 1.7% to 2.43%. These results may contribute to innovative insights into biomass depolymerization and help define optimized parameters for thermochemical conversion, as well as the required biomass composition, with the goal of generating second-generation biofuels in the most cost-effective way.

Keywords: bioenergy; biochar; depolymerization; pyrolysis; thermogravimetric analysis

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1. Introduction

Biomass is biological material directly or indirectly produced by photosynthesis. This includes wood and wood residues, energy crops, plant residues, and organic waste/by-products from industries, agriculture, landscaping, and households. Advanced technologies convert biomass energy into solid, liquid, or gaseous fuels that can be used for heating and/or electricity generation, or as alternative fuel in transportation [1]. Bioenergy is

currently the main source of renewable energy, and studies by the International Energy Agency [2] suggest that modern bioenergy is a key component of the future low-carbon global energy system, necessary to meet climate change commitments.

Bioenergy will play an essential role in many scenarios for developing a low-carbon economy, especially in replacing liquid fossil fuels in transportation, where sufficient volumes of alternative fuels are not available.

Biomass is one of the key renewable energy sources (RESs) and plays a significant role in achieving European climate goals by 2030. According to EU Directive 2023/2413 on the promotion of energy from renewable sources, the renewable energy target for 2030 has been increased from 32% to 42.5% (with a goal to increase it to 45%). EU member states follow specific pathways to fulfil their obligations, as defined in national action plans based on respective energy markets and available resources. In 2022, the share of renewable energy in the EU accounted for 23% of gross final energy consumption in the EU, with bioenergy contributing more than 60% of that [3].

Fast-growing trees and energy crops serve as the primary raw materials for bioenergy. Bioenergy can be categorized into two main types: “traditional” and “modern”. Traditional bioenergy mainly involves burning biomass, such as wood, animal waste, and traditional charcoal. Modern bioenergy technologies include the production of liquid biofuels from purpose-grown biomass in biorefineries, biogas from anaerobic digestion of agricultural and food industry residues, and municipal waste. They also include wood chip and pellet heating systems and technologies like pyrolysis.

Approximately three-quarters of the world’s renewable energy consumption is bioenergy, with more than half provided by traditional biomass use technologies [4]. Biomass, therefore, has significant potential and can be directly burned for heating or energy generation or converted into substitutes for oil or gas. Liquid biofuels are a suitable renewable alternative to gasoline and diesel in the transportation sector.

The energy use of biomass in Slovakia holds great potential due to its geographical conditions, with about 47% of the territory being agricultural land and approximately 41% forest land. This presents a challenge for Slovak farmers as, alongside food production, there are opportunities in energy production and energy carriers, which could contribute 25–30% of total revenues in the future [5].

According to the World Bioenergy Association (WBA) [6], fossil fuels still dominate global energy supplies. In 2021, the total primary energy supply worldwide was 618 EJ, with fossil fuels accounting for 80% (coal 27%, oil 29%, and gas 24%). Nuclear energy contributed 30.7 EJ, representing 5% of the total energy mix. Renewable energy technologies such as solar, wind, hydro, biomass, and geothermal accounted for 15% of the primary energy supply in 2021.

Coal remains a significant contributor to the global energy mix. In 2020, 35% of the world’s electricity was generated from coal-based sources, totalling 9452 TWh. Of the 26,833 TWh of global electricity generation in 2020, 29% came from renewable sources, driven by solar and wind energy, as well as contributions from hydropower and biomass. Hydropower was the largest renewable electricity source, with a 58% share, followed by wind energy at 21%. Bioenergy was the fourth-largest renewable electricity source, producing 658 TWh [7].

To meet international energy and climate goals, renewable energy technologies need to grow at a much faster pace, but efforts are also needed to secure a strategy for phasing out fossil fuel production and use worldwide. The development of total primary energy supplies globally since 2000 is shown in Figure 1.

However, to use woody biomass as an energy source, it is necessary to use it rationally and in a sustainable way [8–10]. On the other hand, there are still some problems in current biomass combustion furnaces, where kinetic analysis is a suitable tool to solve them [11–13].

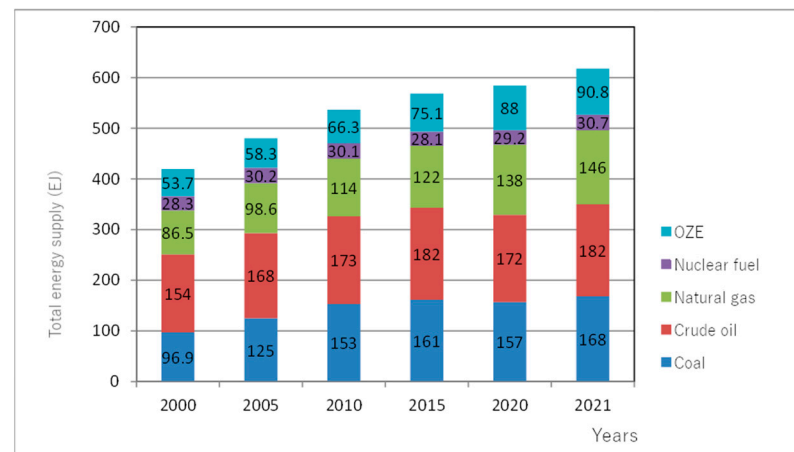


Figure 1. Global primary energy supplies in the world from all sources (edited WBA, 2023 [6]).

Various studies [14–20] observe that the thermal decomposition of the main wood constituents, such as hemicelluloses, cellulose, and lignin, can be divided into two steps. In the first step, in the temperature range of ~ 200 – 400 °C, the combination of total hemicellulose and cellulose decomposition with partial lignin decomposition occurs. The second step could be described as the decomposition of remaining lignin and the combustion of char residues [14,15]. The reason why lignin decomposes slowly under the whole thermal decomposition temperature range is that it contains aromatic matrix which itself increases the degree of the condensation reaction [21–23]. Brodin et al. [24], in a study where decomposition of lignin from different origins was observed, came to the conclusion that a loss of $\sim 40\%$ took place in a temperature range of 200 – 600 °C with maximum material loss at ~ 400 °C.

One of the products resulting from biomass processing is biochar. It is produced by the pyrolysis of sustainably sourced biomass under controlled conditions using clean technology and is used for any purpose that does not involve its rapid mineralization to CO_2 . The condition is that the carbon content in biochar must be higher than 50% of dry matter (DM) [25].

It has the ability to filter water and retain nutrients and can also be used for filtering contaminants in soil [26,27]. Adding biochar to soil offers potential environmental benefits by preventing nutrient loss and thus protecting water quality [28]. Biochar is not only capable of strongly adsorbing many cationic chemicals, such as ammonium ions and various metal ions [29], but can also effectively remove anionic nutrients, such as phosphate, from aqueous solutions [30]. Pyrolysis is a thermochemical conversion process that occurs in the absence of oxygen. While both exothermic and endothermic reactions occur, the latter dominate, requiring external heat. Pyrolysis produces solid (biochar), liquid (bio-oil), and gaseous (synthesis gas) products. Despite some final oxidation products like water and CO_2 , reduced forms such as H_2 , CO, and hydrocarbon gases are present in the pyrolysis gas. Unlike combustion, pyrolysis avoids emissions of SO_2 and NO_x , but it produces H_2S , NH_3 , HCN, and HNCO—highly toxic substances. However, not all nitrogen and sulfur from the raw material transfer to the pyrolysis gas, as some remain in the biochar and oil [31]. The nitrogen, sulfur, and chlorine content in various biomass types is presented in Table 1.

Table 1. Content of nitrogen, sulfur, and chlorine in some types of biomasses [32].

Biomass	N * (mass. %)	S * (mass. %)	Cl * (mass. %)
Wheat straw	0.98	0.07	0.450
Corn husks	0.42	0.04	0.426
Sunflower	0.5	0.1	0.856
Cotton stalks	0.92	0.11	0.159
Wood from fruit trees	0.62	0.06	0.049

* Related to the basis without moisture and ash.

Unlike combustion, pyrolysis retains ash in the coke, preventing the formation of fly ash. The transfer of metals and their oxides into pyrolysis oil or gas is negligible, so they remain in the pyrolysis coke [33]. While pyrolysis is considered an energy recovery process, it consumes heat rather than producing it. Pyrolysis gas, a flammable mixture of H_2 , CO , CO_2 , H_2O , CH_4 , and other gases, can reach a calorific value of up to 15 MJ/Nm^3 , which generally increases with higher pyrolysis temperatures. This gas is mostly used to heat the pyrolysis reactor itself [34].

Pyrolysis oil contains organic acids, sugars, alcohols, ketones, aldehydes, furans, and hydrocarbons such as toluene and naphthalene. It can serve as an alternative liquid fuel with a calorific value ranging from 15 to 20 MJ/kg , often similar to that of the lignocellulosic feedstock used. Being liquid, it is easier to handle than solid fuels. Higher hydrogen and carbon content in the feedstock enhances the bio-oil's calorific value, acidity, and stability [34]. However, materials high in lignin yield lower oil quantities compared to cellulose-rich feedstocks. By separating the components of pyrolysis oil, pure chemicals can be produced.

Pyrolysis coke consists of fixed carbon, inorganic impurities, and condensed pyrolysis products within its porous structure. It has a calorific value of around 34 MJ/kg , comparable to black coal [35]. Due to its large surface area, pyrolysis coke can also be used as an adsorbent to remove dyes or heavy metals from water [36] or as a cost-effective catalyst for cracking tars during gasification [37].

The main advantage of pyrolysis is its ability to produce fuels with higher energy content than the raw material and to convert biomass into various chemicals. However, pyrolysis remains less explored compared to other technologies, and converting pyrolysis products into heat or electricity requires commercial combustion systems. Ongoing research and development in biomass pyrolysis and other renewable resources are critical for creating the ecological technologies of the future [38].

2. Materials and Methods

The organic carbon content in biochar ranges between 35% and 95% of the dry matter, depending on the biomass feedstock and pyrolysis temperature. For example, the carbon content of pyrolyzed straw is usually between 40% and 50%, while wood ranges between 70% and 90% [39].

The aim of the paper is the material (energy) recovery of fast-growing tree species. The research was conducted in collaboration with SUA in Nitra and the AgroBioTech Research Center.

For the material conversion of biomass, a low-temperature decomposition method of organic matter without the presence of oxygen was applied. This technology is primarily used to produce fuels for combustion engines, but also for the material (energy) recovery of biomass. A schematic of the equipment is shown in Figure 2.

The thermal treatment of organic matter in the reactor leads to the decomposition of the input material into three main output components, gas, liquid, and biochar, with the target product of the experiment being biochar and its subsequent use as biofuel. The device is shown in Figure 3.

During the experiment, the process parameters were also verified: process temperature, measured electronically ($^{\circ}\text{C}$), and gas flow rate (m^3/h).

The selected input materials were chips from the fast-growing willow varieties Express, Inger, and Sven. From each of the studied willow biomass samples, 250 to 300 kg were collected. The Swedish willow variety Inger is a hybrid of the Russian clone collected from the Novosibirsk region in 1992 and the Jorr variety. It grows better on dry soils, forms a denser stand with a large number of lateral shoots, and is resistant to leaf rust, rarely affected by insects, and less resistant to frost [40]. The Swedish willow variety Sven is a hybrid of the Swedish varieties Jorunn and Björn. It has fewer upright shoots, lance-shaped leaves, is almost entirely resistant to leaf rust, and is less resistant to pests attacking the shoot tips and frost [40]. The Hungarian willow variety Express was bred at the Szilvánus nursery

research station in Kapuvár, Hungary. The variety requires warm climatic conditions, has a long growing season, grows quickly, and provides a high yield [40].

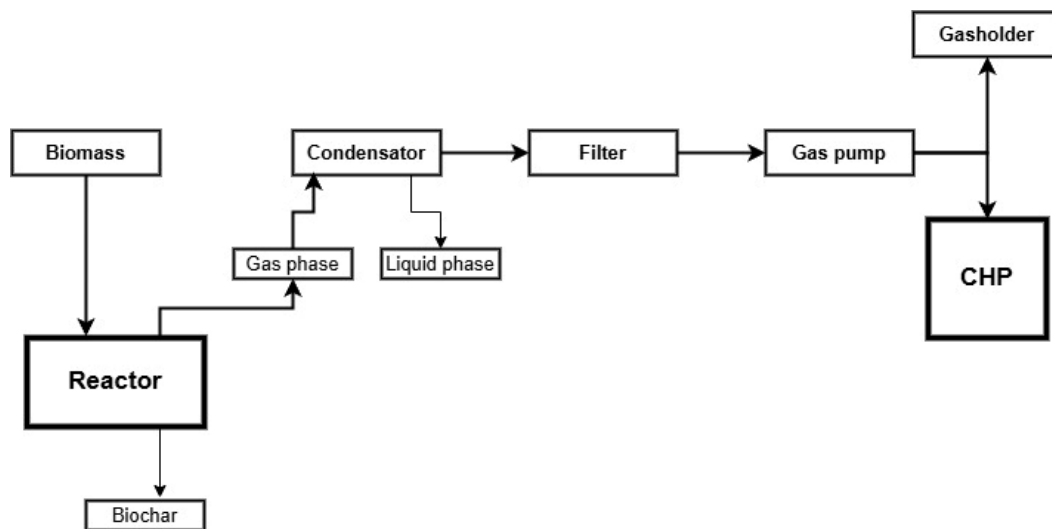


Figure 2. Technological diagram of the pyrolysis unit.



Figure 3. Assembly of the pyrolysis unit. 1—biomass conveyor, 2—reactor, 3—carbon conveyor, 4—condenser.

The biomass was then stored in a hall, where it was chipped to the required fraction of 10 to 15 mm to ensure smooth material movement in the reactor using screw conveyors. A critical parameter in biomass gasification is the dry matter content. Dry matter analysis was conducted using a Kern DBS moisture analyzer (KERN & SOHN GmbH, Balingen-Frommern, Germany). The organic dry matter content was determined according to STN EN 14775 [41].

Wood is the most well-known lignocellulosic material. Wood pyrolysis usually begins at 200–300 °C [42]. The experiments presented were conducted at a temperature of 520 °C. The biomass feeding rate into the reactor was set to 0.5 kg/90 s.

The thermogravimetric method was used to determine the moisture, volatile matter, and ash content in the examined solid biofuels. The laboratory equipment consists of a Nabertherm L9/11/SW/P330 (Nabertherm GmbH, Lilienthal, Germany) furnace and accessories, which include a laboratory-scale Kern EG 420-3NM (KERN & SOHN GmbH, Balingen-Frommern, Germany) and a control computer. The built-in P330 controller allows the programming of selected heating and retention profiles. Parameter settings can also be adjusted manually; however, we used the control computer. The furnace modification allows the measurement of the weight change of the examined sample during the experiment using a digital scale. The device is connected to a computer, where the set and measured data are used to plot the temperature and weight curves on the computer screen for the selected time intervals.

A picture of the device is shown in Figure 4. The main components are the furnace, corundum rod, and digital scale.

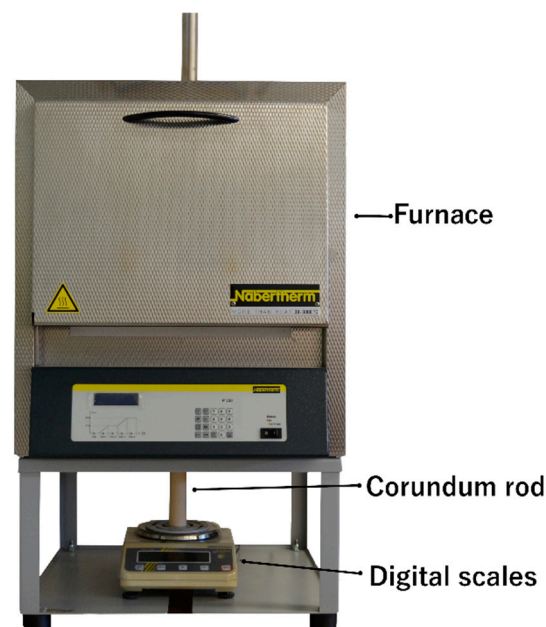


Figure 4. The apparatus used in thermogravimetric study.

The proportions of the individual components are determined according to the following relationships.

Moisture content w :

$$w = \frac{m_1 - m_2}{m_1} \quad (1)$$

Ash content in original sample A' :

$$A' = \frac{m_3}{m_1} \quad (2)$$

Ash content in dry matter p_{ps} :

$$p_{ps} = \frac{m_3}{m_2} \quad (3)$$

Combustible content in original sample h' :

$$h' = \frac{m_4}{m_1} \quad (4)$$

Combustible content in dry matter p_{hs} :

$$p_{hs} = \frac{m_4}{m_2} \quad (5)$$

where: m_1 —original weight of sample, g; m_2 —weight of dry matter, g; m_3 —weight of ash, g; m_4 —weight of combustible content, g.

The technical standard STN EN 15148 [43] is used for determining the volatile matter content in solid biofuels. For determining the ash content in the same materials, the standards STN EN 14775 [41] and STN ISO 1171 [44] are applicable. The experiments conducted were performed in accordance with these standards. At the end of the experiment, the sample was incinerated at a temperature of 815 °C for 60 min. The required temperatures, heating rate, and retention time were set in the respective program for device control. Table 2 presents the parameters during the thermogravimetric measurements.

Table 2. Parameters for gravimetric measurement procedure.

	Time Interval					
	1	2	3	4	5	6
Impact period, minute	60	120	60	60	60	60
Temperature, °C	20–105	105	105–500	500	500–815	815

Source: EN 14775:2010 [41], and ash content determination—STN ISO 1171:2003 [44].

At the beginning of the experiment, the sample under investigation is first heated to 105 °C \pm 2 °C for 60 min and then dried for another 120 min. The weight loss during this interval is used to calculate the moisture content. The weight loss in the fourth interval (500 °C) is considered the volatile combustible matter, while the remaining mass at the end of the experiment consists of ash.

3. Results and Discussion

The result of the experiment on the depolymerization of wood chips is the production of biochar. The wood chips, which were pre-processed into a fraction with a maximum size of 12 mm, were fed into the reactor at regular intervals. Both the wood chips and the produced biochar are shown in Figure 5.



Figure 5. Willow sample before and after processing.

After depolymerization, we obtained the results presented in Table 3. Given that our goal is biochar production, the highest amount of biochar was produced from the Swedish willow variety Sven. The yield and properties of biochar are significantly influenced by the pyrolysis method used and the temperature [45,46].

Table 3. Flow of gas and production of biochar.

Biomass	Express	Inger	Sven
Average gas flow [m ³ /h]	4.54	8.73	3.07
Production of biochar from 1 kg biomass	0.252	0.106	0.256

The elemental analysis of the biochar, presented in Table 4, revealed that the carbon content in the sample was nearly 80%. During each experiment, 20 kg of biomass was processed. After each experiment was completed, the produced biochar was weighed on a Kern platform scale with a resolution of $d = 20$ g. Subsequently, a sample of the dry biochar was taken for elemental analysis. According to [47], biochar produced from plant material contains 70% carbon, with the remainder consisting of nitrogen, oxygen, and hydrogen. Similar results for the analysis of biochar from woody materials are presented in a study by Bird (2017), where the carbon content in biochar from pine chips was 81%, from eucalyptus wood 74%, and from a mixture of softwood 83.7% (Bird 2017). Biochar from willow was also analyzed in a study by Mašek (2013), which found that increasing the pyrolysis temperature leads to higher carbon content, with a carbon content of 70.7% at a temperature of 350 °C. Rasa et al. (2018) pyrolyzed willow at a temperature of 320 °C, and the elemental analysis of the biochar demonstrated a carbon content of 74%. Our results show a carbon content in biochar of nearly 80%, which is likely due to the higher temperature used for biomass processing, as noted in Mašek's (2013) study [48–50].

Table 4. CHNS analysis of biochar from biomass.

Biomass	N %	C %	H %	S %
Sven	1.3	79.3	2.6	0.2
Express	1.0	78.0	2.7	0.2
Inger	1.0	78.3	2.7	0.3

A very important and controlled parameter during depolymerization is the process temperature. Biochar is produced by the pyrolysis of biomass, a process in which organic materials decompose at temperatures ranging from 350 °C to 1000 °C in a low-oxygen environment [25]. Figure 6 illustrates the temperature profiles during the process of each sample. At a set temperature of 520 °C during the thermochemical conversion of the Express willow, the process temperature fluctuated between 510 °C and 524 °C. During the depolymerization of the Inger willow, the temperature ranged between 515 °C and 529 °C, and for the Sven willow, it ranged between 513 °C and 528 °C. Yang (2024) discusses the impact of pyrolysis temperature on the physical and chemical properties of biochar, highlighting how lower temperatures can influence porosity and biochar stability [51].

The average gas flow rate produced from various types of willow is illustrated in Figure 7. The figures show the average gas flow rate during the steady-state process, where 0.5 kg of biomass is fed into the reactor at regular intervals (every 90 s). As indicated by the flow profiles, the lowest average gas flow rate was observed during the thermochemical conversion of the Sven willow variety, 3.07 m³/h. The average gas flow rate during the depolymerization of the Express willow variety was 4.54 m³/h, and the average gas flow rate during the breakdown of the Inger willow variety was 7.83 m³/h.

Figure 8 depicts the gas production process from 0.5 kg of input biomass at a processing temperature of 520 °C. As can be seen from the comparison of the gas flow profiles, there is a difference in gas production as well as in the gasification time for 0.5 kg of biomass. The shortest time, as well as the least gas production, was recorded for the Sven willow variety. The depolymerization time was 1.9 min, and the maximum gas flow rate was 1.84 m³/h. In the case of the Express willow variety, the decomposition time was 3.2 min, and the maximum gas flow rate was 2.7 m³/h. The Inger variety required the longest depolymerization time, with a gasification time of 3.8 min and a maximum gas flow rate of 7.5 m³/h.

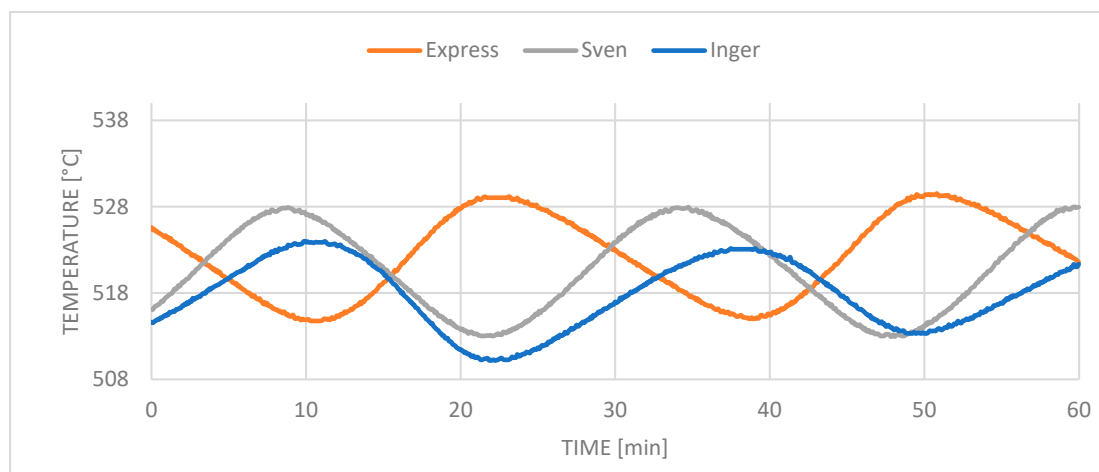


Figure 6. Process temperature profile of each sample.

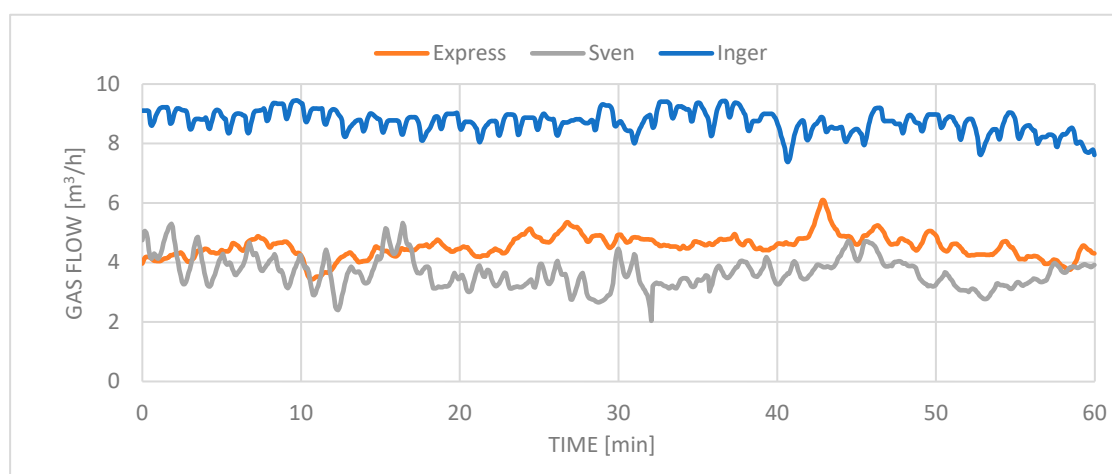


Figure 7. Flow rate of produced gas of each sample.

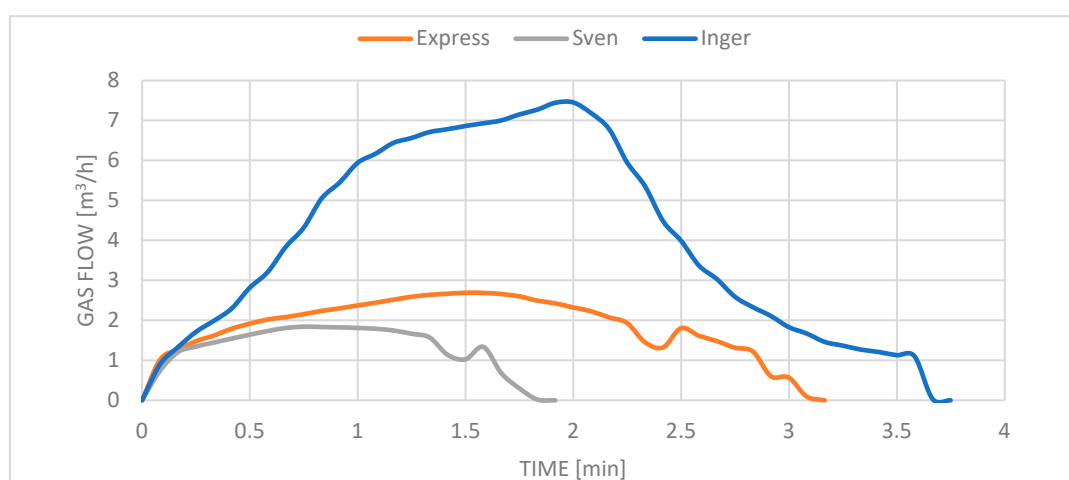


Figure 8. Gas production profile from 0.5 kg of each sample.

Thermogravimetric analysis using the device shown in Figure 4 and calculations according to Equations (1)–(5) yielded the data presented in Table 5. Each sample was examined multiple times, and the average values using descriptive statistics are reported.

Table 5. Moisture, ash, and volatile matter content in biofuels.

Biomass	Express	Inger	Sven
Moisture content wet basis, %	2.001	2.428	1.674
Ash content in dry matter, pps, %	7.210	6.008	7.279
Volatile matter content in dry matter, phs, %	92.790	93.992	92.721

Table 5 presents the average values of the relative moisture content in the original sample and the ash and volatile matter content of the studied dry samples.

The results indicate that the moisture content was very low. The samples were processed using thermochemical conversion and stored in sealed containers. The average dry matter content in the Inger willow sample was 91.83%, and the average organic dry matter content in the dried sample was 99.56%. The average dry matter content in the Sven willow sample was 91.27%, and the average organic dry matter content in the dried sample was 98.33%. The average dry matter content in the Express willow sample was 91.02%, and the average organic dry matter content in the dried sample was 98.43%. The ash content is higher compared to, for example, softwood pellets [8,52].

4. Conclusions

The use of bioenergy can significantly reduce our carbon footprint and thus contribute to improving the quality of the environment. Depending on the desired product at the output, the biomass depolymerization parameters are set. During thermochemical conversion, it is not possible to eliminate the production of coal or gas. In the mentioned experiments, we produced biochar and gas at a temperature of 520 °C in the quantities shown in the results. When evaluating the results, we found that about 25% of biochar was produced from 1 kg of input biomass from the willow of the Express and Sven varieties, and it was about 10% from the willow of the Inger variety. If the emphasis was placed on the production of biochar, the willow varieties Sven and Express are more suitable for this purpose than the Inger variety. If the goal were to produce gas, the willow of the Inger variety is more suitable than the Express and Sven varieties because the average flow of gas produced from the willow of the Inger variety was 8.73 m³/h, which is more than that of the Express variety (4.54 m³/h) and the variety Sven (3.07 m³/h). From the point of view of the speed of depolymerization, it is most advantageous to use willow biomass of the Sven variety, which had the shortest decomposition time, which affects the energy requirement of the thermochemical conversion. The disadvantage is that the average gas flow was the lowest among the studied varieties. Subsequently, the moisture, volatile matter, and ash content were determined through thermogravimetric analysis. We consider the ash content in the dry matter to be significant, with the lowest being in the Inger willow at 6%. The Express and Sven varieties (which are more suitable for biochar production) showed an ash content of 7.2%. The high ash content is primarily due to the pyrolysis process itself, where the proportion is even higher than what is reported by Lokwahrar (2024) [53]. These data affect the choice of combustion equipment and its operation.

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