

TECHNICAL UNIVERSITY IN ZVOLEN
Faculty of Wood Sciences and Technology



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**FIRE AND ENERGETIC PROPERTIES
OF SELECTED FAST-GROWING TREE SPECIES
AND ENERGY CROP SPECIES**



2019

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FOREWORD

This monograph deals with the issue of the use of renewable energy sources, namely biomass, to ensure the continuous supply of energy for the future. This issue is directly related to the need to ensure energy security of both the European Union and the Slovak Republic itself, because bioenergy is also becoming an ever more important option in climate change mitigation policies.

Theoretical knowledge about renewable energy sources (statistical indicators of renewable energy use and legislative background), biomass itself as an energy source, is complemented by an experimental part devoted to description of cultivation requirements and production properties of selected species of fast growing trees (*Paulownia tomentosa*, *Salix viminalis* clone TORA, *Populus x euroamericana* clone MAX 4) and energy crops (*Sida hermaphrodita*, *Arundo donax*, *Miscanthus x giganteus*) and particularly their fire and energy properties to assess their suitability for use as a renewable source for heat and electricity production.

In obtaining experimental results, progressive analytical methods were applied to determine important material and fire properties. The results were discussed with the support of knowledge from international cooperation and using the state-of-the-art knowledge in this field.

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1 INTRODUCTION

The use of renewable energy sources, of which biomass is a significant component, comes back to the very beginnings of human society development and is closely linked to the development of energetics. The rural landscape has provided renewable energy for a long period of development, without the need to import additional energy from other regions. A fundamental change occurred with the rapid development of the economy, mainly thanks to the use of accumulated energy of fossil fuels. The development of the economy subsequently turned the spiral of consumption–production–energy production. (BLUĐOVSKÝ 2005).

Biomass is and will be the cornerstone of renewable energy sources in the European Union's energy forecasts.

The growth in the production and use of biomass for energy purposes is leading to the development of international trade and this market will certainly expand in the future. It is expected that most of the increase in trade with biomass will be in the form of pellets and solid biomass, which generally consists of forest residues. As regards biomass produced in the European Union (EU), the current legal framework, in particular concerning agriculture and forestry, provides some guarantees for sustainable forestry and agriculture. Sustainability in biomass production concerns inter alia the protection of high biodiversity ecosystems and carbon stocks, e.g. in forests. (COM 2010)

Global developments are expected to support the transformation of the economy into a sustainable bio-economics based on the use of renewable raw materials. Although, bioeconomy is not going to be a new industry, rather will join the sectors of forestry, chemicals, energy, and construction and offer sophisticated technological solutions in manufacturing, medicine and industry. (HAJEK ET AL. 2018)

Biomass co-firing is becoming also a promising solution to reduce CO₂ emissions, due to its renewability and carbon neutrality (JUN ET AL. 2015). Therefore, proper knowledge of the energy properties of biomass (fuel) appears to be very important for the correct design of combustion and gasification equipment.

2 RENEWABLE ENERGY SOURCES

The use of renewable energy has many potential benefits, including a reduction in greenhouse gas emissions, the diversification of energy supplies and a reduced dependency on fossil fuel markets (oil and gas in particular). The growth of renewable energy sources may also have the potential to stimulate employment in the European Union (EU), through the creation of jobs in new green technologies.

In general, renewable energy sources include wind power, solar power (thermal, photovoltaic and concentrated), hydro power, tidal power, geothermal energy, ambient heat captured by heat pumps, biofuels and the renewable part of waste.

In this chapter, first, we introduce the information on renewable energy sources, their statistics, and legislation background. In more detail we further introduce the information on forest and agricultural biomass as a renewable energy source in the EU and in the Slovak Republic (SR).

2.1 Statistics focusing the renewable energy sources

In this chapter is introduced the overview of statistics on renewable energy sources in the EU. The source of the data presented here is EUROSTAT (2019).

The statistics presented in this chapter are based on data compiled in accordance with accounting rules set down in the Directive 2009/28/EC on the promotion of the use of energy from renewable sources and calculated on the basis of energy statistics covered by Regulation 1099/2008 on energy statistics, most recently amended in November 2017 by Commission Regulation 2017/2010. The most recent data available on the share of energy from renewable sources are for the reference year 2017.

The primary production of renewable energy within the EU-28 in 2017 was 226.5 million tonnes of oil equivalent (toe). The quantity of renewable energy produced within the EU-28 increased overall by 64.0 % between 2007 and 2017, equivalent to an average increase of 5.1 % per year. (EUROSTAT 2019)

Among renewable energies, the most important source in the EU-28 was wood and other solid biofuels, accounting for 42.0 % of primary renewables production in 2017 (Figure 1, Appendix 1).

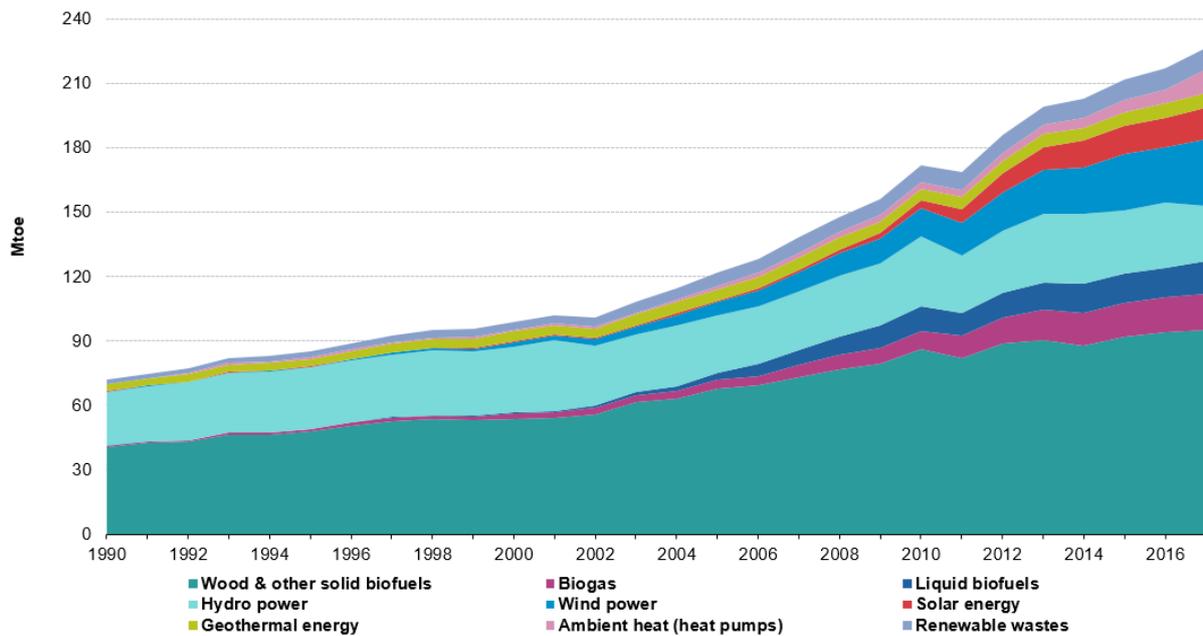


Figure 1 Primary production of energy from renewable sources in EU-28 in period 1990-2017
(Source: EUROSTAT 2019)

Wind power was, for the first time, the second most important contributor to the renewable energy mix (13.8 % of the total), followed by hydro power (11.4 %). Although their levels of production remained relatively low, there was a particularly rapid expansion in the output of biogas, liquid biofuels and solar energy, which accounted respectively for a 7.4 %, 6.7 % and 6.4 % share of the EU-28's renewable energy produced in 2017. Ambient heat (captured by heat pumps) and geothermal energy accounted for 5.0 % and 3.0 % of the total, respectively, while renewable wastes increased to reach 4.4 %. There are currently very low levels of tide, wave and ocean energy production, with these technologies principally found in France and the United Kingdom. (EUROSTAT 2019)

The EU seeks a 20 % share of its gross final energy consumption from renewable sources by 2020. This target is distributed between the EU Member States with national action plans designed to plot a pathway for the development of renewable energies in each of the Member States.

The share of renewable energy in gross final energy consumption is identified as a key indicator for measuring progress under the Europe 2020 strategy for smart, sustainable and inclusive growth. This indicator may be considered as an estimate for the purpose of monitoring Directive 2009/28/EC on the promotion of the use of energy from renewable sources - however, the statistical system in some countries for specific renewable energy technologies is not yet fully developed to meet the requirements of this Directive.

Gross final consumption of energy is defined in the Renewable Energy Directive 2009/28/EC as the energy commodities delivered for energy purposes to industry, transport, households, services (including public services), agriculture, forestry and fisheries, including the consumption of electricity and heat by the energy branch for electricity and heat production and including losses of electricity and heat in distribution and transmission. (EUROSTAT 2019)

Figure 2 shows the latest data available for the share of renewable energies in gross final energy consumption and the targets that have been set for 2020. The share of renewables in gross final energy consumption stood at 17.5 % in the EU-28 in 2017, compared with 8.5 % in 2004.

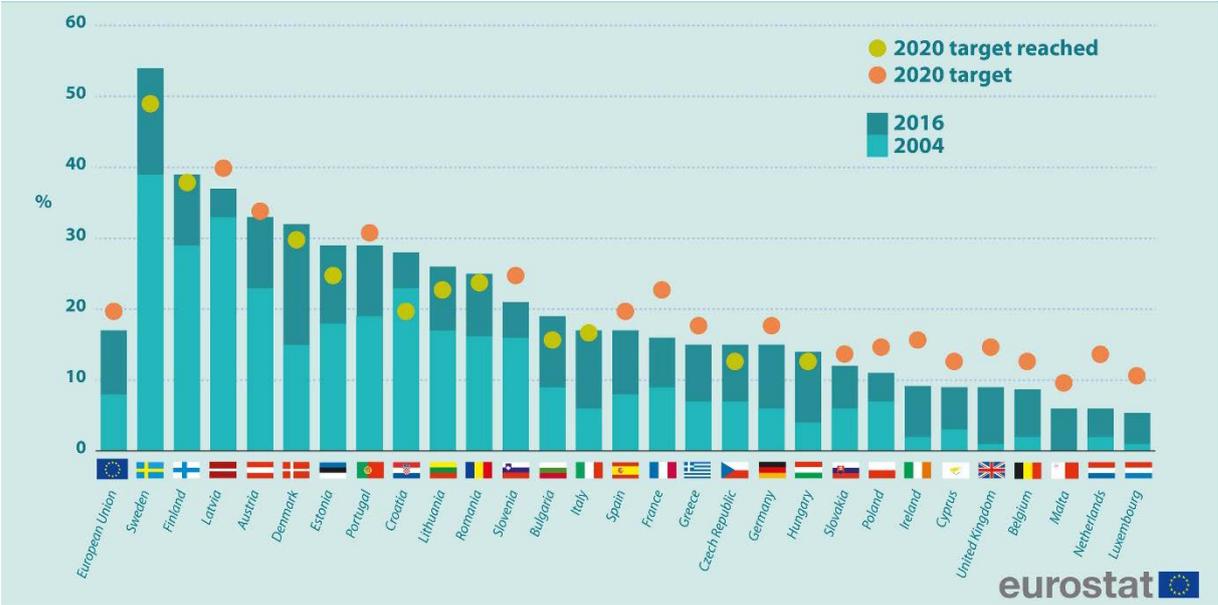


Figure 2 Share of energy from renewable sources in in EU-28 in % of gross final energy consumption in 2017 (Source: EUROSTAT 2019)

This positive development has been prompted by the legally binding targets for increasing the share of energy from renewable sources enacted by Directive 2009/28/EC on the promotion of the use of energy from renewable sources.

The share of energy from renewable sources is divided in three different components: share in electricity, share in heating and cooling and share in transport.

While the EU as a whole is on course to meet its 2020 targets, some Member States will need to make additional efforts to meet their obligations as regards the two main targets: the overall share of energy from renewable sources in the gross final energy consumption (Figure 2) and the specific share of energy from renewable sources in transport (see Figure 3). (EUROSTAT 2019)

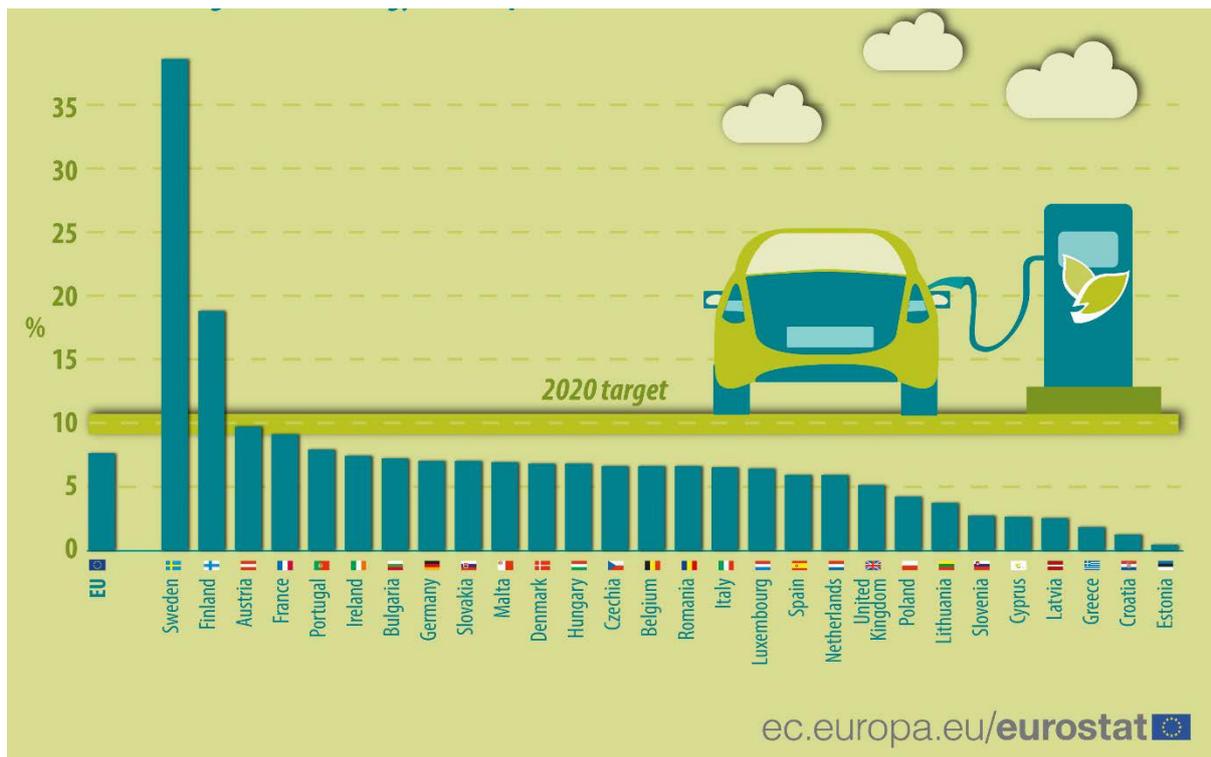


Figure 3 Share of energy from renewable sources in transport in 2017 (Source: EUROSTAT 2019)

In 2017, electricity generation from renewable sources contributed more than one quarter (30.7 %) to total EU-28 gross electricity consumption. Wind power was for the first time the most important source, followed closely by hydro power).

Renewable energy accounted for 19.5 % of total energy used for heating and cooling in 2017. This was a significant increase from 10.4 % in 2004. Increases in industrial sectors, services and households (building sector) contributed to this growth. The share of energy from renewable sources in heating and cooling is presented in Appendix 2. (EUROSTAT 2019)

But Slovak Republic is moving away from its target for the share of renewable energy sources. This is set at 14 % for 2020.

In 2017, however, Slovakia reached only 11.5 %, while the share decreased for the second consecutive year. In 2016, it was 12 %. In 2015, it was 12.9 %. Slovakia returned statistically before 2014, when the share was 11.7 %. (EUROSTAT 2019)

The share of energy from renewable sources in final energy consumption in the Slovak Republic (SR) in period 2004-2016 is shown in Figure 4.

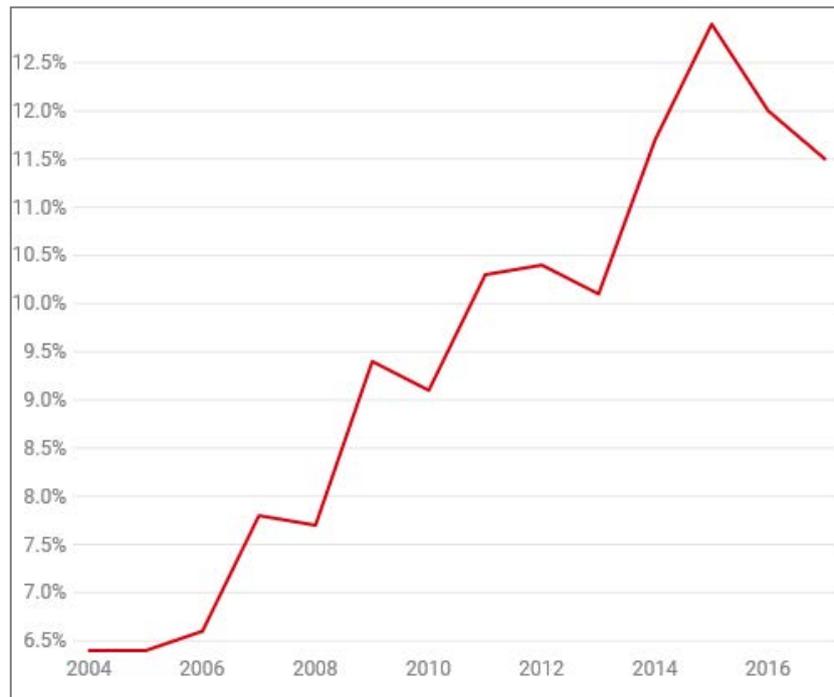


Figure 4 Share of energy from renewable sources in final energy consumption in SR in period 2004-2016
(Source: ENERGIEPORTÁL 2019)

The decrease in the share of renewable energy sources was caused by lower growth in the use of renewable energy sources compared to the growth in final energy consumption. The growth in electricity consumption and, in particular, the significant increase in the use of motor fuels, which caused a dynamic increase in energy consumption, reflects Slovak republic's economic growth. In the long term, the Slovak Republic's priority is energy efficiency, which leads to a reduction in energy consumption and thus to savings in fossil fuels and greenhouse gas emissions.

At the same time, in 2017, the highest increase in energy consumption in Slovakia was recorded by 7 % of all EU Member States. Slovak gross domestic product (GDP) increased this year by 3.2%. This means that the country is failing to separate energy consumption from economic growth and thus enhance energy efficiency.

Of all 28 EU Member States, in the share of renewable energy, the Slovak Republic ended in the ninth place backwards.

According to the latest statistics of EUROSTAT (2019), Slovak Republic is the country with the highest year-on-year increase in final energy consumption – by 7 %.

As energy consumption in the Slovak Republic is growing and renewable sources are not developing, their share inevitably decreases.

In the Slovak Republic, electricity from renewable sources is promoted through a fixed feed-in tariff. Energy companies are obliged to purchase and pay for electricity exported to the grid.

Renewable energy biomass must be given priority connection, and electricity from renewable sources must be given priority dispatch. The grid operator is obliged to extend the grid without discriminating against certain users.

Renewable energy sources are used in addition to electricity production also for heat production. URSO statistics (2019) show that in 2018 the most used fuel for heat production in Slovakia was natural gas. As can be seen from the data in Table 1, its use increased year-on-year most significantly from all fuels to around 8,640 GWh.

Table 1 Renewable energy sources are used in addition to electricity production also for heat production (Source: URSO 2019)

| Year | Natural gas (GWh) | Biomass (Kt) | Coal (Kt) | Biogas (GWh) | Fuel oil (Kt) |
|------|-------------------|--------------|-----------|--------------|---------------|
| 2016 | 8,514 | 1,113 | 571 | 275 | 96 |
| 2017 | 8,141 | 845 | 577 | 326 | 128 |
| 2018 | 8,637 | 877 | 586 | 326 | 128 |

The total volume of heat supply from RES in 2018 was less than 2,000 GWh according to data from the URSO Annual Report (2019). From the combined heat and power (CHP) came 6000 GWh. The distribution of heat supply volume is visualized in Figure 5.

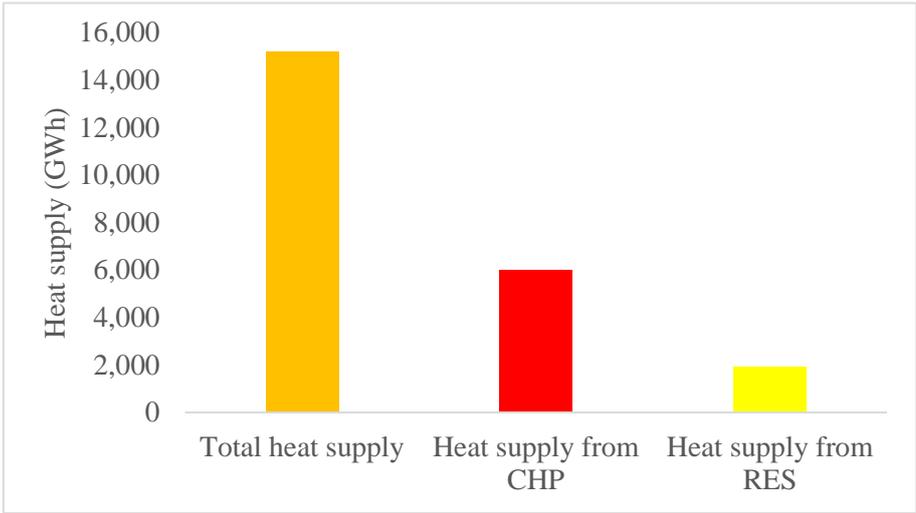


Figure 5 Heat supply in SR in 2018 (Source: URSO 2019)

The support of heat from renewable energy sources mainly takes the form of financial support for investments in the Slovak Republic.

At the end of this subchapter, we would like to point out another fact that is interesting for the present energy and economic community.

Nowadays, the energy and economic communities host strongly polarized views about whether the quantity of fossil fuel resources ultimately available to society is declining and, if so, the potential repercussions of this for societal well-being and economic growth. Much of the argument used by the energy community revolves around the concepts of “net energy” and “energy return on investment” (EROI). For example, while most energy scientists accept the economists' argument that there is a lot of oil left in the ground and that higher prices will encourage its extraction and production, they also point out that when more money is required more energy is required too, and that there is a limit to how much we can pay for oil that occurs as one of approaches using a barrel of oil to extract another barrel of oil. Such net energy analysis is sometimes called the assessment of energy surplus, energy balance, or the EROI.

Energy return on investment (EROI) is a mean of measuring the quality of various fuels by calculating the ratio between the energy delivered by a particular fuel to society and the energy invested in the capture and delivery of this energy. Much of the current EROI analysis literature tends to focus on the net or surplus for a given project, industry, nation, fuel, or resource, e.g. recent discussions on the “energy break even” point of EROI for corn based ethanol, i.e. whether the EROI is greater than 1:1. The apparently different results from this seemingly straight orward analysis generated some controversy about the utility of EROI. But, the variation in these findings is mostly the result of the choice of direct and indirect costs associated with energy production / extraction included within the EROI calculations: i.e. the boundaries of the denominator. (HALL ET AL 2011)

The EROI values for most important fuels, liquid and gaseous petroleum, tend to be relatively high. World oi land gas has a mean EROI of about 20:1 according to LAMBERT ET AL. (2012) and DALE (2010).

Coal internationally has a mean EROI of about 46:1. Analysis of EROI values for nuclear energy suggests a mean EROI of about 14:1. Hydroelectric power generation systems have the highest mean EROI value 84:1of electric power generation systems. (LAMBERT ET AL. 2012).

Wind power has a high EROI value, with the mean perhaps as high as 18:1 (KUBISZEWSKI ET AL 2010) or even 20:1(LAMBERT ET AL 2012). The mean EROI value for ethanol from various biomass sources suggests from 0.64:1 (PIMENTEL AND PATZEK 2005) for ethanol produced from cellulose from wood to EROI value of 48:1for ethanol from molasses in India (VON BLOTTNITZ AND CURRAN 2007). These values result in a mean EROI value of roughly 5:1.

It must be noted, however, that many of the EROI values are below a 5:1 ratio and diesel from biomass is also quite low (2:1). (LAMBERT ET AL. 2012)

Nearly all renewable energy systems appear to have relatively low EROI values when compared with conventional fossil fuels. A question remains as to the degree to which total energy costs can be reduced in the future, but as it stands most “renewable” energy systems appear to be still heavily supported by fossil fuels. Nevertheless they are considerably more efficient at turning fossil fuels into electricity than are thermal power plants, although it takes many years to get all the energy back. (HALL ET AL. 2014)

Further, we are focusing more the legislation governing the use of renewable energy sources.

2.2 Legislation regulating the renewable energy sources use

The European Commission has set out several energy strategies for a more secure, sustainable and low-carbon economy. Aside from combating climate change through a reduction in greenhouse gas emissions, the use of renewable energy sources is likely to result in more secure energy supplies, greater diversity in energy supply, less air pollution, as well as the possibility for job creation in environmental and renewable energy sectors.

The 2020 climate and energy package adopted in December 2008 provided a further stimulus for increasing the use of renewable energy sources to 20 % of total energy consumption by 2020, while calling for energy consumption and greenhouse gas emissions to both be cut by 20 %. Directive 2009/28/EC of the European Parliament and Council on the promotion of the use of energy from renewable sources set an overall goal across the EU for a 20 % share of energy consumption to be derived from renewable sources by 2020, while renewables should also account for a 10 % share of the fuel used in the transport sector by the same date. The Directive changes the legal framework for promoting renewable electricity, requires national action plans to show how renewable energies will be developed in each EU Member State, creates cooperation mechanisms, and establishes sustainability criteria for liquid biofuels (following concerns over their potential adverse effects on crop prices, food supply, forest protection, biodiversity, water and soil resources). A report on the sustainability of solid and gaseous biofuels used for electricity, heating and cooling (SWD 2014) was adopted in July 2014.

On 6 June 2012, the European Commission presented a Communication titled, “Renewable energy: a major player in the European energy market” (COM 2012), outlining options for a renewable energy policy for the period beyond 2020. The Communication also called for a more coordinated European approach in the establishment and reform

of support schemes and an increased use of renewable energy trading among EU Member States. In January 2014, the European Commission put forward a set of energy and climate goals for 2030 with the aim of encouraging private investment in infrastructure and low-carbon technologies. One of the key targets proposed is for the share of renewable energy to reach at least 27 % by 2030. These objectives are seen as a step towards meeting the greenhouse gas emissions targets for 2050 put forward in the Roadmap for moving to a competitive low-carbon economy in 2050 (COM 2011).

One of the 10 priorities of the European Commission (EC) put forward in 2014 was an energy union. It was intended that a European energy union will ensure secure, sustainable, competitive and affordable energy. In February 2015, the European Commission set out its plans for a framework strategy for a resilient energy union with a forward-looking climate change policy in a Communication (COM 2015). The Communication proposes five dimensions for the strategy, one of which is decarbonising the economy.

On 11 December 2018, the EU adopted Directive 2018/2001/EU on the promotion of the use of energy from renewable sources. The new regulatory framework includes a binding renewable energy target for the EU for 2030 of 32 % with an upwards revision clause by 2023. This will allow Europe to keep its leadership role in the fight against climate change, in the clean energy transition and in meeting the goals set by the Paris Agreement.

The legislative environment in the field of renewable energy sources (RES) in the Slovak Republic has recently undergone significant changes made by the establishment and adoption of new legislation or amendments to existing laws. The reasons why new laws are constantly being adopted or some parts of them are changing. First, it is the efforts of the EU Member States to meet common emission reduction targets. The binding targets adopted by the EU Member States can be achieved if, first, common legislation is represented by directives. Member States are obliged to implement the obligations arising from the common legislation (common directives) into their national legislation. Other reasons for changing some of the statutes of the RES legislation are due to the liberalization of the energy sector, the introduction of market mechanisms in the electricity sector, and the knowledge gained through the real operation of renewables. (OZE 2019)

In Slovakia, the primary legislation consists of Act of the National Council of the Slovak Republic No. 656/2004 Coll. Energy Act / Zákon NR SR č. 656/2004 Z. z. Zákon o energetike. This Act defines the basic processes related to electricity and RES. It defines the basic concepts, the performance of state administration. Conditions for issuing a license for electricity production from RES, conditions for the construction of energy facilities

(including facilities for electricity production when electricity is produced from RES), rights and obligations of a producer of electricity from RES, rights and obligations of the transmission and distribution system operator to which the producer of the electricity from RES is connected and through which the transmission or distribution of electricity produced from RES is carried out to the final consumption point. Under this Act, support for RES is achieved through the priority access, connection, transmission, distribution and supply of electricity produced from RES. However, the producer must respect the technical and commercial conditions of access and grid connection, which are specified in the tertiary legislation.

The secondary legislation consists of the Government Regulation No. 211/2010 / Nariadenie vlády Slovenskej republiky č. 211/2010, laying down the rules for the functioning of the electricity market and the Act no. 309/2009 Coll. on the Promotion of Renewable Energy Sources and High Efficiency Cogeneration and on Amendments to Certain Acts / Zákon č. 309/2009 Z. z. Zákon o podpore obnoviteľných zdrojov energie a vysoko účinnej kombinovanej výroby a o zmene a doplnení niektorých zákonov.

Government Regulation No. 211/2010 (Electricity Market Rules), by its very nature, supplements the “Energy Act” and specifies some of its provisions. These market rules lay down the conditions for connection, access, transmission and distribution of electricity. It defines when it is possible to connect the producer to the system, where it is possible to carry out the distribution of electricity produced also from RES, the necessary contractual relations necessary to connect the production equipment. The contractual relations named in the Market Rules are further specified in tertiary legislation. The electricity market rules further define and develop functional processes related to market participant deviation, registration of daily supply diagrams, etc.

The Act no. 309/2009 Coll. specifies: the method of support and conditions for the promotion of electricity production from renewable energy sources, electricity by high-efficiency cogeneration, biomethane; rights and obligations of producers of electricity from renewable energy sources, electricity from cogeneration, electricity from high-efficiency cogeneration, biomethane; the rights and obligations of other electricity and gas market participants; and, the rights and obligations of the legal person or the natural person who places on the market fuels and other energy products used for transport purposes.

The tertiary legislation includes in particular: Rules of Operation of the transmission System Operator; Operating Rules of the Distribution System Operator; Technical Conditions of the Transmission System Operator; Technical Conditions of the Distribution System Operator; URSO Decisions; URSO Decree no. 2/2008 and its amendments.

2.3 Biomass as a source of energy

Biomass is one of the key renewable sources of energy that is produced from organic matter. It includes wood, agricultural crops and waste, and other "living" material that can be used to produce heat and energy.

DZURENDA AND JANDAČKA (2010) define biomass as a matter of biological origin, which includes plant biomass grown in soil and water, animal biomass, production of animal origin and organic waste.

According to Directive 2001/77/EC definition, the biomass means a biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste.

According to LIESKOVSKÝ AND GEJDOŠ (2016), the biomass is generally understood as all living and organic matter in a given system that was originated and develops as a product of life processes (development, growth, reproduction) of living organisms. According to this definition, it provides a very wide range of its possible systematic sorting and distribution. In terms of its origin we can talk about plant biomass (phytomass), animal biomass (zoomass) and municipal and industrial waste.

Biomass in terms of origin can be divided into: plant (dendromase, phytomass); animal (zoomase); municipal and industrial waste of biological origin.

Dendromass is an organic matter of woody and shrubby plants consisting of wood, bark and green matter (DZURENDA AND JANDAČKA 2010).

Phytomass is a biomass of plant origin (HUTŇAN 2012).

According to the source of biomass production we divide it into: forest biomass (fuel wood, stumps, roots, branches, bark, sawdust); agricultural biomass (phytomass – cereal straw, cereals, hemp, etc.), zoomase – fats, excrements, etc.; municipal and industrial waste of biological origin.

From the point of view of energy use, biomass is divided into purpose-grown biomass for energy use and waste biomass.

Under the energy use purpose-grown woody biomass we mean fast-growing trees (poplar, willow, alder, acacia, birch).

Waste biomass includes wood and wood waste from forestry (fuel wood, bark, stumps, small wood, cones) and waste from the wood-processing industry, as well as vegetable waste from primary agricultural production and landscape maintenance (straw, remains after shrubbery

removal, hay, remains from vineyards and orchards), livestock wastes (livestock manure, feed remains), municipal organic waste (sewage sludge, organic fraction of municipal solid waste), organic waste from food production (meat-wastes, dairies, distilleries and canning wastes).

The most common industrial biomass can be grown from numerous types of plants, including *Miscanthus*, switchgrass, hemp, corn, poplar, willow, sorghum, bamboo, sugarcane, and a variety of tree species, ranging from eucalyptus to oil palm (palm oil). (JAWAID ET AL. 2017)

Regardless of source, biomass materials can be divided into two broad categories: woody and non-woody. Forests provide only woody materials; agriculture sources provide both woody and non-woody biomass for bioenergy production. (JAWAID ET AL. 2017)

Biomass is the plant material derived from the reaction between CO₂ in the air, water and sunlight, via photosynthesis, to produce carbohydrates that form the building blocks of biomass. Typically, photosynthesis converts less than 1 % of the available sunlight to stored, chemical energy. The solar energy driving photosynthesis is stored in the chemical bonds of the structural components of biomass. (MCKENDRY 2002).

In photosynthesis, the effective amount of solar energy is known and measurable. For the production of glucose (C₆H₁₂O₆), it is used to store 2.872 kJ of energy. Oxygen is produced as a by-product of this process. The combustion heat of glucose is of 2.817 kJ (0.78 kWh), provided that the combustion takes place in a closed system, that is, without deducting the condensation heat of the water. The accumulated energy in wood can therefore be reused to a high extent in combustion. (JONAS AND HANEDER 2001)

If biomass is processed efficiently, either chemically or biologically, by extracting the energy stored in the chemical bonds and the subsequent “energy” product combined with oxygen, the carbon is oxidised to produce CO₂ and water. The process is cyclical, as the CO₂ is then available to produce new biomass. The value of a particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. (MCKENDRY 2002)

Biomass formation is closely linked to the process of photosynthesis. Photosynthesis has become an essential prerequisite for the biological existence of carbon-based life.

Biomass, in the context of its energy recovery, can be used for direct combustion or other transformations with subsequent energy recovery.

Combustion in this term is a thermochemical method using so-called dry processes of biomass processing. These consist of the decomposition of organic material by the action of heat, while generating flammable gases, followed by subsequent oxidation and release

of energy. The resulting combustion product is heat, carbon dioxide, ash and water in the form of water vapour.

The choice of biomass (i.e. woody or herbaceous species) for energy production purposes depends upon the end-use, bio-conversion portion of interest, e.g. combustion, gasification, pyrolysis, fermentation or mechanical extraction of oils.

Some dendromass and phytomass species are amendable to nearly all the potential conversion technologies. Oil seed rape can be processed via combustion, gasification, pyrolysis or mechanical extraction. Wood and cereal crops are suitable for combustion, gasification, pyrolysis and fermentation.

The attention paid to woody and herbaceous species varies around the world, taking into account the soil and climatic factors that affect growth. In Europe, much attention has been focused on the C₃ woody species, especially those grown as short rotation coppice (willow, poplar and forestry residues). Of the herbaceous species, the perennial C₄ grass, *Miscanthus*, has created considerable interest. *Miscanthus* has been identified as the ideal fuel crop, providing an annual crop, being easy to grow and harvest and when harvested dry, gives a high dry-matter yield. (MCKENDRY 2002)

Looking back at the recent past, also in the Slovak Republic, biomass for energy purposes was not an interesting topic until 2000. Traditionally, it was previously considered as an additional source of energy to meet local heating needs, mostly in areas without fossil fuel infrastructure. Until 1999, there was no domestic demand for forest fuel chips and their annual production ranged from 2 – 3 thousand tons (i.e. 2 – 3 Kt). (ORAVEC 2010)

The pioneer in this area was Slovenské energetické strojárne (SES), a. s., Tlmače in Slovakia, which reconstructed the boiler room in 2001 and adapted the equipment for the combustion of chips. According to the TREND newspaper (published on 04.11.2003), at that time it was 20 thousand tons of wood chips per year, covering the heating needs of buildings and part of the Lipník housing estate in Tlmače. The use of wood chips in SES Tlmače was also solved to a large extent by the problem of the Levice Forest Enterprise (LZ), which were looking for sales opportunities for not very attractive tree species such as Turkey oak (*Quercus cerris*) and black locust (*Robinia pseudoacacia*) at that time.

Since that time, much has changed in the timber market. The amount of logging in the Slovak forests has been increasing in the past 15 years. Planned and actual logging is increasing in Slovakia, particularly due to an increase in the share of stands of higher (ruby) age. The unbalanced age structure in the forests of Slovakia causes cyclical changes

also in the development of logging possibilities. It is anticipated that they will decline already around 2030 but depending on the extent of incidental felling. (MP SR 2018)

In 2000, there was logged approximately 5.5 mil. m³, while it was more than 9.3 mil. m³ in 2017. The trend of decreasing quality timber on the market and an increase in the share, especially of the 5th grade timber assortments, is visible. To a large extent, wood degradation is also due to a high proportion of incidental felling, which regularly exceeds 50 % (57 % in 2015), with a significant proportion of felling being found in coniferous forests. (GEJDOŠ, LIESKOVSKÝ 2017)

According to the document "Utilization of wood for energy purposes / Využitie dreva na energetické účely", the total consumption of solid wood fuel biomass (fuel wood, chips, fine-grained and lump residues after processing and handling of wood, briquettes and pellets) amounted to 3.05 mil. tons (3.05 MMt) in 2017. The key consumers of wood fuels, which are the dominant renewable energy source in Slovakia, are the wood-processing and plant and paper industry, the population, central heating sources and the energy sector. The heat produced is mainly used for heating and industrial purposes. The proportion of wood fuels in the total consumption of primary energy sources in the Slovak Republic was of 1.9%. (MP SR 2018)

The heat producers associated in the Slovak Association of Heat Producers / Slovenský zväz výrobcov tepla (SZVT) heat 38 places together, for which approximately 257,000 tons of timber are used annually (i.e. 2.14 % of harvested wood). If the heat producers only used branches and wood waste for heating, it would still not be even 10% of the total harvested wood plant.

Another nine electricity producers from biomass, who are not associated with the SZVT, utilize approximately 530,000 tons (530 Kt) of wood annually – approximately 4.17 % of total timber harvesting. Indication of how much wood is used for individual heating of households is not available. (ORAVEC 2018)

Further we introduced basic facts about forest and agricultural biomass to be used for production of heat and energy.

2.3.1 Forest biomass as a source of energy

Biomass, i.e. dendromass, principal producer for energy needs is forestry.

Figure 6 illustrates a typical example of forest biomass to be processed and further used for energy purposes.



Figure 6 Typical example of forest biomass as a source of energy (Source: FORESTPORTAL 2015)

The decisive legal document for forest management in the Slovak Republic is the Act No. 326/2005 Coll. on forests, as amended / Zákon č. 326/2005 Z. z. Zákon o lesoch. The Act defines the areas of forest land and forest protection, professional and differentiated forest management, forest use and the requirement of sustainable forest management. The current forestry and agriculture legislation also address land use issues related to the sustainability of forest biomass (also dendromass) production and has a direct impact on its energy use. (KPMG 2016)

Table 2 presents data representing the development in the dendromass stock specified for energy use.

Table 2 Development of the dendromass stock for energy use (Source: NLC 1991 – 2018)

| Year | Forest chips ¹⁾ | | Wood fuel and other ²⁾ | | Total | |
|------|----------------------------|-------|-----------------------------------|-------|-------|--------|
| | (Kt) | (TJ) | (Kt) | (TJ) | (Kt) | TJ |
| 2017 | 580 | 5,510 | 845 | 8,028 | 1,425 | 13,538 |
| 2016 | 610 | 5,795 | 830 | 7,885 | 1,440 | 13,680 |
| 2015 | 615 | 5,843 | 835 | 7,933 | 1,450 | 13,775 |
| 2013 | 620 | 5,890 | 820 | 7,790 | 1,440 | 13,680 |
| 2010 | 250 | 2,375 | 695 | 6,602 | 945 | 8,977 |
| 2005 | 120 | 1,140 | 640 | 6,080 | 760 | 7,220 |
| 2000 | 5 | 48 | 471 | 4,475 | 476 | 4,522 |
| 1990 | 2 | 19 | 368 | 3,496 | 370 | 3,515 |

¹⁾ Wood chips and wood for the production of wood chips;

²⁾ Fuel wood and wood used for energy from waste, harvest residues and dead trees.

The expected significant increase in the proportion of renewable energy sources and the use of underproductive agricultural land for the cultivation of energy stands creates a significant increase in the potential of energy-efficient biomass in Slovakia. At the same time, it will be possible to support the further development of the fuel dendromass market. The amendment to the Act on forests introduced concepts such as energy stands and forest

plantations. Energy stands are purpose-built forests with the aim of maximizing biomass production in the first 15 years, while also fulfilling other forest functions, especially soil conservation, erosion control and partly landscape creation. Biomass produced in this way should be used mainly for energy production.

A definition of forest plantation has been added to § 2 “Definition of basic terms / Vymedzenie základných pojmov”. A forest plantation shall mean a forest stand with maximum production of timber for industrial use, consisting of one or two tree species with regular spacing and the same age, usually at sites with high production potential. (EXPLANATORY STATEMENT / DÔVODOVÁ SPRÁVA 2007)

In energy stands and forest plantations it is not possible to effectively use the management methods as in conventional forests. For example, it is unreasonable to require the provision of conventional management operations in such forest stand. For that reason, the application of the conventional stand management obligation is excluded in these cases. At the user's request, the stands can be reclassified to energy stands during the recovery of the Forest Management Program (PSL). In 2006, almost 550 ha of forest were reclassified this way in the OZ Levice (management unit of Forests Slovakia, S.E.). These were mostly the coppices of black locust (96.1%) and Turkey oak (1.2%). These coppices are restored by the clear cutting connected with the maximum utilization of the stump and root sprouting of the above-mentioned tree species (MESSINGEROVÁ ET AL. 2016).

Current resources of wood on non-forest ground are mainly the tree stands on long-term unused agricultural land (so-called “white areas”), streamside stands and trees in the open country, including linear planting vegetation, e.g. windbreaks, trees around roads.

Legislative conditions for planting fast-growing trees on agricultural land are determined directly by the zákon č. 220/2004 Z. z. Zákon o ochrane a využívaní poľnohospodárskej pôdy a o zmene zákona č. 245/2003 Z. z. o integrovanej prevencii a kontrole znečisťovania životného prostredia a o zmene a doplnení niektorých zákonov / Act no. 220/2004 Coll. on the protection and use of agricultural land and on the amendment of Act no. 245/2003 Coll. on integrated pollution prevention and control and on amendments and supplements to certain acts. For the purposes of this Act, fast-growing trees on agricultural land shall mean the plantation of fast-growing trees to produce wood biomass, on an area with extent more than 1,000 m², for a maximum of 20 years.

The planting of fast-growing trees may be established on agricultural land classified according to the code of a certified soil-ecological unit in the 5th to 9th quality group or on agricultural land contaminated by dangerous substances, about assignment

of which the agricultural soil protection authority decided according to § 8 par. 5 or on agricultural land classified according to the code of a creditable soil-ecological unit in the 3rd or 4th quality group, if the agricultural land is located in a floodplain, is wet or exposed to wind erosion. The plantation of fast-growing trees cannot be established on areas situated in the 3rd to 5th degree of nature and landscape territorial preservation.

The tree stands on “white areas” formed mainly by succession of trees are located on an area of ca. 275,000 ha with a total wood supply of 36.6 MMm³ (timber stock without bark). The current stock of coniferous trees is of 12.7 MMm³, hard deciduous trees of 9.1 MMm³ and soft deciduous trees of 14.8 MMm³. The assortment structure of stands on “white areas” is represented by a higher proportion of fibre wood and wood for energy use compared to stands on forest land. Due to their localization, stands on “white areas” are easily accessible and terrain conditions enable the use of efficient timber logging technologies. (ORAVEC, BARTKO, SLAMKA 2012)

Another possibility of increasing biomass production is plantation of fast-growing trees. The establishment of fast-growing trees plantations supports other unique and important environmental and ecological benefits that can provide enough raw material for the energy industry. At the same time, if certain decisions are taken into account in addition to production when planning a fast-growing trees plantation, they finally can have a positive impact on the landscape, biodiversity, soil, and water cycle in the ecosystem. The use of this method of targeted energy biomass extraction is a combination of forestry and agriculture and brings new opportunities supporting regional energy self-sufficiency.

With the increasing demands for biomass for energy purposes, the issues of production and targeted cultivation of fast-growing tree plantation (known also as short rotation coppice – SRC) are becoming topical. In the future, demand for wood as a raw material for heating and electricity production is expected to increase. This increase will mainly be influenced by the situation on the fuel market and will be supported as a target of national and European energy policy. Energy chips from fast-growing tree species can thus make a significant contribution to the European targets related to increasing the proportion of renewable energy sources. (MESSINGEROVÁ ET AL. 2016).

An important factor that can influence the future plantation of the fast-growing trees is sufficient potential area for their establishment. The potential of plantation establishment is both on the forest and in the agricultural ground fund.

In 2017, the area of utilized agricultural land was of 1,910,654 ha. Slovak Republic accounts for 38.8% of agricultural land in the total land area (MP SR 2018). In addition,

the distribution of agricultural land in the Slovak Republic is also characterized by a high proportion of agricultural land in mountain and foothill areas with rugged terrain and unfavourable climatic conditions.

Under such conditions, intensive agricultural production is not efficient today. However, it creates the preconditions for the possibility of diversification of production, one alternative of which is the production of biomass for energy purposes.

In the medium term horizon, it is possible to consider with planting of energy stands on area of 30,000 ha (according to the balance of suitable areas and trees by afforestation of areas after their felling, i.e. 24,000 ha and 6,000 ha of aspen forest), of which energy chips accounted for 70% and fibre wood for 30% of production at the 15-year-long rotation period. (MP SR 2018)

The most frequently planted tree species on plantations are various clones and varieties of poplar (*Populus sp.*) and willow (*Salix sp.*). Current legislation does not directly limit plantation owners and users to the use of a clone or varieties, but the cultivation of non-origin tree species is in violation of the Act no. 543/2002 Coll. on nature and landscape protection / Zákon č. 543/2002 Z. z. Zákon o ochrane prírody a krajiny. Appropriate selection considering habitat conditions is a prerequisite for meeting production expectations. In establishing fast-growing tree plantations is the site selection no less important factor. The site is characterized mainly by climatic region, altitude, ground water level, soil depth and its skeletons. In the case of forest soils, data from forest management programmes can be used as a basis for site selection, supplemented, if necessary, with data on soil properties and current nutrient reserves. On agricultural land, it is advisable to analyse the mechanical and chemical properties of the soil and compare the data with the information published on the portal “podnemapy.sk”.

The willows and poplars have relatively low soil quality demands but require sufficient water supply. Either it is in the form of rainfall, where the annual rainfall total is over 500 mm and over 300 mm during the vegetation season. Rainfall deficit on the site can be compensated by high groundwater level. Fast-growing trees have a distinct root system and can reach groundwater to a depth of 4 m. Growth is also dependent on the supply of mineral nutrients, therefore additional nitrogen fertilization is recommended to support growth. Optimum yields are achieved on weakly acidic to neutral soils. The pH should therefore not be less than 5.5.

The re-cultivation of the terrain and removal of the original vegetation is one of the most demanding activities in the initial phase of fast-growing trees plantation. In particular, ground belonging to the Forest Ground Fund is often occupied with shrubs and pioneer trees that need

to be removed. One way to deal with an undesirable crop quickly and efficiently is to remove them mechanically using various tractor adapters such as soil cutters and crushers.

On weeded areas, it is necessary to assign the application of mechanical weeding or chemical agents. Neglecting this stage of soil preparation, prior to plantation, results in increased weed protection costs in the first years since plantation establishment and often also causes a significant reduction in the number of planted plants root taking.

Planting density for a 2 – 3-year harvesting cycle varies depending on tree species and variety. In principle, these are very dense stands, with 5,000 to 16,000 plants per 1 ha usually. With the number of plants, the spacing between rows changes. The advantage of this method of planting is the possibility of fully mechanized harvesting. The disadvantage can be the restrictions on the choice of location, as the area may have a maximum slope of 15% and for economic reasons its extent should not be less than 2 ha. Multi-annual harvesting cycles, which are usually harvested every 4 to 5 years, have a planting density of between 1,000 and 5,000 plants per ha. This method is suitable for smaller plantations or areas on steep slopes. Subsequent harvesting is carried out by hand-held chain saw or other commercially available forestry logging machines. In contrast to the very short rotation, there is the possibility of temporarily storing trees at the edge of the plantation, resulting in reduced moisture and improved energy parameters of the biomass produced. The line spacing should be from 2.8 to 3 m. This width allows a smooth passage of machines assisting in plantation cultivation and harvesting (JAUSCHNEGG, METSCHINA, LOIBNEGGER 2009).

Selection of varieties, the clones respectively, depends on the specific needs of the plantation owners, users and the climatic conditions of the site. It also depends on the availability of plants. Their producers need at least one year to be able to provide enough cuttings of the desired variety. Once it is known what variety is required, they can shorten the rods on the fast-growing trees plantation and get one-year shoots to produce plants in the coming winter. There are currently around 25 certified varieties available in the EU, of which about 10 are now commercially available. Approximately one or two new varieties are bred annually. Information on the specific characteristics and suitability of willow or poplar clones should be provided by producers (DIMITRIOU, RUTZ 2015).

In general, the biomass yields per 1 ha of plantation are higher in poplar populations than in willows. It should also be noticed that, as a rule, yields for the first harvest do not reach the maximum production capacity of cultivated trees, but then production grows up to 15 years. From this time on, a gradual decline in biomass production can be expected, and after

20 – 25 years the plantation needs to be re-cultivated, supplemented with missing nutrients and new plantings are implemented.

The production of dendromass and dry matter per 1 ha of plantation are the most important indicators in the cultivation of stands for energy use.

For example, POLLÁK ET AL. (2018) reported that, in the case of willow, the highest and most balanced dendromass production in the three crop cycles was achieved by SHERWOOD variety. The total production in 9 years was of 325.1 t with an average production of 108.37 t over a three-year cycle. SHERWOOD, GUDRUN, TORA varieties achieved dendromass production over 300 t in 9 years, with an average of over 100 t in 3-year cycle.

The SHERWOOD variety reached the highest annual increase of 50.2 t of dry matter in 9-year cycle, with an average annual increase of 16.73 t in 3-year cycle. Overall, the lowest average dendromass production ($77.03 \text{ t}\cdot\text{ha}^{-1}$) as well as the lowest average dry matter increment ($11.83 \text{ t}\cdot\text{ha}^{-1}$) was achieved by the ULV variety from stands established in 1994. 1 Several authors mention the average annual increase in dry matter of 12 t as the limit of profitability of willow plantation. The results of the study show that out of the five varieties studied, three varieties - SHERWOOD, GUDRUN and TORA are the production bases as a suitable source for commercial dendromass plantation.

In the Slovak Republic, as in many European countries, there has been an increased interest in the cultivation of fast-growing clones of *Paulownia* in recent years. This interest is largely based on the information on the production potential of the *Paulownia* hybrid clones, which are promoted by many domestic and foreign sites of seedlings of these clones. According to this information, the volume and value production of plantations of the *Paulownia* clones is incomparably higher than the production of any native woody plants, respectively clones of cultivated poplar and willow trees. (JANKOVIČ ET AL. 2016)

As stated MUTŇANOVÁ (2015), the cultivation of *Paulownia* clones brings along with the benefits also risks, its uncontrollable spread to the landscape, as the *Paulownia* plants have a high ability to regenerate with sprout shoots. In case of commercially marketed clones, there are declared that they have non-germinal seeds, so there is no risk of spreading, as is known e.g. for the *Paulownia tomentosa* species. This is already considered invasive in some European countries and several such sites of its spontaneous spread have also been reported in southern and western Slovakia. Since all *Paulownia* clones bloom and can produce fruits and seeds, pollination from *Paulownia*

toментosa cannot be excluded and, in such a case, the risk that a certain percentage of seeds could be germinating, which could increase their spread potential. (JANKOVIČ ET AL. 2016)

2.3.2 Agricultural biomass as a source of energy

Agricultural biomass, i.e. phytomass, is a subset of biomass produced directly from agricultural activities, including cereal grains, sugar crops, oilseeds, other arable crops and crop by-products such as straw, vegetative grasses, farm forestry, and livestock by-products, e.g. manure and animal fats.

An example of agricultural biomass is introduced in Figure 7.



Figure 7 Example of agricultural biomass (Source: Sustainable Agriculture 2016)

Agriculture is the source of non-woody materials used to make bioenergy, such as cellulosic materials like plant leaves, stems, and stalks; sugar; starch (i.e. grains); and oil-producing plant materials (e.g., soybeans). Agriculture-based biomass materials come from annual commodity crops like corn and soybeans, residues collected after harvest of annual crops grown for food or feed, and perennial crops such as grass and tree crops.

Of all the types of unprocessed biomass, straw and energy crop biomass are most suitable for utilization in large commercial heat and power generation plants. The amount of straw that may be collected for the needs of electrical power generation. Of all cereal and other plant species, the power industry primarily uses straw. Rye, wheat, rape, buckwheat, fava bean, sunflower straw and corncobs are particularly valuable.

Agriculture has the potential to help meet the growing energy and raw material needs of society in a sustainable manner as a part of the vision towards a biobased economy, resulting in lowering greenhouse gas (GHG) emissions, and bringing benefits to soil, water quality and biodiversity.

Agricultural biomass can only be considered sustainable if it is economically efficient and profitable, socially viable, provides a net benefit to improving environmental performance

and rural development. In the same time time, in wider context of trade liberalisation and sustainable development, it must also be compatible with policy goals for agriculture, environment, energy.

According to the previously published data by JOINT RESEARCH CENTRE (2018), the total average agricultural biomass produced in the EU-28 for the period 2006 – 2015 is estimated at 956 million tons of dry matter per year (MMt·a⁻¹). The amount of 514 MMt (54%) are primary products (biomass produced as grains, fruits, roots, tubers etc.), which economic value is the principle motivation for their cultivation (economic production). The other 442 MMt of biomass (46%) are secondary products such as dry biomass from leaves and stems (residue production); these can also generate farm income, for instance when used for animal bedding or for bioenergy production.

The production of agricultural biomass in the EU has increased slightly during the period 1998 – 2015. This is the result of a progressive increase in the yields of the main cereals (e.g. maize) due to improvements in agro-management, and a general expansion of the area used for oilseed cultivation. The inter-annual variability of total biomass production is largely determined by weather conditions. Adverse weather extremes affected cereal growth in the main producing countries in the year 2003, which saw an extremely cold winter and a long heatwave during the summer, and in 2007, when Eastern Europe experienced a severe drought. These conditions resulted in relatively low total biomass production for those years. Conversely, 2004 and 2014 were the years with the highest levels of agricultural biomass production, as favourable weather conditions prevailed during the growing season in most Member States. (JOINT RESEARCH CENTRE 2018)

Cereals (258 MMt·a⁻¹ or 50 %) and plants harvested green (156 MMt·a⁻¹ or 30 %) dominate economic production, jointly accounting for about 80 % of total biomass production, followed by sugar and starchy crops (40 MMt·a⁻¹), and oilseed crops (27 MMt·a⁻¹). Dedicated energy crops (crops grown exclusively for energy production, not included in any of the other crop groups) represent less than 0.1 % of total biomass production. With a share of 74 % (329 MMt·a⁻¹), cereals also dominate residue production. Oilseed crops contribute 17 % (73 MMt·a⁻¹).

In both of these crop groups, the biomass of residues is higher than economic production. About 75 % of both the economic products and their residues (384 MMt·a⁻¹ and 323 MMt·a⁻¹ respectively) is produced in seven Member States: France, Germany, Poland, Italy, Spain, the UK and Romania. (JOINT RESEARCH CENTRE 2018)

Energy crops are a versatile fuel source that when utilized in substitution of fossil fuels can reduce the GHG impact of energy generation. Most energy crops grown specifically for the bioenergy sector are produced using conventional farming techniques. The crops may be dried, chopped, chipped, pelletized, or baled to produce fuels that can be directly combusted within small-scale stove or boiler systems, within dedicated biomass energy plants, or even cofired with coal within conventional power plants.

Energy crops are specifically grown for use as a fuel and are therefore designed to maximize energy yields per hectare at the lowest cost possible. (NUAMAH ET AL. 2012)

Into this category, we assign herbaceous energy crop, i.e. grass species such as *Miscanthus x giganteus*, *Sida hermaphrodita* or *Arundo donax*.

Herbaceous energy crops, also referred to as grassy or forage energy crops, are high-yielding lignocellulosic crops that remain in cultivation for several seasons and are harvested, on average once a year, after taking two to three years to reach full productivity. Energy crops within this definition are perennial in nature, so that they can be cut and harvested for biomass over successive years without re-cultivation or sowing, and the whole crop can be harvested and used for energy production.

According to FERNANDO ET AL. (2017) and ADAMS, LINDEGAARD (2016) IN BALAMAN (2019), they have several advantages over other types of energy crops, such as, they have efficient solar energy conversion resulting in high yields, need low agrochemical inputs, have a low nutrient and water requirement due to their extensive rooting system, which holds onto fertilizers and water, have low moisture levels at harvest, and plants with perennial growth habits also have the benefits of low establishment costs and fewer annual operations.

These include grasses such as switchgrass, *Miscanthus*, bamboo, sweet sorghum, wheatgrass, tall fescue, kochia, etc.

Among them, switchgrass and *Miscanthus* are the most commonly used biomass resources because they are adaptable to many climatic zones, require relatively low water and nutrients, are adaptable to low-quality land, and have a minimum of 10 years productive life (10 years for *Miscanthus*, 10 – 20 years for switchgrass). (ALLEN ET AL. 2014 IN BALAMAN 2019)

Also, they have positive environmental impacts because of their deep roots and ground cover, so that the cultivation of them in marginal soils has the potential to restore soil properties (fertility, structure, organic matter) and reduce erosion (STEWART ET AL. 2015 IN BALAMAN 2019).

3 FIRE AND ENERGY PROPERTIES OF BIOMASS

It is the inherent properties of the biomass source that determines both the choice of conversion process and any subsequent processing difficulties that may arise. However, the choice of biomass source is also influenced by the form in which the energy is required and it is the interplay between these two aspects that enables flexibility to be introduced into the use of biomass as an energy source.

This chapter of the monography is focused on introduction of essential physical, chemical, fire and thermal, i.e. also energetic properties of woody and herbaceous biomass to be used as a source of energy. This is further supplemented with introduction of selected standardized and non-standardized, i.e. progressive analytical methods to investigate the essential physical, chemical, fire and thermal properties of biomass and to derive other properties to describe the process of biomass combustion and its energetic potential more accurately.

3.1 Biomass physical, chemical, fire and thermal properties

Dependent on the energy conversion process selected, particular material properties become important during subsequent processing. The main material properties of interest, during subsequent processing as an energy source, are related to: moisture content (intrinsic and extrinsic), calorific (heating) value, proportions of fixed carbon and volatiles, ash/residue content, alkali metal content, cellulose / lignin ratio. For dry biomass conversion processes, the first five properties are of interest, while for wet biomass conversion processes, the first and last properties are of prime concern. (MCKENDRY 2002)

Among physical properties of biomass influencing the fire and energy properties of biomass to be used for energy purposes we assigned: moisture content.

Reduction in the moisture content of biomass material may be required to achieve several purposes in energy applications. The moisture content also has an impact on transport and storage of biomass material. There is also a direct, and strong relationship between how dry biomass fuel is and its energy content, or calorific value. (FOREST RESEARCH 2019)

In combustion systems any water content in the fuel must be driven off before the first stage of combustion can occur, requiring energy, and thus reducing overall system efficiency and potentially reducing combustion temperature below the optimum. Reduction in combustion temperature below the optimum may result in incomplete combustion of the fuel giving rise to the emission of tars and creosote which may condense in the flue, especially if it is long or includes changes of direction, and particulates. The water may also re-condense in the flue,

and all these may lead to corrosion of the flue and the gradual accretion of material leading to the potential for eventual blockages or fire. (FOREST RESEARCH 2019)

High moisture content of biomass has a much lower net energy density by mass, owing to the weight of the water, but also by volume owing to the energy required to evaporate the water. This means that transport is less efficient as a significant proportion of the load is water.

Storage is also less efficient, with less net energy available, but also storage of high moisture content biomass brings other problems with greater risk of composting, causing loss of biomass and potentially a fire risk from elevated temperatures and mould formation. Good ventilation and air flow help to minimise these problems. (FOREST RESEARCH 2019)

Two forms of moisture content are of interest in biomass: intrinsic and extrinsic moisture. Intrinsic moisture is the moisture content of the material without the influence of weather effects. Extrinsic moisture is characterized by the influence of prevailing weather conditions during harvesting on the overall biomass moisture content. In practical terms, it is the extrinsic moisture content that is of concern, as the intrinsic moisture content is usually only achieved, or applicable, under laboratory conditions. (MCKENDRY 2002)

Important in respect of the prevailing weather conditions at the time of harvesting, is the potential contamination of the harvested biomass by soil and other detritus, which can in turn have a significant deleterious impact on other “material“ properties during subsequent treatment or processing. The parameters of interest that are affected by such contamination are the ash and alkali metal content of the material. (MCKENDRY 2002)

Other factors aside, such as conversion to alcohol or gas / oil, the relationship between biomass moisture content and appropriate bio-conversion technology is essentially straight forward, in that thermal conversion requires low moisture content feed stock (typically < 50 %), while bio-conversion can utilise high moisture content feedstock. Thermal conversion technologies can also use feedstock with high moisture content but the overall energy balance for the conversion process is adversely impacted. On this basis, woody and low moisture content herbaceous species are the most efficient biomass sources for thermal conversion to liquid fuels, such as methanol. For the production of ethanol by biochemical (fermentation) conversion, high moisture herbaceous species, such as sugar cane, are more suited. Such species can also be fermented via another biochemical process, anaerobic digestion, to produce methane. (MCKENDRY 2002)

The calorific value (CV) of a biomass is an expression of the energy content, or heat value, released when burnt in air. The calorific value is usually measured in terms of the energy content per unit mass, or volume; hence $\text{MJ}\cdot\text{kg}^{-1}$ for solids, $\text{MJ}\cdot\text{l}^{-1}$ for liquids, or $\text{MJ}\cdot\text{N}^{-1}\cdot\text{m}^{-3}$ for gases.

The calorific value of a fuel can be expressed in two forms: the gross calorific value (GCV), or higher heating value (HHV) and the nett calorific value CV (NCV), or lower heating value (LHV). The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapour and therefore represents the maximum amount of energy potentially recoverable from a given biomass source. The actual amount of energy recovered will vary with the conversion technology, as will the form of that energy, i.e. combustible gas, oil, steam, etc. In practical terms, the latent heat contained in the water vapour cannot be used effectively and therefore, the LHV is the appropriate value to use for the energy available for subsequent use. (MCKENDRY 2002)

When quoting a calorific value, the moisture content needs to be stated, as this reduces the available energy from the biomass. It appears normal practice to quote both the calorific value and crop yield based on dry matter tons (dmt), which assumes zero percent moisture content. If any moisture is present, this reduces the calorific value proportional to the moisture content. (MCKENDRY 2002)

Besides the calorific value of biomass, also biomass heating values were investigated.

According to MCKENDRY (2002) heating value in defining the biomass fuel energy content is used for numerical simulations of thermal systems to evaluate combustion quality. Biomass heating value is tightly connected with elemental composition and affected by the variation in cell wall composition and ash.

Chemical and thermal analyses methods are often applied to assess the proportions of fixed carbon and volatiles content.

The volatiles content, or volatile matter of a solid fuel, is that portion driven-off as a gas (including moisture) by heating (to 950 °C for 7 min).

The fixed carbon content, is the mass remaining after the releases of volatiles, excluding the ash and moisture contents.

Laboratory tests are used to determine the volatiles matter and fixed carbon contents of the biomass fuel. Fuel analysis based upon the volatile matter content, ash and moisture, with the fixed carbon determined by difference, is termed the proximate analysis of a fuel. The significance of the volatile matter and fixed carbon contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified or oxidised, depending on how the biomass is to be utilized as an energy source. This type of fuel analysis is of value for biological conversion processes only once the fuel is produced, enabling a comparison of different fuels to be undertaken. (MCKENDRY 2002)

Elemental analysis of a fuel, presented as C, N, H, O and S together with the ash content, is termed the ultimate analysis of a fuel. Comparison of biofuels with fossil fuels, such as coal, shows clearly that the higher proportion of oxygen and hydrogen, compared with carbon, reduces the energy value of a fuel, due to the lower energy contained in carbon-oxygen and carbon-hydrogen bonds, than in carbon-carbon bonds. (MCKENDRY 2002)

Pyrolysis and combustion behaviour are important characteristics of biomass, which can be used to efficiently design a reactor or boiler for bioenergy production. Those profiles can also be used to obtain the lignocellulose composition of biomass (hemicellulose, cellulose and lignin) and to study how those constituents behave at different temperatures (CARRIER ET AL. 2011) [3]. The proportion of lignin in biomass can also be used as an indicator of the heating value due to its relatively lower oxygen concentration than holocellulose. (LEWANDOWSKI AND KICHERER 1997; DEMIRBAS 1997, 2005; COLLURA ET AL. 2005, 2006; MICHEL ET AL. 2006; VILLAVERDE ET AL. 2009)

The chemical breakdown of a biomass fuel, by either thermo-chemical or bio-chemical processes, produces a solid residue. When produced by combustion in air, this solid residue is called “ash” and forms a standard measurement parameter for solid and liquid fuels. The ash content of biomass affects both the handling and processing costs of the overall, biomass energy conversion cost. During biochemical conversion, the percentage of solid residue will be greater than the ash content formed during combustion of the same material. For a biochemical conversion process, the solid residue represents the quantity of non-biodegradable carbon present in the biomass. This residue will be greater than the ash content because it represents the recalcitrant carbon which cannot be degraded further biologically but which could be burnt during thermo-chemical conversion. Dependent on the magnitude of the ash content, the available energy of the fuel is reduced proportionately. In a thermo-chemical conversion process, the chemical composition of the ash can present significant operational problems. This is especially true for combustion processes, where the ash can react to form a “slag”, a liquid phase formed at elevated temperatures, which can reduce plant through put and result in increased operating costs. (MCKENDRY 2002)

The alkali metal content of biomass, i.e. Na, K, Mg, P and Ca, is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockage of airways in the furnace and boiler plant. It should be noted that while the intrinsic silica content of a biomass source may be low, contamination with soil introduced during harvesting can increase the total silica content significantly, such that while the content of intrinsic silica

in the material may not be a cause for concern, the increased total silica content may lead to operational difficulties. (MCKENDRY 2002)

The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water-soluble substances, hydrocarbons, ash, and small amounts of alkali, alkaline, and heavy metals and other compounds. Among all these components, cellulose, hemicelluloses, and lignin are the three principal components.

According to MCKENDRY (2002), biomass contains varying amounts of cellulose, hemicellulose, lignin and a small number of other extractives.

Woody plant species are typically characterised by slow growth and are composed of tightly bound fibres, giving a hard external surface, while herbaceous plants are usually perennial, with more loosely bound fibres, indicating a lower proportion of lignin, which binds together the cellulosic fibres: both materials are examples of polysaccharides; long-chain natural polymers. The relative proportions of cellulose and lignin is one of the determining factors in identifying the suitability of plants species for subsequent processing as energy crops.

Cellulose is a glucose polymer, consisting of linear chains of (1,4)-D-glucopyranose units, in which the units are linked 1-4 in the β -configuration, with an average molecular weight of around 100,000.

Hemicellulose is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methyl glucuronic and galacturonic acids, with an average molecular weight of <30,000. In contrast to cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly, but non-covalently, to the surface of each cellulose microfibril. Hemicellulose differs from cellulose, in consisting primarily of xylose and other five-carbon monosaccharides.

Lignin can be regarded as a group of amorphous, high molecular weight, chemically related compounds. The building blocks of lignin are believed to be a three-carbon chain attached to rings of six carbon atoms, called phenyl-propane. These may have 0, 1 or 2 methoxyl groups attached to the rings, giving rise to three structures, termed I, II and III, respectively. The proportions of each structure depend on the source of the polymer, i.e. structure I, is found in plants such as grasses; structure II in the wood of conifers; while structure III is found in deciduous wood. Cellulose is generally the largest fraction, representing about 40 – 50 % of the biomass by weight; the hemicellulose portion represents 20 –40 % of the material by weight. Both woody and herbaceous plant species have specific growing conditions, based on the soil type, soil moisture, nutrient balances and sunlight, which will determine their suitability and productive growth rates for specific, geographic locations. Many types

of perennial grasses, such as sugar cane and cereals like wheat and maize, have widely different yields, depending on the growing conditions: thus wheat can be grown in both hot and temperate climates with a wide range of rainfall, whereas sugarcane can be grown successfully only in warm, moist climatic conditions.

The proportions of cellulose and lignin in biomass are important only in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon-containing plant material present as cellulose is greater than for plants with a higher proportion of lignin, a determining factor when selecting biomass species for biochemical processing. To produce ethanol, a biomass feedstock with a high, cellulose / hemicellulose content is needed to provide a high, $l \cdot t^{-1}$, yield. While the lignin content represents a potentially large energy source, current techniques involving hydrolysis / enzymatic systems cannot convert the lignin to syngas. (MCKENDRY 2002)

Among fire and thermal (energetic) properties of biomass belongs the activation energy, which has a significant influence on combustion process, fire initiation and which influences the thermal degradation process of specific materials. To calculate the activation energy, there are several methods to be applied. Those range from simple methods (e.g. Arrhenius equation to much more complex iso-conversional methods (e.g. Ozawa-Flynn-Wall, Kissinger-Akahira-Sunos or Friedman, ASTM-E698-05), which requires to dispense with the results of thermogravimetry, differential thermogravimetry and differential scanning calorimetry and other progressive instruments and methodologies results to calculate the activation energy and the combustion process kinetics much more complexly and precisely.

An important characteristic of biomass is also its bulk density, or volume, both as produced and as subsequently processed. The importance of the as produced, bulk density is in relation to transport and storage costs. The density of the pro-cessed product impacts on fuel storage requirements, the sizing of the materials handling system and how the material is likely to behave during subsequent thermo-chemical / biological processing as a fuel / feedstock. (MCKENDRY 2002)

3.2 Standardized analytical methods for investigating the fire and energetic properties of biomass

In this category of methods we assigned the spontaneous ignition temperature fire tests, calorific value analysis (gross calorific value and heating value), moisture content, ash content

and elemental analysis in regards to essential fire and energetic properties of biomass calculation.

The procedure according to STN ISO 871: 2006 is used for determination of spontaneous ignition temperature. Plastics - Determination of ignition temperature using hot-air furnace.

According to this standard, the spontaneous ignition temperature is understood the lowest temperature at which, under defined test conditions, ignition will occur by heating, without the presence of any source of ignition.

The principle of the test consists in heating a sample of the material in the hot-air furnace (Figure 8) at different temperatures in the heating chamber, and the ignition temperature is determined as the temperature at which ignition of the released gases occurred.

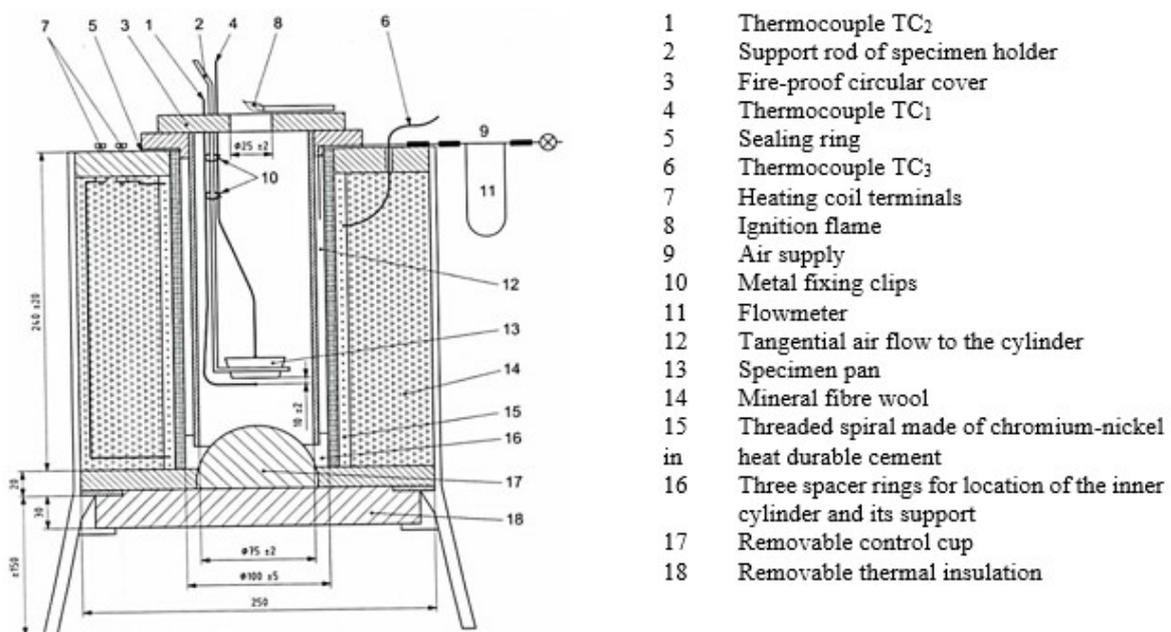


Figure 8 Hot-air furnace (Source: STN ISO 871:2006)

Materials in any form, including composites, may be used for the test, but it is essential that the form is described in detail in the test protocol.

For materials with a density of more than $100 \text{ kg}\cdot\text{m}^{-3}$, a sample mass of $3.0 \text{ g} \pm 0.2 \text{ g}$ shall be used. The materials may be tested in the form of granules or powder, as commonly supplied for moulding. The materials in the form of boards are cut into squares with maximum dimensions of $20 \text{ mm} \pm 2 \text{ mm}$ and stacked to the height required to achieve the required sample weight. The foil materials shall be rolled to a strip with a width of $20 \text{ mm} \pm 2 \text{ mm}$ and the necessary length to achieve the required sample weight.

In case of the lightweight materials with a density less than $100 \text{ kg}\cdot\text{m}^{-3}$, any outer layer shall be removed, and the sample shall be cut into blocks with dimensions $(20 \text{ mm} \pm 2 \text{ mm}) \times (50 \text{ mm} \pm 5 \text{ mm})$.

Enough material is required to make at least two tests.

The samples shall be conditioned at a temperature of $23 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and a relative humidity of $50 \pm 5 \%$ for a minimum of 40 hrs in accordance with ISO 291 before testing.

The procedure for determining the spontaneous ignition temperature specified by the above standard begins with the adjustment of the air flow rate. This is set at $25 \text{ mm}\cdot\text{s}^{-1}$ by adjusting the actual air flow rate q_v over the entire cross-section of the inner cylinder at the furnace temperature to the calculated value ($\text{l}\cdot\text{min}^{-1}$) based on the equation (1):

$$q_v = 6.62 \times \frac{293}{T} \quad (1)$$

Where:

T – Temperature (K)

It shall be ensured that the air flow rate is kept within $\pm 10 \%$ of the calculated value.

The electrical current supplied to the heating coil shall be adjusted by means of a control transformer with respect to the temperature T_3 until the air temperature T_2 remains constant at the level of the required initial test temperature.

The sample holder is then raised, and the opening of the cover pan and sample is placed in a ring holder. The sample is inserted into the furnace, taking care to position the TC_1 and TC_2 thermocouples correctly. The time measuring device is turned on. Further, it is necessary to wait for ignition of the gases released by the heated material for 10 min. After 10 min, the temperature T_2 is lowered or increased by $50 \text{ }^\circ\text{C}$, depending on whether ignition has occurred and the test is repeated with a new sample.

Ignition is evident by burning the sample by flame or by glowing. For some materials, ignition may be difficult to detect visually, especially in cases where the combustion takes place by glowing rather than by flame. In such cases, reliable evidence is a faster rise in temperature T_1 than T_2 , accompanied by visual observation.

The spontaneous ignition temperature shall be the lowest air temperature T_2 at which flame burning or glowing of the sample is observed within 10 min.

For the purpose of determining the induction period, it is recommended to proceed as follows.

When determining the spontaneous ignition temperature range, the tests shall be started at a temperature about $10 \text{ }^\circ\text{C}$ lower than the highest temperature within the thermal range

and shall continue to reduce the temperature by 10 °C in each case to a temperature at which no ignition occurs for 10 min. The ignition temperature shall also be the lowest air temperature T_2 at which, during 10 min, flame burning or glowing of the sample has been observed.

The calorific value of biomass is commonly determined according to the STN EN ISO 18125:2017 Solid biofuels – Determination of calorific value standard. The calorific value can be expressed as: gross calorific value at constant volume, net calorific value at constant volume and net calorific value at constant pressure.

Gross calorific value at constant volume is the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified. The products of combustion are assumed to consist of gaseous oxygen, nitrogen, carbon dioxide and sulphur dioxide, of liquid water (in equilibrium with its vapour) saturated with carbon dioxide under the conditions of the bomb reaction, and of solid ash, all at reference temperature.

Net calorific value at constant volume is the value of specific energy of combustion, in joules, for unit mass of the fuel burned in oxygen under conditions of constant volume and such that all the water of the reaction products remains as water vapour (in a hypothetical state at 0,1 MPa), the other products being as for the gross calorific value, all at the reference temperature (the international reference temperature for thermochemistry of 25 °C).

Net calorific value at constant pressure is the value of specific heat (enthalpy), in joules, for unit mass of the fuel burned in oxygen under conditions of constant volume and such that all the water of the reaction products remains as water vapour (at 0.1 MPa), the other products being as for the gross calorific value, all at the reference temperature.

When the gross calorific value is being determined, a weighted portion of the analysed sample of the solid fuel is burned in high-pressure oxygen in a bomb calorimeter under specified conditions. First, the effective heat capacity of the calorimeter, i.e. the amount of energy required to cause unit change in temperature of the calorimeter is determined in calibration experiments by combustion of certified benzoic acid under similar conditions, accounted for in the certificate. The corrected temperature rise is established from observations of temperature before, during and after the combustion reaction takes place. The duration and frequency of the temperature observations depend on the type of calorimeter used. Water is added to the bomb initially to give a saturated vapour phase prior to combustion, thereby allowing all the water formed, from the hydrogen and moisture in the sample, to be regarded as liquid water.

The gross calorific value is calculated from the corrected temperature rise and the effective heat capacity of the calorimeter, with allowances made for contributions from ignition energy, combustion of the fuse(s) and for thermal effects from side reactions as the formation of nitric acid. Furthermore, a correction is applied to account for the difference in energy between the aqueous sulphuric acid formed in the bomb reaction and gaseous sulphur dioxide, i.e. the required reaction product of sulphur in the fuel.

The net calorific value at constant volume and the net calorific value at constant pressure of the fuel are obtained by calculation from the gross calorific value at constant volume determined on the analysed sample. The calculation of the net calorific value at constant volume requires information about the moisture and hydrogen contents of the analysed sample. In principle, the calculation of the net calorific value at constant pressure also requires information about the oxygen and nitrogen contents of the sample.

For determination of biomass moisture content, the following three standards can be applied: STN EN ISO 18134-1: 2015 Solid biofuels. Determination of moisture content. Oven dry method. Part 1: Total moisture; STN EN ISO 18134-2: 2015 Solid biofuels. Determination of moisture content. Oven dry method. Part 2: Total moisture. Simplified method; and STN EN ISO 18134-3: 2015 Solid biofuels. Determination of moisture content. Oven dry method. Part 3: Moisture in the analytical sample for general analysis.

The simplified method of biomass (biofuel) moisture content is often used. Using this procedure, the sample of biomass is dried at a temperature of 105 ± 2 °C in air atmosphere until constant mass is achieved and the percentage moisture calculated from the loss in mass of the sample. For this purpose, the drying oven, capable of being controlled (manufacturer's specification) at a temperature within the range of 105 ± 2 °C and in which the air atmosphere changes between three times and five times per hour. The air velocity should be such that the sample particles are not dislodged from their drying container.

The difference in the procedure comparing to the reference method STN EN ISO 18134-1 is that the effect due to buoyancy is neglected in this method. The weight of a tray when still hot is, due to buoyancy, less than the weight of the cold tray. The magnitude of the buoyancy effect depends of the size and the weight of the tray.

The two main types of analytical procedure used to determine the ash content of biomass are based on this principle: dry ashing and wet ashing. The method chosen for a particular analysis depends on the reason for carrying out the analysis, the type of material analysed and the equipment available. Ashing may also be used as the first step in preparing samples for analysis of specific minerals.

The ash content is expressed as a percentage on dry fuel basis. An ash content is one of the main parameters characterizing fuel. A muffle furnace (Figure 9) can be used to determine the ash content of various biofuel types (e.g. wood chips, wood pellets, briquettes etc.) that are used in CHP plants, district heating facilities or for individual heating. The method can be used to determine the ash content for the less frequently used fuels (e.g. buckwheat and sunflower husks) too. By knowing the ash content of the fuel, it is possible to evaluate combustion efficiency and potential application in heat generation.

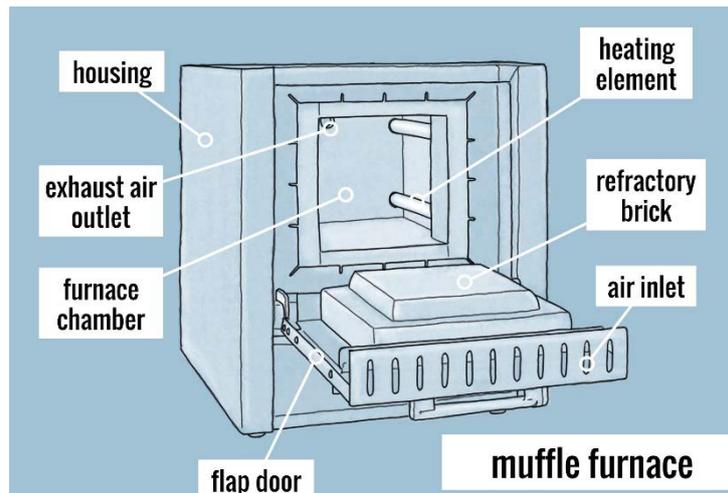


Figure 9 Muffle furnace (Source: WIRING DIAGRAM 2019)

Determination of the ash content is typically performed according to STN EN ISO 18122:2015 Solid biofuels. Determination of ash content, which is based on dry ashing approach.

For the analysis procedures it is crucial to carefully select a representative sample, which composition does not change significantly prior to analysis. Typically, samples of 1 – 10 g are used in the analysis of ash content. Solid materials are finely ground and then carefully mixed to facilitate the choice of a representative sample. Before carrying out an ash analysis, samples that are high in moisture are often dried to prevent spattering during ashing. Other possible problems include contamination of samples by minerals in grinders, glassware or crucibles which meet the sample during the analysis. For the same reason, it is recommended to use deionized water when preparing samples.

Dry ashing procedures use a high temperature muffle furnace capable of maintaining temperatures of between 500 and 600 °C. Water and other volatile materials are vaporized and organic substances are burned in the presence of the oxygen in air to CO₂, H₂O and N₂. Most minerals are converted to oxides, sulphates, phosphates, chlorides or silicates. Although most minerals have low volatility at these high temperatures, some are volatile and

may be partially lost, e.g. iron (Fe), lead (Pb) and mercury (Cu). If an analysis is being carried out to determine the concentration of one of these substances, then it is advisable to use an alternative ashing method that uses lower temperatures.

The biomass sample is weighed before and after ashing to determine the concentration of ash present. The ash content (%) can be expressed on either a dry (1) or wet basis (2):

$$\text{Ash (dry basis)} = \frac{m_{\text{ash}}}{m_{\text{dry}}} \times 100 \quad (1)$$

$$\text{Ash (wet basis)} = \frac{m_{\text{ash}}}{m_{\text{wet}}} \times 100 \quad (2)$$

Where:

- m_{ash} – Mass of the ashed sample
- m_{dry} – Original mass of the dried sample
- m_{wet} – Original mass of the wet sample

Recently, progressive analytical instruments have been developed to dry ash samples based on microwave heating. These devices can be programmed to initially remove most of the moisture (using a relatively low heat) and then convert the sample to ash (using a relatively high heat). Microwave instruments greatly reduce the time required to carry out an ash analysis, with the analysis time often being less than an hour. The major disadvantage is that it is not possible to simultaneously analyse as many samples as in a muffle furnace.

The elemental analysis can be performed according to the STN EN 15289:2011 Determination of total content of sulphur and chlorine and STN EN 15104: 2011 Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods.

3.3 Progressive analytical methods for investigating the fire and energetic properties of biomass

Among the progressive analytical methods to study the fire, thermal and energy properties of biomass we assigned the thermal analysis (especially thermogravimetry and differential scanning analysis), gas chromatography combined with pyrolysis (Py-GC-MS) and numerical modelling of biomass fast pyrolysis modelling using the Computer Fluid Dynamics (CFD) tools.

In general, thermal analysis (TA) comprises a group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program.

First, we introduce the brief introduction of thermal analysis history.

In 1763, Joseph Black was the first to distinguish between latent and sensible heat and between temperature (quality of heat) and heat (quantity of heat).

Regarding the substances investigated, the origin of modern thermal analysis (TA) methods are the clay minerals. Antoine Laurent de Lavoisier was probably the first who performed a TA study that would correspond to today's requirements. During his studies of mass changes upon oxidation, he also investigated a clay mineral under heating. (FEIST 2015)

Lavoisier's main aspect was the mass change, but later it was rather the aspect of temperature or heat that led Henri Le Chatelier to publish his important work on clays (LE CHATELIER 1887).

Further crucial contributions to today's TA are the difference measuring principle of thermocouples, the use of an inert reference substance, and the phase rule of Josiah Willard Gibbs. (FEIST 2015)

Previously, doing classical or conventional TA meant to follow the temperature of a sample upon heating and / or cooling, i.e. to record dependencies $T = f(T)$ or $T = f(t)$. In the field of heterogeneous equilibria, mostly of inorganic systems, this was rather easy to practise in the student's lab classes first for single-phase, then for binary systems.

Later on, TA transformed into difference thermal analysis (DTA), primarily, after introduction of a thermally inert reference substance subjected to the same heating or cooling program as the sample and, secondarily, by the development of the difference measuring setup. Instead of $T = f(T)$ it is followed now $DT = f(T)$.

Power-compensated DSC became undoubtedly state-of-the-art of modern scanning calorimetry which is certainly also a consequence of the enormous progress made in measurement and evaluation software during the last two decades. Due to its higher caloric sensitivity, DSC rather than DTA is the appropriate tool for investigating structure transitions in polymers.

Further, we continue with introduction of thermal analysis theory.

In general, three groups of physical parameters to be measured (mass, temperature or heat flux, mechanical and other parameters) allow for a classification of the thermal analysis methods (Figure 10).

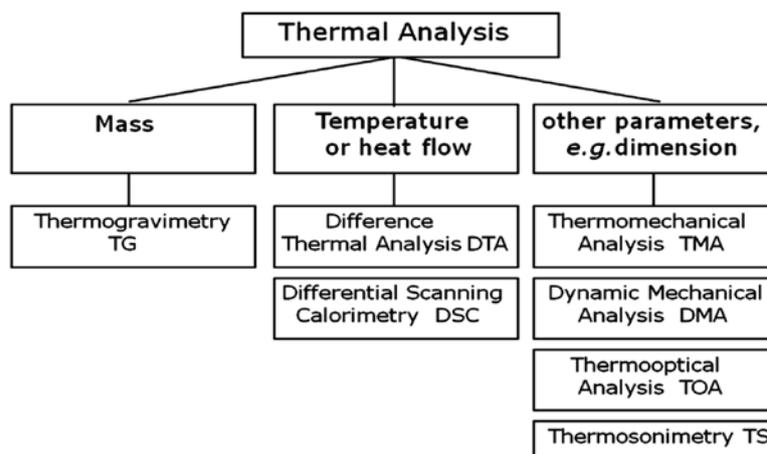


Figure 10 Classification of thermal analysis methods (Source: FEIST 2015)

Methods based on thermal analysis techniques such as DSC, TGA, TMA, DMA are extremely important for characterizing the materials and compounds used in renewable energy resources. Thermal analysis is mainly used to measure the thermal stability, oxidative stability, and curing behaviour of materials. In addition, it is an important tool for optimizing processes in biomass plants or for quality control in the biofuels industry.

The most important effects that can be analysed by DSC are the glass transition, melting behaviour, and the enthalpy of cure.

TOA (Thermo Optical Analysis) is the method of choice for the visual observation of samples, for example during crystallization and to detect cloud point effects. It is also named thermomicroscopy.

In its simplest variant is realized in the form of the heating microscope for the determination of melting points. Besides a simple microscopic inspection of the temperature-depending changes (e.g. the beginning transparency of melting crystals), it allows following structure transitions in the solid state in polarized light upon heating or cooling. Today, TOA is predominantly applied in pharmaceutical chemistry. A recent development of TOA utilizes LED light conductors and a video camera for detecting melting points via the light transmission of melting solids (METTLER TOLEDO 2009)

The main applications of TGA are content analysis, thermal stability and evaporation behaviour.

Thermomechanical Analysis (TMA) measures the dimensional changes of a sample as it is heated or cooled in a defined atmosphere (Figure 11).

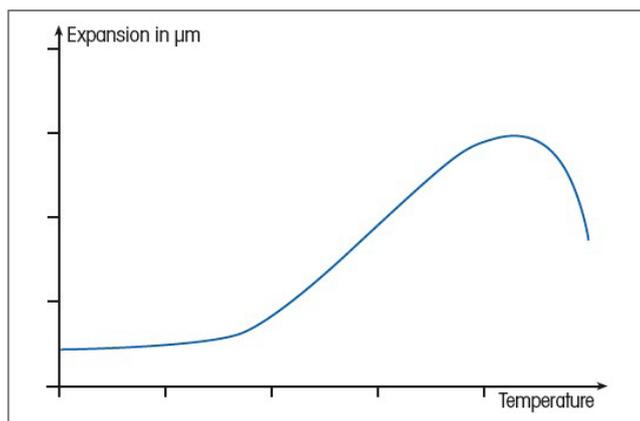


Figure 11 Graphical representation of TMA analysis results (Source: METTLER TOLEDO 2019)

Dynamic Mechanical Analysis (DMA) measures the mechanical properties of viscoelastic materials as a function of time, temperature and frequency when they are deformed under a periodic stress (Figure 12).

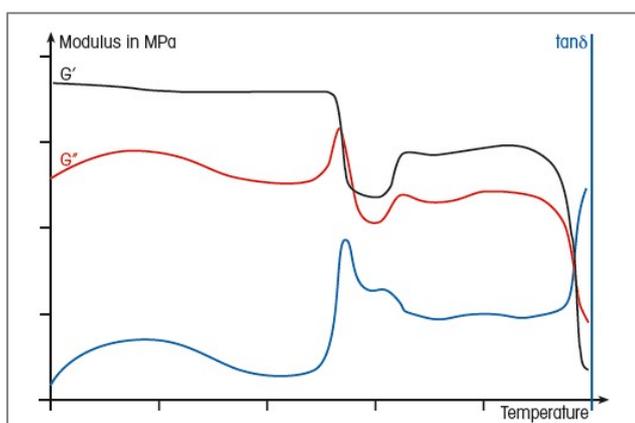


Figure 12 Graphical representation of DMA analysis results (Source: METTLER TOLEDO 2019)

Further we introduce more the TGA and DSC methods of thermal analysis.

Thermogravimetric analyses

Thermogravimetric analysis (TGA) is a type of thermal analysis used to model pyrolysis and combustion profiles of biomass by measuring the mass of a sample as a function of time when the sample undergoes a specific heating pattern. The mass loss (mg) over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability in general.

TGA technique measures the mass of a sample as it is heated, cooled or held at a constant temperature in a defined atmosphere. Thermogravimetric analysis (TGA) is ideal for characterizing the thermal properties of materials such as plastics, elastomers and thermosets, mineral compounds and ceramics as well as for chemical and pharmaceutical products.

Thermogravimetry (TG) is one of the basic methods in thermal analysis. It is a technique in which the mass of a substance is measured as a function of temperature while a substance is subjected to a controlled temperature program. The resulting dm vs. T curve provides information regarding thermal stability and composition of the initial sample, the intermediate products that may form and the composition of solid residue, if any. To get useful information, the sample should evolve a volatile product as a result of various physical and chemical processes taking place in the sample on heating. This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption; as well as chemical phenomena including chemi-sorptions, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction). Sometimes performed simultaneously with DTA/DSC and sometimes performed separately. (PANDYA 2018)

Applications of TG method are in analysing material properties such as thermal stability, oxidation and / or combustion, thermogravimetric kinetics, operation in combinations with instruments.

The principle of TG analysis is specified in the STN EN ISO 11358-1:2015-04 Plastics. Thermogravimetry (TG) of polymers. General principles. According to this standard, a test sample is heated as specified rates with a controlled temperature programme, and the change in mass is measured as a function of temperature. Alternatively, the sample is kept at a given constant temperature and the change in mass is measured as a function of time over a given period. During measurement the test sample is held in a controlled inert or oxidising atmosphere. In general, the reactions which cause the mass of a test sample to change are decomposition or oxidation reactions or the volatilisation of a component. The change in mass is recorded as a thermogravimetric (TG) curve. The change in mass of a material as a function of temperature and the extent of this change are indicators of the thermal stability of the material. TG data can therefore be used to evaluate the relative thermal stability of polymers of the same generic family and polymer-polymer or polymer-additive interactions, using measurements made under the same test conditions.

The sample to be analysed may be liquids or solids. Solids may have the form of powders, pellets, granules or cut pieces. Preferably, the mass of the test sample shall be in the range of 10 mg to 100 mg.

A number of commercial instruments suitable for thermogravimetric measurements are available. The basic apparatus consists of the thermobalance and purge gas, i.e. dry air or oxygen (oxidizing conditions) or a suitable inert gas with an oxygen content of 0.001 %

by volume or less (non-oxidising conditions). In either case, the water content of the purge gas shall be less than 0.001 % by mass.

Derivative thermogravimetry (DTG) is difference thermogravimetry ratio of measurement of dm (mass loss or mass increase) at heating / cooling / isotherm, interpretation by dm over temperature (T) or time (t); $(-dm/dt)$.

In majority cases subsequent decomposition process give overlapping decomposition stages. Thus, dissimilarly to the decomposition pattern of a certain decomposition reaction is not yet finished when another (higher temperature one) commences. In most of cases a reliable qualitative and quantitative evaluation of the TG curve is impossible without having its first derivative (i.e. DTG curve). The DTG peak height at any temperature gives the rate of mass loss (dm/dT in $mg \cdot min^{-1}$). With DTG curve T_i , T_f and T_{max} (the temperature of the maximum mass loss rate) can be precisely determined in overlapping reactions. The first thermobalance capable of recording TG and DTG curves simultaneously was developed by PAULIK ET AL. (1954).

The DTG method has its application in thermogravimetric analysis of liquids, the derivate of the TG curve with respect to time (the DTG curve) is directly correlated with the differential equations of the rate of change in weight. With the aid of DTG curve, which in the case of derivatography is the derivative of the TG curve with respect to time, the apparent evaporation surface and the heat of evaporation of the liquid can be calculated on the basis of dx/dT .

Differential Thermal Analysis is a thermo-analytic technique that is similar to differential scanning calorimetry (DSC). DTA is a technique in which the temperature difference between a substance and a thermally inert reference material is measured as a function of the temperature (T), while the substance and reference material are subjected to a controlled temperature program. Here, the material under study and an inert reference are made to undergo identical thermal cycles, (i.e. same cooling or heating program) while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve, or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample. DTA is the oldest thermo-analytical method.

DTA curve can be used only as a fingerprint for identification purposes but usually the applications of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres. It is widely used in the pharmaceutical and food industries. It is used in cement chemistry, mineralogical research and environmental studies.

The principle of thermogravimetry (TG) method is set in STN EN.

TGA is often used together with Differential Scanning Calorimetry (DSC) because the two techniques provide complementary information, which often facilitates the interpretation of a thermal analysis experiment (Figure 13).

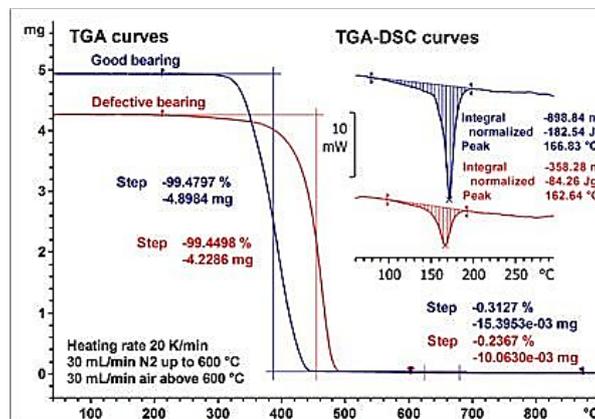


Figure 13 Graphical representation of TG-DSC analysis results (Source: METTLER TOLEDO 2019)

The gaseous products that are evolved can be analysed using hyphenated techniques, for example by coupling a Fourier transform infrared spectrometer (FTIR) or a mass spectrometer (MS) to the thermobalance of the TGA instrument.

The properties and behaviour that can be measured by the TGA technique include composition, purity, decomposition reactions, decomposition temperatures, and absorbed moisture content.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) is another type of thermal analysis that measures the endothermic or exothermic behaviour of biomass as a function of temperature or time when the biomass is subjected to a specific heating pattern. It is most commonly used to model pyrolysis processes (STENSENG ET AL. 2001).

DSC measures the heat flow produced in a sample when it is heated, cooled, or held isothermally at a constant temperature. From all thermal analysis techniques, DSC is the most frequently used in routine and high performance-applications alike. (METTLER TOLEDO 2019)

Simply, it allows to determine the energy absorbed or released by a sample as it is heated, cooled or held at constant temperature (Figure 14).

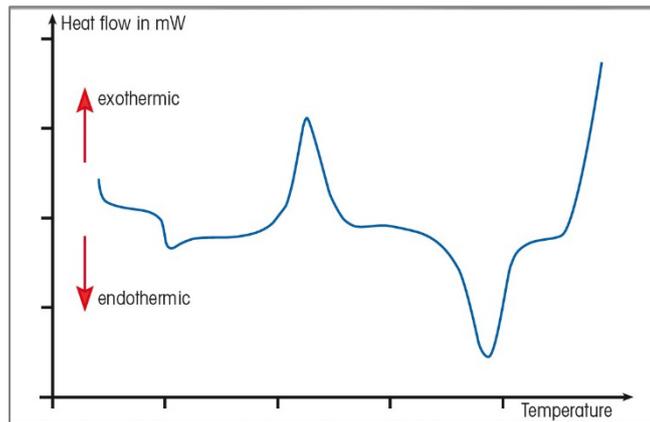


Figure 14 Graphical representation of DSC analysis results (Source: METTLER TOLEDO 2019)

Figure 15 shows the principal setup of two variants of DSC. In case of the historically older heat flux DSC, both crucibles (i.e. pans with a flat bottom, possibly with a lid) are connected via a heat-conducting metal band which leads to a rapid compensation of the temperature differences.

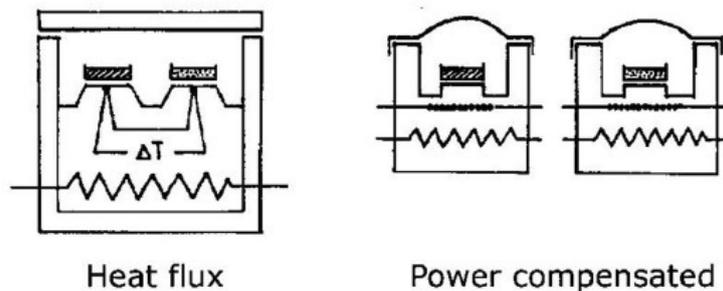


Figure 15 Principal setup of two variants of DSC (Source: METTLER TOLEDO 2019)

The heat flux establishing this compensation is the measuring signal. It is obvious that such a kind of measuring setup is less dependent on outer influences, e.g. from the thermal asymmetry or from the carrier gas flow. Sample and reference can also be heated separately. In this case, the measuring signal is the different heating power required for keeping both at the same temperature.

DSC analysis is used for numerous applications in a wide range of industries. Examples include glass transition determination and the investigation of chemical reactions, melting and crystallization behaviour. Other DSC applications deal with the influence of additives, fillers or the processing of materials. The characteristic shape of the individual DSC curves is used for quality control.

The DSC sensors determine the quality of the measurement and are thus the most important components of the instrument. Better sensitivity means that it is possible to detect smaller thermal effects in the sample or conversely to use smaller amounts of sample.

Another important performance property in a DSC experiment is the baseline. The baseline should be free of artefacts or drift because effects like these could overlay or hide true sample effects.

In a DSC experiment, the heat flow from the furnace to the sample is measured relative to the heat flow to a reference material. The sample is placed in a crucible, or pan, which sits directly on top of the sensor. Both the sample and reference crucibles are surrounded by a heated chamber or furnace. The sample and reference crucibles are identical except that the reference crucible is usually empty. For quantitative heat flow measurements, the crucible containing the sample must have excellent thermal conductivity and be in optimum contact with the sensor. The geometry of the crucible and the material used are therefore very important irrespective of the kind of sample that is measured. Depending on the sample and measurement requirements, other crucibles may also be needed. A common application is to measure a sample in a closed atmosphere and at a higher pressure than ambient. These measurements can be performed using the high-pressure crucible. DSC measurements can be performed dynamically using a linear temperature ramp, isothermally, or with temperature modulation. Temperature scans are used to investigate temperature-dependent processes such as the glass transition, crystallization, melting, and curing reactions. Isothermal temperature experiments are mainly used to determine the oxidation induction time of materials or to study chemical reactions. Temperature-modulated experiments allow to separate reversing and non-reversing effects, for example the glass transition from simultaneously occurring reactions or evaporation. Special atmospheres such as pure oxygen or nitrogen are often used in specific applications to accelerate or prevent the decomposition of samples. (METTLER TOLEDO 2019)

According to the standard STN EN ISO 11357-1 Plastics. Differential scanning calorimetry (DSC) - Part 1: General principles, the sample shall be in the liquid or solid state. Solid-state samples may be in any form which fits into the crucible (e.g. powder, pellets, granules, fibres) or may be cut from bigger pieces to a suitable size. The sample shall be representative of the sample being examined and shall be prepared and handled with care. Care shall be taken to avoid any contamination of the sample. If the sample is taken larger pieces by cutting, care shall be taken from larger pieces by cutting, care shall be taken to prevent heating, polymer orientation or any other effect that may alter the sample properties. Operations such as grinding that could cause heating, polymer or reorientation and could therefore change the thermal history of the sample shall be avoided of thermal analyses.

Typical sample masses are between 2 mg and 40 mg.

Pyrolysis

Biomass as a form of energy source may be utilized in two different ways: directly by burning the biomass and indirectly by converting it into solid, liquid or gaseous fuels. Pyrolysis is an indirect conversion method and can be described in simpler terms as a thermal decomposition of biomass under oxygen-depleted conditions to an array of solid, liquid and gaseous products, namely biochar, bio-oil and fuel gas. However, pyrolysis of biomass is a complex chemical process with several operational and environmental challenges.

Pyrolysis is the thermal degradation of macromolecules in the absence of air and generates oils and gases, which are suited for chemical utilization or generation of energy. (ARVANITOYANNIS 2008)

Pyrolysis of organic feedstocks produces three products including a liquid (bio-oil), a syngas, and a solid (biochar). Bio-oil is created during pyrolysis because natural polymeric constituents (i.e. lignin, cellulose, fats) are broken down into volatile gasses containing O- and H- containing forms. These gasses can be later re-condensed along the pyrolysis continuum into bio-oil or recycled to facilitate energy required for upstream feedstock drying and carbonization. Carbonization furthers the removal of polar functional groups and rearrangement of ring/linear-shaped organic structures into polycondensed aromatic sheets in the resultant biochar (CHEN ET AL. 2008; KEILUWEIT ET AL. 2010 IN NOVAK, JOHNSON 2019).

The biomass pyrolysis process is conducted under very low oxygen concentrations, at pyrolysis temperatures ranging from 300 to 1,100 °C, using variable residence times, i.e. seconds to hours (MANYA 2012). Low oxygen levels are necessary for carbonization to occur while minimizing CO₂ and NO_x production (ANTAL, GRØNLI 2003).

The pyrolysis process has different modes of processing including slow/fast pyrolysis, flash pyrolysis, and gasification. Slow pyrolysis, such as with traditional kilns, exposes feedstocks in a batch thermal mode for days to a week. Fast pyrolysis uses a traditional method of advancing the feedstock through a retort/oven for several minutes using a continuous feed system. In the flash pyrolysis procedure, feedstocks are exposed to a burst of thermal energy, usually from 1 to 5 s. Finally, gasification exposes the feedstock to high temperatures up to 1,100 °C to maximize conversion into syngas materials. Final product recovery under these modes includes bio-oil, biochar, and gases (MANYA 2012; BOATENG ET AL. 2015).

In general, flash pyrolysis yields are 60 % biochar and 40 % bio-oil and syngas, while fast pyrolysis yields show higher bio-oil recoveries with minimal biochar leftovers. Slow pyrolysis produces almost equal yields of bio-oil, biochar, and syngas (LAIRD ET AL. 2009).

Biochars produced for agronomic purposes prefer a slow pyrolysis mode to maximize biochar yields (SONG, GUO 2012).

Among the progressive analytical methods to study the pyrolysis of the woody and herbaceous biomass, particularly two methods are used: GC-MS-Pyrolysis and modelling the hydrodynamic behaviour of particles in pyrolysis.

Fast pyrolysis, the rapid thermal decomposition of organic material in the absence of oxygen, is a process that can be used to convert biomass into liquid fuels and chemicals. When performed at the micro-scale, pyrolysis is useful for characterizing biomass structure, as well as determining the pyrolysis products that can be generated from specific biomass feedstocks. Indeed, microscale pyrolysis coupled with on-line analysis of the pyrolysis vapours by GC-MS, so-called Pyrolysis-GC-MS (Py-GC-MS), is a technique that can be used to characterize the structure and composition of the various components of lignocellulosic and microalgal biomass based on their pyrolysate distributions. Pyrolysates produced also provide insight into the range of products that can be expected when biomass feedstocks are subjected to thermal decomposition processes. (WARE 2013)

The scheme of Pyrolysis – Gas Chromatography – Mass Spectrometry (Py-GC-MS) is introduced in Figure 16.

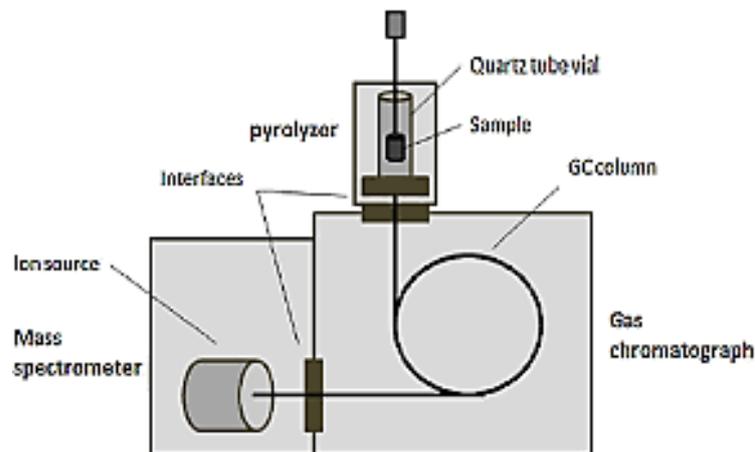


Figure 16 Schematic presentation of the Py-GC-MS device (Source: GIRADIN ET AL. 2017)

According to WARE (2013), Py-GC-MS is a rapid, microscale pyrolysis technique that can be used to monitor the relative abundance of condensable pyrolysates formed from pyrolysis of biomass and its constituents. The relative abundance of these pyrolysates may also influence the properties of the bio-oil obtained and hence influence its application for uses. Therefore, Py-GC-MS can be used to infer information about the composition of a feedstock as well as the potential products it can generate upon thermochemical processing.

Py-GC-MS is a technique that uses a microscale pyrolysis unit to pyrolyze organic material on a micro- to milligram scale. Various forms of Py-GC-MS exist and the reactor configurations and parameters for analysis can be optimized for the types of samples and the information sought. While reactors are sometimes constructed by researchers, commercial models are available from companies such as CDS Analytical and Frontier Laboratories. Biomass is typically analysed by Py-GC-MS by subjecting it to pyrolysis in a quartz tube or boat cell inside a heated chamber or a metal coil (such as platinum), the latter offering maximum heating rates and heat transfer to the biomass particles.

The product vapours then pass through heated filters or sorbent media or go directly to the GC through a heated transfer line to prevent condensation of vapours. The pyrolysis units are purged with an inert gas, Helium (He), which is also the carrier gas for the GC-MS. Carrier gas flow rates are typically on the order of $50 \text{ mL}\cdot\text{min}^{-1}$, allowing for rapid transfer of pyrolysates from source to GC. Combined with the use of sorbent media or short transfer lines, Py-GC-MS in the presence of GC carrier gas can allow for analysis of the primary pyrolysates formed. However, some condensation and secondary reactions are difficult to avoid, although good reproducibility is usually achievable providing there are no cold spots or leaks within the unit.

Py-GC-MS has been widely used to study the structure and composition of lignocellulosic biomass and its separated components. It has also been used to understand the mechanisms and kinetics associated with the thermal decomposition of biomass. Whole biomass separated components and various model compounds of biomass components have all been analysed by Py-GC-MS to explain the origin and formation of pyrolysates. Most studies have focused on lignocellulosic biomass and its components whereas few studies have focused on Py-GC-MS analysis of microalgae species. Py-GC-MS studies have been supported by other techniques used to study biomass structure and composition. Chemical degradation techniques, spectroscopic analysis and thermogravimetric analysis have all shown that Py-GC-MS analysis can give consistent information about biomass composition.

Py-GC-MS of whole biomass has been used to analyse thermal decomposition products from many types of biomass. Pyrolysates monitored were indicative of the presence of the various components present in each of the biomass species.

Py-GC-MS has also been supported by studies comparing pyrolysis products from biomass in larger scale reactors. Pyrolysates from spruce and beech pyrolyzed in a larger scale reactor were like those analysed by Py-GC-MS analysis of various biomass feedstocks in a study by AZEEZ ET AL. (2010).

Separate components of lignocellulosic biomass have also been studied using Py-GC-MS. Py-GC-MS studies of cellulose and dextran have been performed in order to elucidate the mechanisms and kinetics associated with the thermolysis of these polysaccharides in biomass. (LIN ET AL. 2009; PATWARDHAN ET AL. 2009, 2011)

Lignin extracted from various types of biomass has also been studied using Py-GC-MS in order to understand its thermolysis, structure, monomeric composition and the differences in these characteristics between the native and extracted lignin. (SAIZ-JIMENEZ AND LEEUW 1985; VAN DER HAGE ET AL. 1993; JIANG ET AL. 2010; PATWARDHAN ET AL. 2011; HU ET AL. 2013)

Lignin extracted using various techniques from different biomass sources was subjected to Py-GC-MS and thermogravimetric analysis in a study by BREBU ET AL. (2013).

Py-GC-MS data suggested that lignin from hardwood biomass types generated similar pyrolysates even if the lignin extraction techniques were different. KIM ET AL. (2013) extracted lignin from poplar wood using assorted techniques and Py-GC-MS analysis indicated some differences in the pyrolysate distributions of the lignin examined.

For numerical modelling of biomass fast pyrolysis in a reactor scale, the Computer Fluid Dynamics (CFD), as an indispensable tool, is used to understand the underlying physics involved in the fast pyrolysis.

Many studies have been carried out both on experimental and numerical aspects in the biomass fast pyrolysis, but the exact reaction mechanism and the kinetics involved in the pyrolysis reaction remain uncertain. Thus, several studies have been attempted for developing the kinetic model for biomass fast pyrolysis (CHAN ET AL. 1985; SRIVASTAVA ET AL. 1996; BABU AND CHAURASIA 2003). These studies assumed that three major products including gas, char, and organic liquid (tar) are obtained from the competitive pyrolysis reaction of a single component of biomass. The scheme of such a kinetic model is called as simple kinetic scheme.

For the simple kinetic scheme, many studies have already been reported in the literature (PAPADIKIS ET AL. 2009; SHARMA ET AL. 2015).

PAPADIKIS ET AL. (2009) have studied fast pyrolysis in a bubbling fluidised bed reactor using a Euler-Euler-Lagrangian approach.

Recently, SHARMA ET AL. (2015) have studied the pyrolysis process using the simple kinetic scheme in a fluidised bed reactor. CFD study of biomass fast pyrolysis was carried out by XUE ET AL. (2011) using the global kinetic scheme for biomass pyrolysis.

XIONG ET AL. (2013 a,b, 2014 a,b) have developed a generalised numerical framework for biomass pyrolysis in a fluidised bed reactor with interphase transport coefficients using global kinetic scheme. Same authors have also investigated the different devolatilization schemes including simple kinetic scheme with only primary biomass decomposition, simple kinetic scheme and global kinetic scheme for biomass pyrolysis (XIONG ET AL. 2014c).

They have found that the product yields from the global model were best predictions. Recently, the same authors have studied the impact of bed hydrodynamics on the yield prediction during biomass pyrolysis (XIONG ET AL. 2016).

BRUCHMILLER ET AL. (2012) have studied the thermo-chemical decomposition of biomass using a semi-global multicomponent mechanism by a discrete element model (DEM) approach. They have also investigated a parametric study of the fluidisation velocity, temperature and the moisture content on the yield.

For advanced kinetic scheme, recently, MELLIN ET AL. (2014) have studied the fast pyrolysis of biomass in a pilot-scale fluidised bed based on multi-fluid Eulerian method.

In the study of RANGANATHAN AND GU (2016), a numerical model was developed for the biomass fast pyrolysis process using sand as the bed material. They concerned with CFD modelling of biomass fast pyrolysis in a fluidised bed reactor. Initially, they conducted a study to understand the hydrodynamics of the fluidised bed reactor by investigating the particle density and size, and gas velocity effect. With the basic understanding of hydrodynamics, the further extended their study to investigate the different kinetic schemes for biomass fast pyrolysis process. The Eulerian-Eulerian approach they used to model the complex multiphase flows in the reactor.

4 EXPERIMENT

Experiment represents is a core part of this scientific monography. The aim of the experiment was to analyse the fire and energetic properties of selected species of woody and herbaceous biomass to specify the rating of its suitability for energy production purposes.

This chapter is divided to totally three principal chapters describing the test samples, methodological approaches applied, and introduction and discussion of the achieved results.

4.1 Tested fast-growing tree species and energy crop species

Totally six biomass species suitable to be used as a source of energy underwent the testing. There were tested three woody biomass species: *Populus x euroamericana* clone MAX 4, *Salix viminalis* clone TORA and *Pawlonia tomentosa*; and three energy crop species: *Sida hermaphrodita*, *Miscanthus x giganteus* and *Arundo donax*.

The samples of *Salix viminalis* clone TORA and *Populus x euroamericana* clone MAX 4 were taken from the existing plantations of the University Forest Enterprise of the Technical University in Zvolen territory.

The samples of *Paulownia tomentosa*, and herbaceous energy crops *Sida hermaphrodita*, *Arundo donax*, *Miscanthus x giganteus* were taken from the plantations belonging to the Agricultural Co-operative Dolné Saliby.

Further, we introduce the essential information of those woody and herbaceous biomass species.

4.1.1 *Populus x euroamericana* clone MAX 4

Populus is a genus of 25 – 35 species of deciduous flowering plants in the family *Salicaceae*, native to most of the Northern Hemisphere. English names variously applied to different species include poplar, aspen, and cottonwood.

Populus sp. are characterized by their rapid growth and high dendromass production. For this reason, they are suitable wood for bioenergy. For this purpose, various cultivated hybrids are grown, which are among the fastest growing trees in Slovakia. Their softwood is well workable into various forms of fuel, which is also used for paper and veneer production. About 110 poplar species are known, of which only 3 species are native to Slovakia: *Populus tremula*, *Populus alba* and the *Populus nigra*. In addition to the mentioned species, there is also a hybrid of poplar (*Populus x canadensis*) in Slovakia.

Populus x euroamericana MAX 4 (Figure 17) is a clone which originates in Japan and was created by crossing *Populus maximowiczii* × *Populus nigra*.



Figure 17 *Populus x euroamericana* (Source: BOMENGIDS 2019)

The leaves are as broad as the length of the main vein on the lush shoots, broadly ovate, with a short tip at the top. The edge of the leaf is shallowly crenate and strongly undulating. The blade is bright green on the upper side with a lighter, distinctly whitish vein. (ČÍŽEK, ČÍŽKOVÁ 2009)

Blade-based glands are poorly developed, usually two in each. Very short haired petiole grows to about half the length of the main vein. The leaves on the side shoots are smaller, round, with a base broadly wedge-shaped and with a more pronounced, spirally curved tip. (ČÍŽEK, ČÍŽKOVÁ 2009)

The buds are conical, up to 13 mm long, adjacent to the shoots, with a sharp tip covered with a drop of light brown balsam. It sprouts very early and the colour of the leaves is light green. Annual lush shoots are in the upper part of brown green to grey-green with irregular lighter spots. They are almost circular on the cross-section, with up to five slightly rounded edges

at the top. Lenticels are whitish in colour and elongated in shape, up to 3 mm long. (ČÍŽEK, ČÍŽKOVÁ 2009)

The stem of young trees is continuous and straight. The bark remains smooth for a long time, initially light gray-green, later light yellow-gray with whitish lenticelas. The crown is broadly oval, sparse with fine branching. (ČÍŽEK, ČÍŽKOVÁ 2009)

Poplar could easily be agamic propagated. Genetic selection and improvement of growth capacity and healthy individuals have been very efficient. They can be grown for biomass production, as carbon sinks to mitigate carbon dioxide production and for buffering against nutrient leakage. At the beginning of the 1900`s the first industrial poplar plantations were established in Italy (FAO 1980).

Natural hybrids of native and North American species were the most commonly planted trees. Plantations are usually established on fertile soils with rotation periods of 10–15 years and a spacing of 4 × 4 m (GUZINA ET AL. 1979). The rotation period of poplar plantations, however, is dependent on the initial plant density and growth rate (KRAUTER ET AL. 2003).

Poplar stumps are removed after tree felling as a way of avoiding the risk of pathogen attacks on seedlings in the new plantation (VERANI ET AL. 2008). After harvesting a poplar stand, there are at least two alternatives for the site:

- Utilize the sprouting capacity of the poplar stumps. The sprouts can be harvested in a 5 – 10 years rotation or thinned leaving only one sprout per stump for later harvest of plant wood.
- Extract the stumps with or without parts of the root system to allow subsequent re-planting of trees or cultivation of cereals.

When choosing a suitable species or clone for commercial forestry, the level of basic density is an important factor. The basic density indicates the amount of dry weight solid wood by tree volume.

Poplar can be planted using a variety of methods: poles (2.0–3.0 m stout poles), stakes or wands (0.75–1.0 m), un-rooted cuttings (0.4–0.5 m) or rooted cuttings (0.8–1.0 m); (CHARLTON ET AL. 2007). If poplar poles are planted to a depth of 0.8 m, a deep taproot forms (SPINELLI ET AL. 2005). In Italy these stumps are harvested using a special tool, which removes the stump and taproots without the lateral roots. The shape of a root system is determined by site conditions (STOKES AND MATTHECK 1996). A shallow root system develops even in species that usually produce deep roots if the soil has a high-water table. According to KÖSTLER ET AL. (1968) the root-system of poplar is shallow with a root length of up to 40 m. In addition, STOKES AND MATTHECK (1996) reported a shallow root system for poplar. In Sweden, only rooted cuttings have been used to establish poplar plantations. Thus, the stumps did not have roots and most of the lateral roots were found between 5 and 30 cm below ground level. The mean root length of the course (≥ 50 mm) roots was 6.71 m.

In a study by FAULKNER (1976) the root system of *Populus x euroamericana* clone was found between 5 and 20 cm below ground level and in a study of 12-year-old Veronese poplar (*Populus deltoides* × *nigra*) stands in New Zealand most of the coarse roots (≥ 2 mm) were found within the top 40 cm of the soil profile (MCIVOR ET AL. 2009).

LIESKOVSKÝ (2015) was concerned with the determination of *Populus x euroamericana* MAX4 clone production capabilities. In order to obtain empirical material, plots were monitored in 2013, in which 284,000 cuttings were planted on a reduced area of 35.5 ha.

The determination of production characteristics of woody plants was based on the application of the general principles of dendrometric quantities determination with the application of the direct measurement method on the plots according to a pre-prepared sampling plan. The average stem diameter was measured at 1.3 m with an electronic diameter with accuracy of 0.1 mm. The height was measured with a height gauge and determined to an accuracy of 0.1 m. The results of the survey showed that the average yield on the monitored area was 95.9%, the diameter of the average stem at $d_{1.3}$ was 7.8 mm and the average height 1.48 m.

FORTIER ET AL. 2019 stated that after 6 years of growth, total aboveground biomass production (stems + branches + leaves) reached $112.8 \text{ t dm}\cdot\text{ha}^{-1}$ and total leafless biomass production (stems + branches) reached $101.1 \text{ t dm}\cdot\text{ha}^{-1}$ at this site, while stem wood volume attained $237.5 \text{ m}^3\cdot\text{ha}^{-1}$. Yields as low as $14.2 \text{ t dm}\cdot\text{ha}^{-1}$ for total biomass and $24.8 \text{ m}^3\cdot\text{ha}^{-1}$ for total stem volume were also observed at the Magog site. Highest yields were obtained on the most fertile sites, particularly in terms of NO_3 supply rate. Mean stem volume per tree was highly correlated with NO_3 supply rate in soils ($R^2 = 0.58$, $p < 0.001$). Clone effects were also detected for most of the variables measured. Total aboveground biomass and total stem volume production were high for clone 3729 (*Populus nigra* × *Populus maximowiczii*) ($73.1 \text{ t dm}\cdot\text{ha}^{-1}$ and $134.2 \text{ m}^3\cdot\text{ha}^{-1}$), although not statistically different from clone 915311 (*Populus maximowiczii* × *Populus balsamifera*). However, mean whole-tree biomass (including leaves) was significantly higher for clone 3729 (38.8 kg dm per tree).

According to KLASNJA ET AL. (2006) varying densities and the number of trees per unit area determine the main characteristics of sizes, quantity and structural composition of the yielded biomass. Thus, in the plantation with one-year rotation, average diameter amounts 2.0 to 2.8 cm, height 3.0 to 3.5 m. In the plantations with two rotations, average diameters are 8.6 to 12.8 cm and height 12.3 to 14.4 m. This is also the main reason why volume percentage of bark in total biomass in the plantations with one-year rotations is about 47%, and in the plantations with two rotations the share of bark is about 16 %.

Further, under planting density of 40,000 plants per ha production cycle is one year, attaining small dimensions and also yields ($15 - 80 \text{ m}^3\cdot\text{ha}^{-1}$). In the plantations established with density 1.20×0.50 , i.e. 16,670 plants, production cycle was 2 years and yields were $25 - 55 \text{ m}^3\cdot\text{ha}^{-1}$ (ca. 50,000 trees per hectare). Plantations established with plant spacing 1.80×0.80 to 2.0×2.0 , i.e. 2,500 – 7,000 plants per hectare provides the yields of $40 - 60 \text{ m}^3\cdot\text{ha}^{-1}$. Their production cycle is of 3 – 4 years.

The reported maximum yields lie between 20 and 35 t·ha⁻¹·y⁻¹ (BEALE, HEYWOOD 1997). Other authors introduce the yields of 10 – 12 t·ha⁻¹·y⁻¹ Central Europe and North America temperate regions (SCHOLZ AND ELLERBROCK 2002; KAUTER ET AL 2003; DECKMYN ET AL. 2004; FISCHER ET AL. 2005).

4.1.2 *Salix viminalis* clone TORA

Salix sp. grown as short rotation coppice (SRC), are being developed as sources of biomass for the production of bioenergy, biofuels and high value products for the chemical industries especially across Europe, north-eastern and midwestern U.S. and Canada (KEOLEIAN AND VOLK 2005; VOLK ET AL. 2006; KUZOVKINA ET AL. 2008; KARP 2014). Advantages of using *Salix* for biomass production include fast growth and high biomass production, ability to re-sprout after multiple harvests, ease of vegetative propagation from dormant woody cuttings, a wide genetic base for breeding and a positive greenhouse gas (GHG) balance. (KEOLEIAN AND VOLK 2005; VOLK ET AL. 2006; KUZOVKINA ET AL. 2008; KARP AND SHIELD 2008; DJOMO ET AL. 2011; KARP 2014)

Salix viminalis (Figure 18) is a ligneous and shrubby plant, having a rapid growth up to 3 – 3.5 cm per day and a lifespan of 20 – 25 years. In 2 – 3 years it can grow at shoots height of 6 – 7 m with a shoots base diameter of 6-8 cm. Beginning with the 2 – 3rd year a yield of at least 35 t·ha⁻¹·year⁻¹ (wet) biomass can be obtained in form of raw biomass – bales, chips, or straight rods and pellets or briquettes.



Figure 18 *Salix viminalis* (Source: ALCHETRON 2018)

It develops very well under temperate climate conditions, with average annual temperatures of 8 – 12 °C. It does not demand that much light, if the recommended densities are satisfied. Tolerates frost up to -30 °C and moderate drought. It can be grown on different soil types, supporting a pH between 3.5 and 10, the ideal value being in range 5.5 to 7.5. It has a zero tolerance to salty soils. (BALKAN GREEN ENERGY USE 2016)

Yields depend on soil quality, climate and water availability. Out of these elements water availability is the by far the most required for the yield maximization. In given sense, if there are no natural conditions perfectly suitable, irrigation needs to be implemented in order to reach maximal yields and profit.

Soil preparation for *Salix* plantation begins in the year before the establishment of the plantation by removing the weeds by administration of non-selective (total) herbicides. After removing the vegetation, the land is deeply mellowed after it was ploughed and (disc/roto) harrowed. Once the soil is prepared basic fertilization may be carried out. At early spring land should be ready for hosting *Salix* cuttings.

Salix as a species is autochthonous over East Europe though with a different genome. Due to intense hybridization (and NOT genetic modification) many varieties are available today. All of them bear benefits of extremely fast growth, high yields and low soil requirements.

For the establishment of the plantation there are selected energetic willow varieties and hybrids, each adapted to specific soil and climate conditions. Planting material – cuttings, must be of good quality and certified.

Usually accepted time for planting is during the spring as early as possible, when there is moisture in the soil. Planting is done in twin rows with distances in between, to allow the access for maintenance, harvesting and transport mechanization. Axial plants distance in the row is 75 cm, distance between two rows is 75 cm while the space between twin neighbouring rows is 1.5 m. This way a planting density of c.a. 14,000 cuttings per ha is obtained.

Planting can be done mechanically or manually.

High yields may be established in most of the East Europe, even on low quality soils, in case there is enough water through vegetative season. Climate changes have caused rapidly growing arid conditions thus making irrigation a must consider it.

On properly maintained plantations with the irrigation system in place annual yields of 60 – 70 t·ha⁻¹ (wet mass at harvesting) may be reached. Optimal harvesting frequency is every second year, thus making harvesting mass of 130 or more t·ha⁻¹. To gain more tangible image it would require a bundle of *Salix* to weight ca. 9 kg since there are 14,000 plants·ha⁻¹. Without irrigation over last 5 – 6 years average yields reached at the most 30 – 35 t·ha⁻¹·year⁻¹ on well administered plantations. (BALKAN GREEN ENERGY USE 2016)

The first harvesting is usually performed in the 2nd or 3rd year, i.e. when the yield exceeds 25 – 30 t·ha⁻¹. Harvesting frequency is in direct relation to the yield and defers from region

to region whereas in Western Balkans harvesting frequency should be performed bi-annually. Harvesting happens when the plants shed their leaves, in the vegetative rest period from November until March. (BALKAN GREEN ENERGY USE 2016)

Specialized machines cut the rods in various shapes: in form of chips, which are collected in trailers and piled in sheds, wrapped in round bales of 400 – 500 kg stored in open space or as straight shoots – depending on the end user requirements. Moisture content at harvest is about 45 – 50 % and more. After a storage period of about 2 – 3 months bales left on the field due to draught and the sun spontaneously decrease moisture to 10 % – 20 % requiring no sheds. Such stored biomass does not lose any quality in time.

Besides the above ground biomass, *Salix* has also an extensive below ground root system, which increases in size as the plant ages (MATHEWS 2001; PACALDO 2013). The root system stores essential carbohydrate reserves needed primarily for respiration and growth, and, to a lesser extent, symbiotic associations and exudation (LAMBERS 1987; DICKMANN AND PREGITZER 1992). Mobilisation of carbohydrate reserves in the roots and cut stump are particularly important for re-sprouting of shoots after coppicing (DICKMANN AND PREGITZER 1992; SENNERBY-FORSSE ET AL. 1992; TSCHAPLINSKI AND BLAKE 1994; VON FIRCKS AND SENNERBY-FORSSE 1998; REGIER ET AL. 2010).

Estimates of below ground biomass production and the allocation of total plant biomass to above and below ground pools in willow are limited as roots are notoriously difficult and time consuming to sample. Studies are generally restricted to a small number of genotypes sampled at a few points during growth, often on roots and shoots of different ages which makes comparisons problematic.

RYTTER (2001) studied roots of 1 – 3 year old plants of *Salix viminalis* in lysimeters. Annual net primary productivity of root biomass increased from 1 to 3 years, but the actual allocation below ground declined each year from 25 – 30 % to 10 – 12 % of total biomass in 1- and 3-year old plants, respectively. Both values increased markedly if fine root turnover was included in the estimation.

Knowledge of below ground biomass in perennial crops such as willow is important for understanding the GHG balance of bioenergy systems, as the roots have considerable potential to contribute towards the carbon (C) sequestration potential of the crop (ZAN ET AL. 2001; LEMUS AND LAL 2005; SARTORI ET AL. 2006; RYTTER 2012; AGOSTINI ET AL. 2015).

4.1.3 *Paulownia tomentosa*

The fast-growing woody crops are a very important source for the generation of the bioenergetics biomass. *Paulownia sp.* is a plant part of this group, and because of its fast growth, multiple values and high adaptability with climate conditions, is set recently in the centre of the intention. *Paulownia* is one of the fastest growing species in the world with low concentration of ash, sulphur (S) and nitrogen (N) and high calorific energy from its wood. It is considered as an energetic crop adequate to produce the solid bicarbonates and the bioethanol. (ICKA ET AL. 2016)

Paulownia (Figure19) is recognized with many names like Princess Tree, Empress Tree, Royal tree, Kiri Tree, Phoenix tree etc. (INNES 2009; BIKFALVI 2013).



Figure 19 *Paulownia tomentosa* (Source: VAN DER BERK NURSERIES 2019)

Paulownia genus includes 6 – 17 species (depending on the taxonomic authorities) (ATES ET AL. 2008; WOODS 2008). It is a member of monogenetic family of *Paulowniaceae* often related to *Scrophulariaceae* (WOODS 2008; INNES 2009) or *Bignoniaceae* (INNES 2009).

The most important species of this genus are *Paulownia albiphloea*, *Paulownia australis*, *Paulownia catalpifolia*, *Paulownia elongata*, *Paulownia fargesii*, *Paulownia fortunei*, *Paulownia kawakamii*, and *Paulownia tomentosa* (YADAV ET AL. 2013).

The original home of *Paulownia* is Southeast Asia. The first Paulowia, namely *Paulownia tomentosa*, which original area of expansion is represented by Central and Western China (ZHAO-HUA ET AL. 1986; ROLOFF & BÄRTELS 1996), was introduced to Central Europe in 1834 (KIERMEIER 1977) as an ornamental tree.

MÁRTONFI (1997) stated that *Paulownia tomentosa* has been grown as an ornamental tree in Slovakia since approximately 1870 and currently the number of adults grown mostly in parks. There are only slightly more than 100 trees in the whole territory. BARANČOK ET AL. (1999) referred the *Paulownia tomentosa* as one of the first *Paulownia* planted in Slovakia,

in the Chateau Park in Hlohovec. Its age is estimated at 200 years (height of 12 m, stem perimeter of 441 cm, crown diameter of 6 m). GOJDIČOVÁ ET AL. (2002) in the List of non-natives, invasive and expansive vascular plants classified *Paulownia tomentosa* as a frequently run riot taxon.

The original species of *Paulownia tomentosa* is 10 – 20 m tall, with a spherical thin crown. Its bark is smooth, brownish gray or gray, with large, reddish-yellow lenticels, the young branches are rusty brownish fuzzes, later glaucous. The buds are fuzzy, with striking leaf scars. The leaves are deciduous, opposite, pedicellate, stems densely hairy, up to 35 cm long. The blade is 15 – 30 (40) × 15 – 30 cm large, broadly ovate to heart-ovate, with a heart-like base, whole-edge or 3-lobed on the margin, at the top clear, initially green or dark green, velvety hairy, matt rube dense grey fuzz. The flowering is formed by a multi-erect upright broom, 20 – 35 cm long. Spindle and buds are rusty hairy. The flowers are large, fragrant, pink to pale blue-violet. It blooms in May-June, before the leaves sprout. The fruit is a woody, two-capsule multi-seed capsule, 2 – 4 × 1.5 – 2 cm large, with a narrow tip on.

They are mainly tropical and subtropical plants and some monocotyledonous plants, e.g. corn, millet but also sugar cane. C₄ plants have a different anatomical leaf structure than most temperate zone plants (so-called C₃ plants). They have two types of chloroplasts - mesophyll and chloroplasts of the vascular bundle, which allows more economical use of CO₂.

Paulownia trees are fast-growing trees, which are characterized in particular by large leaves, which enable the assimilation of solar energy (C₄ photosynthesis) very efficiently and also contribute significantly to the storage of CO₂, which can also contribute significantly to mitigating climate change in global warming. They can grow under extreme conditions, with the temperature range for growing individual *Paulownia* clones from -33 to +48 °C, annual rainfall of around 500 mm, and soil pH from 5 to 8.9. The trees have a deep root system, for example, with the Spanish clone R112 (OXYTREE), the root system is reported to reach a depth of 9 m.

Paulownia trees can be grown, depending on the variety (clone), for timber production or specifically for biomass production only. When the stem is trimmed, new stems grow out of the remaining stump and root, and after unification the new sprout shoot is able to fully replace the original tree. The younger ones are growing even faster just because of the existence of a functioning large root system.

In natural conditions in 10 years *Paulownia* sp. develops a stem with diameter of 30 – 40 cm, measured 1,2 m from the earth, producing a volume of 0.3 – 0.5 m³ (YADAV ET AL., 2013; ATES ET AL. 2008). According ATES ET AL. (2008) and ANGELOV (2010),

each Paulownia tree aged 5 – 7 years old can generate 1 m³ timber in a surface with density of 2,000 plants per ha, offering a total production of 330 t·ha⁻¹. In the areas planted with a smaller number of plants per surface unit can reach a production of 150 t·ha⁻¹.

According to JANKOVIČ ET AL. (2016), clone OXYTREE has the stem perimeter of 80 – 85 cm already in the 3rd year. In the 6th year, the stem has the perimeter of 35 cm and height of 16 m.

Paulownia growers also report that during a 6 to 7-year growth cycle, the processing of leaves and branches into biomass can be monetized, and after the growth has been harvested, the timber can be harvested and monetized up to 3 times for 20 years and finally it is possible to monetize the root itself.

An important economic aspect of plantation is the use of *Paulownia* clones as a source of timber and fuel wood, biomass and feed. In addition to rapid growth, they are also characterized by high quality wood, which is light but relatively hard (also called aluminium among the trees). Wood production ranges from 0.4 to 0.6 m³ of wood from a 5 to 7-year-old tree. The popularity of this wood on the world market was ensured by its dimensional stability and high ignition value. The average wood density is about 0.35 g·cm⁻³, it is easy to dry it by air, without serious corrosive drying defects. It has a high strength-to-weight ratio, low shrinkage coefficient, and does not warp or crack. It is resistant to rot. The wood is light and yet extremely strong, well-workable, mostly without knots, with a silky lustre. It can be used in construction, joinery, furniture, musical instruments, shipbuilding, aircraft, paper, plywood, etc. sawn wood is also sold for special solid wood products, OSB boards, veneers and plant to produce fine paper, biomass (fuel), etc.

Paulownia timber is estimated to be adequate for its usage to the cellulose plant industry and as solid biofuels (YADAV ET AL. 2013; ATES ET AL. 2008).

By-products are large leaves, which can serve both as pet food (e.g. cattle, ostriches, hares) and as a substitute for soil chemical fertilizers due to the high protein and nitrogen content of the leaves. The leaves are large in their youth, later smaller. The literature states that a 10-year-old tree can produce up to 30 kg of dry foliage per year and 400 kg of young branches that need to be cut to the desired height, which can be used to produce biomass.

The root, which is collected after the plantation, is used by manufacturers of musical instruments and sports equipment. The flowers are large (20 – 30 cm), strongly scented, rich in pollen and honey, so it is also used in apiculture.

Paulownia timber has low thermo-conductivity (0.26 – 0.36 kJ·m⁻¹·hr⁻¹·C⁻¹) and natural resistance against fire and damages (EL-SHOWK ET AL. 2003), it is resistant against the wood

worms and termites because of the high content of tannins (ANGELOV 2010). Because of the fast growth and the high cellulose concentration up to 440 g cellulose per kg (YADAV ET AL. 2013)

Calorific value of *Paulownia* biomass is higher than that of coal (and forest biomass) ($20.9 \text{ kJ}\cdot\text{g}^{-1}$), lower with air pollutants as sulphur, lower compound compared to other biomasses and the fast growth factor and the renewable factor make this plant suitable for environmental profitability (LAWRENCE 2011).

Paulownia is recommended to be cultivated at altitudes up to 700 m above sea level. The plant is not very sensitive to soil type, but it is important that the soil is deep and drained well. Heavy clay soils or very acid soils are not suitable for it. Trees need a lot of light. *Paulownia* does not benefit from high groundwater levels and should be at least 1.5 m below ground level. Given the high-water requirements, especially in the first three years after planting, it is necessary to ensure the irrigation of young plants. Older plants could be grown without irrigation after creating a robust and deep root system. Before planting, it is recommended to plough and fertilize the soil – preferably by a well-matured manure. When planting seedlings, it is advisable to add to each well hydrogel, respectively mycorrhizal agent. After the planting is finished, the area should be grubbed up and returned to agricultural crops.

4.1.4 *Sida hermaphrodita*

The common name for *Sida hermaphrodita* (Figure 20) is Virginia mallow or Virginia fanpetals, referring to its origin in Northern America. However, *Sida* is hardly found in Virginia, and its main area of distribution is in the adjacent states to the west and north.



Figure 20 *Sida hermaphrodita* (Source: BIOENERGY CROPS 2013)

Botanically, the genus *Sida* belongs to the *Malvaceae* family, hence the reference to mallow in one of its common names.

It thrives on moist but opens to partially shaded habitats on riverine terraces and floodplains, including disturbed situations along railroad banks and roadsides (SPOONER ET AL. 1985 IN NAHM, MORHART 2018).

Due to its specific habitat preferences, *Sida* is considered a rare species in its natural range of distribution. It is a perennial herb with shoots that emerge in April from a well-developed rhizome, its buds being situated at the base of the stems of the previous year.

It seems likely that *Sida* reproduces both sexually via seed germination, but also asexually via spreading rhizomes (ENVIRONMENT CANADA, 2015). In general, during an estimated plantation lifetime of 20 years, *Sida* is deemed rather unsusceptible toward pests and diseases, although it can be affected by *Sclerotinia sclerotiorum* (HALLER, FRITZ 2015; REMLEIN-STAROSTA ET AL. 2016). It can withstand temperatures of up to $-35\text{ }^{\circ}\text{C}$ without problems (BORKOWSKA ET AL. 2006). Still, *Sida* can be considered a thermophilous species in Central Europe (FRANZARING ET AL. 2015 IN NAHM, MORHART 2018), and although it is generally considered resistant to temporary droughts (SMOLIŃSKI ET AL. 2011 IN NAHM, MORHART 2018).

Its growth performance appears to react more sensitively to reductions of water availability than other non-woody energy crops (JANKOWSKI ET AL. 2016 IN NAHM, MORHART 2018).

Sida flowers abundantly, from July onwards until the first frost, thus providing ample pollinator resource. It can yield up to 120 kg honey per hectare (BORKOWSKA ET AL. 2006 IN NAHM, MORHART 2018). But not only insects seem to profit from *Sida*. In a study in which the number of earthworms and their total biomass were determined in the soil under seven different perennial crops including *Sida* and maize, both parameters reached their maximum under *Sida*, thus pointing to its potential to valorise also the soil ecologically (EMMERLING 2014). Although *Sida* produces similar amounts of biomass as short-rotation crops, its water demand amounts to only half of the water demand of woody short rotation crops such as willow (BORKOWSKA, MOLAS, 2012 IN NAHM, MORHART 2018). Moreover, compared to barley and potato, it did not influence the soil moisture content significantly (CETNER ET AL. 2014 IN NAHM, MORHART 2018). In general, perennial crops such as short-rotation crops, and thus, flowering *Sida* plants in particular, can be expected to reduce soil erosion and nitrate leaching, to improve the soil quality, to increase biodiversity, and to upgrade the landscape experience for people in open arable settings (BUTLER MANNING ET AL. 2015 IN NAHM, MORHART 2018).

Sida can grow more than 4 m in height within one vegetation period and is able to develop more than 40 shoots per 1 m^2 (BORKOWSKA, MOLAS, 2012 IN NAHM, MORHART 2018). In short, *Sida* can be expected to generate a variety of ecosystem services, whilst simultaneously producing considerable amounts of utilizable biomass under favourable growth conditions.

In the year of the establishment of a plantation, the biomass yield of *Sida* is typically low. In the second or third year, it increases considerably. Nevertheless, this increase depends on the soil and weather conditions, fertilizers applied, and careful weed control. It might also depend on the method chosen for the establishment, using seeds, seedlings, and root cuttings. In general, root cuttings seemed to result in the highest biomass productivity (BORKOWSKA, MOLAS 2012; TWORKOWSKI ET AL. 2014).

Sida's annual biomass productivity ranks between 8.7 and 20.3 t of dry matter per 1 ha ($\text{t dm}\cdot\text{ha}^{-1}$).

In most cases, the annual yield of *Sida* exceeded $\text{t dm}\cdot\text{ha}^{-1}$ after the first two years of growth. (NAHM, MORHART 2018).

Regarding the comparison with other perennial energy crops, the amounts of dry biomass rank in the same dimensions as that of other solid fuel feedstock plants such as short-rotation crops and *Miscanthus*.

In direct experimental comparisons, *Sida's* biomass productivity exceeded that of willow clones considerably (BORKOWSKA & MOLAS 2012, 2013 IN NAHM, MORHART 2018) and produced also higher amounts of dry matter compared to *Miscanthus* (SLEPETYS ET AL. 2012 IN NAHM, MORHART 2018).

In other studies, its biomass yield was lower compared to that of *Miscanthus* (KUŚ ET AL., 2008; BORKOWSKA, MOLAS 2013 IN NAHM, MORHART 2018) and that of willow (KUŚ ET AL. 2008 IN NAHM, MORHART 2018). These findings signify that *Sida's* biomass productivity is dependent on soil and climate characteristics, but in general, it can compete well with better known and already established energy crops. (NAHM, MORHART 2018)

The greatest interest in *Sida* lies in its potentials to be used as a renewable energy source. Hence, *Sida* was frequently investigated regarding its thermophysical and biochemical properties in the context of direct combustion and biogas production. When used as solid fuel, parameters often determined are the higher heating value (HHV) and the lower heating value (LHV). In ten studies considered in this review, the HHV of *Sida* ranked between 16.5 and 19.5 $\text{MJ}\cdot\text{kg}^{-1}$ dry matter (dm) at an average of $18.4 \pm 0.9 \text{ MJ}\cdot\text{kg}^{-1} \text{ dm}$; the LHV between 14.0 and 17.2 $\text{MJ}\cdot\text{kg}^{-1} \text{ dm}$ at an average of $16.1 \pm 1.2 \text{ MJ}\cdot\text{kg}^{-1} \text{ dm}$ (BORKOWSKA ET AL. 2009, 2016; WRÓBLEWSKA ET AL. 2009; SMOLIŃSKI ET AL. 2011; SZYSZLAK-BARGLOWICZ ET AL. 2012; STOLARSKI ET AL. 2013, 2014; FRANZARING ET AL. 2014; TWORKOWSKI ET AL. 2014; SIAUDINIS ET AL. 2015; JABLONOWSKI ET AL. 2016). Whilst the HHV of *Sida* biomass appeared to be rather constant from November until April in one study, the LHV

increased from 9.7 to 15.0 MJ·kg⁻¹ within this time span (STOLARSKI ET AL. 2014), presumably owing to the changing water content of the biomass.

Similarly, the amount of crude fibers in *Sida* biomass was strongly correlated with an increase of the HHV (SIAUDINIS ET AL. 2015), which is lower during the vegetation period when the *Sida* plants have leaves and flower. The amount of neutral detergent fibers, cellulose, hemicelluloses, and lignin in *Sida* material harvested during the flowering stage accounted for 60.2 % of dry matter (POKÓJ ET AL. 2015), whilst it amounted to about 80 % when cut in October (SLEPETYS ET AL. 2012). It even reached 88.1 % in another study, in which, however, the time of harvest was not given (MICHALSKA ET AL. 2015). In accordance with these findings, the contents of cellulose and lignin in the stems remained rather stable from June until December, whilst they increased during that time in the leaves (JABLONOWSKI ET AL. 2017).

Also, the ash content of field-grown *Sida* varies throughout the growing season, but typical ash contents of *Sida* analysed after harvesting between November and March fluctuated around 3 % of dm (e.g. STOLARSKI ET AL. 2014; JABLONOWSKI ET AL. 2017), ranging from 2.5 % (TWORKOWSKI ET AL. 2014) to 4.2 % (KACPRZAK ET AL. 2010). The latter source showed in addition that the ash content of *Sida* depended on the type and the amount of fertilizer applied. The ash high melting point of *Sida* exceeded 1,500 °C in one study, presumably because of its relatively high contents of CaCO₃ and other molecules that only melt at high temperatures, and the simultaneous presence of only very few low-melting potassium silicate compounds (JABLONOWSKI ET AL. 2017).

The water content of *Sida* stems determined in November can still exceed 40 % of dm (STOLARSKI ET AL. 2014). In January and February, at harvesting time, it can be expected to amount to 20 – 25 % of dm (STOLARSKI ET AL. 2014; TWORKOWSKI ET AL. 2014), and it can drop to about 10 % in March and April (LISOWSKI ET AL. 2011; JABLONOWSKI ET AL. 2017).

Several authors assessed the content of elements in *Sida* dry matter, digestates, or ashes (SZYSZLAK-BARGLOWICZ, PIEKARSKI 2009; KACPRZAK ET AL. 2010; BARBOSA ET AL. 2014; STOLARSKI ET AL. 2014; SZYSZLAK-BARGLOWICZ 2014; SIAUDINIS ET AL. 2015; WIERZBOWSKA ET AL. 2016; JABLONOWSKI ET AL. 2017). For example, carbon contents of *Sida* biomass remained rather constant from December until April, fluctuating around 49 % of dm (STOLARSKI ET AL. 2014). Values for the carbon (C) content in two other studies amounted to 45.9 and 47 %, and the nitrogen (N) content to 0.3 and 0.2 %, respectively (WRÓBLEWSKA ET AL. 2009; MICHALSKA ET AL. 2015).

In sum, the chemical composition of *Sida* is considered favourable for combustion in comparison with herbaceous biomass (SIAUDINIS ET AL. 2015), and problems related to ash melting such as slagging or bed agglomeration are expected to be negligible, as *Sida*'s combustion properties seem similar to those of woody biomass (JABLONOWSKI ET AL. 2017).

Regarding the energy expenses and energy yield of *Sida* cultivation, SIAUDINIS ET AL. (2015) performed a comparative analysis. Depending on the time of the year, *Sida*'s energy output amounted to 105 GJ·ha⁻¹, whilst that of cup plant reached 236 GJ·ha⁻¹. In another study, JANKOWSKI ET AL. (2016) determined an energy yield of *Sida* that reached 152 GJ·ha⁻¹, and it was considerably lower than that of other crops tested, such as *Miscanthus* and maize. The energy yields determined for *Sida* by SIAUDINIS ET AL. (2015) and JANKOWSKI ET AL. (2016) are much lower than that determined by JABLONOWSKI ET AL. (2017), who reported 440 GJ·ha⁻¹. This difference can be attributed to the considerably higher yield at the site studied by JABLONOWSKI ET AL. (2017). The *Sida* dry matter yield per ha that resulted in 440 GJ·ha⁻¹ was 23.4 t dm·ha⁻¹, whilst it amounted to only 6.2 t dm·ha⁻¹ across all treatments in the study of SIAUDINIS ET AL. (2015), and to 8.2 t dm·ha⁻¹ as an average of three years, when in addition, the biomass was harvested already during summer (JANKOWSKI ET AL. 2016).

4.1.5 *Miscanthus x giganteus*

Miscanthus x giganteus (Figure 21) is a highly productive, sterile, rhizomatous C₄ perennial grass that was collected in Yokohama, Japan in 1935 by Aksel Olsen. It was taken to Denmark where it was cultivated and spread throughout Europe and into North America for planting in horticultural settings. (LEWANDOWSKI ET AL. 2000; LINDE-LAURSEN 1993; SCALLY ET AL. 2001 IN ANDERSON ET AL. 2011)



Figure 21 *Miscanthus x giganteus* (Source: VICTORIANA NURSERY 2019)

Over time, it has been known as *Miscanthus sinensis* 'Giganteus', *Miscanthus giganteus*, *Miscanthus ogiformis* Honda, and *Miscanthus sacchariflorus* var. *brevibarbis* (Honda) Adati. (CLIFTON-BROWN ET AL. 2008 IN ANDERSON ET AL. 2011)

Miscanthus x giganteus is a perennial grass that utilizes the C₄ photosynthetic pathway. However, it is unique among C₄ species that are typically susceptible to damage at cold temperatures (LONG 1983). It retains high photosynthetic activity at low temperatures and remains highly productive in cold climates (LEWANTOWSKI ET AL. 2000; LINDE-LAURSEN 1993; BEALE ET AL 1996; NAIDU ET AL. 2003).

Owing to its high productivity across a variety of conditions, *Miscanthus x giganteus* has been grown successfully from the Mediterranean climates of Spain to as far north as Scandinavia. (CAROLL, SOMERVILLE 2009).

As a perennial grass, *Miscanthus x giganteus* generally reaches maximum productivity in its third year of production (CLIFTON-BROWN, LEWANDOWSKI 2000). During the establishment year, *Miscanthus x giganteus* can be planted from rhizomes or micro-propagated plantlets in April or May (BULLARD ET AL. 1995).

PYTER ET AL. (2007), introduced the yields of *Miscanthus x giganteus* under midwestern U.S. conditions. In the first year, the plant does not achieve maximum yield. After establishment, shoots emerge from the below-ground buds in April. By May, established plants reach nearly 2 m and canopy closure occurs by late May to early June (HEATON ET AL. 2008; DOHLEMAN, LONG 2009) enabling the grass to outcompete weeds and making weed control unnecessary (DOHLEMAN ET AL. 2009). Stand maturity is typically achieved after 2 or 3 years (CLIFTON-BROWN ET AL. 2001). Mature plants grow 3.5 – 4 m tall, with root structures reaching approximately 1.8 m deep. (CAROLL, SOMERVILLE 2009)

Full plant senescence begins after a killing frost occurs as early as September through mid to late October (PYTER ET AL. 2007).

Miscanthus x giganteus should be harvested following full senescence, and harvestable dry matter yield declines with the time left in the field beyond full senescence (LEWANDOWSKI, HEINZ 2003). At that point in order to avoid weather-related biomass losses over the winter (PYTER ET AL. 2007).

The oldest European plantation of *Miscanthus x giganteus* is a 25-year stand in Denmark and the estimated lifetime of a plantation is 25 years (LEWANDOWSKI ET AL. 2003)

Harvesting technology for *Miscanthus x giganteus* is currently an active area of research, but very little work has been published to date. Typically, modern hay-harvesting equipment, including cutters, conditioners and balers, is suitable for the harvest of *Miscanthus x giganteus*

in many situations. However, the equipment must be operated more slowly than in hay crops owing to the density and toughness of the *Miscanthus x giganteus* stems.

Biomass is typically harvested in late fall or winter, after the biomass dries in the field. Heaton reported that biomass moisture levels decreased from near 50% in October to below 10% in February; bales of biomass stored under cover can remain in good condition for at least 3 years (HEATON 2006).

Most of the literature reporting dry biomass yield for *Miscanthus x giganteus* originates from European studies. Ceiling peak biomass yields in established stands of *Miscanthus x giganteus* have approached 40 t dm·ha⁻¹ in some European locations, although it may take 3 – 5 years to achieve these ceiling yields (MIGUEZ ET AL. 2008).

Across Europe, harvestable yields of up to 25 t dm ha⁻¹ from established stands of *Miscanthus x giganteus* have been reported in areas between central Germany and southern Italy, while peak yields in central and northern Europe have ranged between 10 – 25 t dm·ha⁻¹, and in excess of 30 t dm·ha⁻¹ in southern Europe (LEWANDOWSKI ET AL. 2000).

HEATON ET AL. (2004) published a quantitative review of established *Miscanthus x giganteus* stands across Europe. They reported a mean peak biomass yield of 22 t dm·ha⁻¹, averaged across N rates and precipitation levels.

The major elemental composition based on dry matter in *Miscanthus* includes 47.1 to 49.7 % of carbon (C), 5.38 to 5.92 % of hydrogen (H,) and 41.4 to 44.6 % of oxygen (O), which reflects the variation of three major lignocellulosic components to some extent. (LEWANDOWSKI AND KIRCHERER 1997; HODGSON ET AL. 2011; LYGIN ET AL. 2011)

Mineral content including K, Cl, N, and S plays an important role in affecting biomass combustion quality. K and Cl enrichment can reduce ash melting point and cause corrosion issue. (BROSSE ET AL. 2012)

High concentrations of nitrogen (N) and sulphur (S) can result in emissions of NO_x and SO₂. Mineral content varies significantly depending on different genotypes, harvest time, locations, and even fertilization. Delayed spring harvest time benefits the *Miscanthus* combustion quality due to relatively lower K, Cl and N elemental level.

Harvestable *Miscanthus* yields (dry matter) have been estimated to be in the range of 2 to 44 t·ha⁻¹, yields of 27 to 44 t·ha⁻¹ have been reported in Europe and U.S. Midwestern locations, and 10 to 11 t·ha⁻¹ of small-scale trials at spring harvest in Montreal Canada. (PYTER ET AL. 2007, 2009; HEATON ET AL. 2008; SCURLOCK 1998)

However, there is very limited data in the literature from other continents.

The mass yield depends on many factors: genotypes, soil types, nutrients used, crop age, bioclimatic location, and the weather during the growing season. Many *Miscanthus* genotypes have been evaluated for their yields. *Miscanthus* × *giganteus* has great potential for biomass yields compared with other genotypes and is non-invasive. Higher yield can be achieved in the southern Europe irrigated area than northern Europe due to its higher average temperature and abundant global solar radiation.

4.1.6 Arundo donax

According to RIGGI ET AL. (2019), Giant reed (*Arundo donax* L.) is a perennial grass attracting the interest of scientific and industrial community due to its multipurpose attitude related to high biomass yield, phyto depuration properties, strong adaptation capacity to environmental conditions, greenhouse gas (GHG) emissions mitigation, and lower tillage requirement than traditional crop (COSENTINO ET AL. 2006, 2008, 2014; ANGELINI ET AL. 2009; MANTINEO ET AL. 2009; FABBRINI ET AL. 2019; HAWORTH ET AL. 2019).

Arundo donax diffusion at a commercial scale is counteracted by many challenges recently reviewed by GE ET AL. (2016).

Arundo donax L. (Figure 22), which is known as invasive species, (GE ET AL. 2016) deserves a special attention owing to tolerate deficient environment (CORNO ET AL. 2014), excessive growth rate (BOSCO ET AL. 2016), high biomass yield (KOLODZIEJ ET AL. 2016), ease of cultivation, and response to waste amendments (SMITH AND SLATER 2010). Moreover, energy generated from giant reed was reported to be much greater than energy expenditures in the production of biomass (ANGELINI ET AL. 2009; PARI ET AL. 2016). The ability of re-growth after cutting reduce production cost of *Arundo donax* following the plantation, but high biomass harvest increases nutrient removal from land and makes nitrogen fertilizer the major cost item for the cultivation (MANTINEO ET AL. 2009). At the same time, there has been a growing interest in using organic wastes directly in crop production to allow waste minimization and nutrient recycling as a sustainable waste management strategy (LAG-BROTONS ET AL. 2014). Therefore, nutrient-rich wastes, such as PAS, could be more sustainable option to meet long-term nutrient demand of high biomass yield and perennial energy crops that remove plenty of nutrients from the soil at each harvest cycle (BOSCO ET AL. 2016). Although poultry wastes have been scarcely studied as a natural fertilizer source for energy crops, the available data obtained from waste sources on biomass yields are promising (OCIEPA-KUBICKA ET AL. 2016).



Figure 22 *Arundo donax* (Source: MILLER 2004)

Regarding the environmental concern, there are numerous studies in literature reporting the pollutants transfer from waste amendments, such as sewage sludge and composts to the biomass feedstocks, as well as plant nutrients and trace elements at different experimental conditions. For instance, OCIEPA-KUBICKA ET AL. (2016) reported that application of sewage sludge to giant *Miscanthus* increased the plant tissue concentration of heavy metals (e.g. Zn, Cd, Pb, and Ni) as compared with conventional fertilization.

Likewise, JEGUIRIM ET AL. (2010) cultivated *Miscanthus* and *Arundo* plants with fertilization rates ranging from 10 to 300 t·ha⁻¹·y⁻¹ and found that biomass samples produced similar gaseous emissions in the combustion test.

The main constrains include potential negative environmental impacts (invasive species attitude), negative biomass quality traits (limiting transformation processes), but also limited experiences in crop management strategies (starting from propagation high costs).

Furthermore, being sterile, this species has a limited genetic variability (BALOGH ET AL. 2012; MARIANI ET AL. 2010), dramatically reducing the potential support of genetic improvement to its diffusion as a multipurpose crop. Nevertheless, high correlations between parent–progeny for some biometrical traits (culm height and diameter) have been assessed and they could be proposed as drivers for clonal selection (PILU ET AL. 2014).

Differences in biomass quality traits (ash content, biomass methane and biogas potential) have recently emerged in large collections of *Arundo donax*, from different geographical areas in Europe and China (AMADUCCI AND PEREGO 2015; COSENTINO ET AL. 2016; CURT ET AL. 2018). The ranges of observed differences between clones, and the genetic control of ash and hemicellulose content, reported in some energy crop (FABIO ET AL. 2017), sustain further studies to ascertain the heritability of these characters.

Photosynthetic capacity markedly characterizes giant reed with its high assimilation rate, uncommon for a C₃ species, and for its tolerance to stressing environmental condition (NACKLEY ET AL. 2014). However, the studies conducted on leaf level gas exchange, punctually measuring photosynthesis and transpiration rate, were not able to reveal relevant differences between clones (HAWORTH ET AL. 2017 a,b,c).

Nevertheless, knowledge on the relationship between soil water availability and physiological and productive traits could greatly contribute to describe plant responses to environmental drivers, but also to precisely define crop needs in term of irrigation. In this view, eco-physiological studies, within agricultural context, could support plant selection process to contribute to ideotype definition and mining (HAWORTH ET AL. 2018a). In a recent work, FABBRINI ET AL. (2019) proposed for semi-arid environment with dry and hot season, the stomatal resistance as a selection driver discriminating between ecotypes with different attitude to regulate water transpiration.

The physiological responses to soil water status tend not to be linear (JONES 2007), and species-specific thresholds could be ascertained for assimilation rate, leaf transpiration and stomatal conductance (FLEXAS ET AL. 2004; COSENTINO ET AL., 2016; ROMERO-MUNAR ET AL. 2018; HAWORTH ET AL. 2018b). In this view, gas exchange response-curve to environmental variables could contribute to obtain a deeper interpretation of eco-physiological dynamic, escaping the effects of momentary ambient conditions. According to RASCHER ET AL. (2000), the so-called cardinal points obtained in light response curve, resulting from a set of different light level measurements, provide highly useful data for the eco-physiological characterization of plant ecophysiology.

Yield potential varied significantly between clones, as MOROCCO (26.4 t·ha⁻¹) emerged as the most productive. Expressing the yield of Sicily and Tuscany as a percentage of the best performing MOROCCO, the relative performances were equal to 83 % and 70 %, respectively. The observed values, related to a 2 year old *Arundo donax*, were similar to those reported by COSENTINO ET AL. (2006, 2014), HIDALGO AND FERNANDEZ (2000) and ERICKSON ET AL. (2012), but slightly lower when compared to 30 t·ha⁻¹ reported by DRAGONI ET AL. (2015) for a two-year crop, and significantly lower to 38–40 t·ha⁻¹ reported by ANGELINI ET AL. (2009) for a mature crop elder then 4 years.

The harvest period affected significantly the biomass production, and the lower yield was obtained with the late harvest (76 % of the early yield). This result is similar to the results obtained in the same environment by BORIN ET AL. (2013), who reported that the late harvest was about 77 % lower relatively to the early one. The author argued that this reduction could

be ascribed to leaves and stalks falling to the ground when the harvest was delayed from autumn to late winter.

Interestingly, in study of RIGGI ET AL. (2019), irrigation appeared as the less affecting factor for yields, as the rain-fed treatment reached 89% of the performance reported by well-watered treatment. In contrast, an open field experiment involving nine ecotypes of different provenance (Italy, Greece, France) grown in a Xeric Mediterranean environment, showed that the ratio of rain-fed to irrigated yield ranged between 54 % and 76 % (CURT ET AL. 2018). The unusually large amount of precipitation occurred starting from September, surely masked the irrigation effects. Nevertheless, these reduced differences could be also explained by the capacity of the rain-fed treatment to grow, in our environment, in autumn/winter and to achieve a full recovery of net assimilation after soil water restoring. Stem height (described for the same experiment by HAWORTH ET AL. 2019) showed a higher daily increment in the stressed treatment following the late summer precipitations. Therefore, the rain-fed plants were able to maintain a higher photosynthesis and, in turn, a higher growth rate later in the year compared with irrigated plants that, in contrast, began to senescence earlier.

RIGGI ET AL. (2019) also noticed clear differences in biometric traits among clones, where MOROCCO showed higher values of stem height and basal diameter and a low leaves yield, while Tuscany exhibited higher stems density (number·m⁻²). These results confirmed the data already recorded during the establishment of the crop (previous year – data not reported) and are in keeping with the results reported by ZEGADA-LIZARAZU ET AL. (2018) obtained

with the same clones used in their experiment. They observed taller plant, a significant minor number of tillers (-38%) and 27 % higher dry biomass in the Moroccan ecotype than in Tuscany one, cultivated for two consecutive years in well-watered condition in rhizotrons. The authors stated that the higher productivity of MOROCCO clone could be related to the plant higher volume (i.e. height and diameter) and suggested that these traits should be taken into account in ecotypes selection activities.

COSENTINO ET AL. (2006), PILU ET AL. (2014), and FABBRINI ET AL. (2019) indicated that stem height and basal diameter had a moderate-to-high heritability. Consequently, these could be useful traits for clonal selection activities. Moreover, the Moroccan ecotype had more xylem vessels with a higher diameter and a lower structural density than the Tuscan ecotype (HAWORTH ET AL. 2017b), allowing a higher hydraulic conductivity that may favour rapid growth. Furthermore, clonal selection may take advantage also of inheritable phenotypic traits,

such as leaf area index, stem dry mass, stem density, number of nodes per stem, stem height and diameter, described by FABBRINI ET AL. (2019).

The use of *Arundo donax* as biofuel shows some difficulties connected to the high ash content that reduces thermal conversion efficiency and may cause problems to combustion process (COULSON ET AL. 2004; SMITH AND SLATER 2011). Nevertheless, new transformation processes and biorefinery approach for added value compound extraction contribute to expand the potential use of the crop escaping quality limitation (ANTONETTI ET AL. 2015).

The amount of ash, remarkable when compared with other energy crops, comes mainly from leaf tissues (COULSON ET AL. 2004; MONTI ET AL. 2008; NASSI O DI NASSO ET AL. 2010). AMADUCCI AND PEREGO (2015) reported significant difference among clones for the plant ash content ranging from 5.3 % to 8.1 %. MONTI ET AL. (2008) reported values for ash content of 11.3 % and 3.2 % for leaves and stems, respectively. Furthermore, CORNO ET AL. (2014) indicated a decrease in the total plant ash content along the growing season, ranging from 9.9% dry mass for the May samples to 3 % dry mass for the March samples. In comparable field conditions, SCORDIA ET AL. (2012) reported a value of 5.9 % in the whole plant ash content of the late harvest. (IN RIGGI ET AL. 2019)

In respect to the studied quality aspects, MOROCCO emerged for its positive traits. The lower ash content associated with the reduced leaves biomass indicates that this clone may potentially have the higher thermal conversion efficiency. (RIGGI ET AL. 2019)

Moreover, the lower ash content measured at late harvest in the whole biomass can also influence the technical decisions concerning crop management. According to RIGGI ET AL. (2019) results, the amount of ash in leaves were 17.0 and 10.7 % on dry matter basis for early and late harvest, respectively, whereas stems showed values around 4% irrespectively of the harvest dates. The observed reduction in the leaf yield at late harvest resulted in a relevant reduction in total amount of ash per hectare (about 45 % of the total ash content of the early harvest, i.e. 0.84 vs. 1.85 t·ha⁻¹, respectively). Therefore, the yield reduction observed in late harvest produced a quality improvement of the biomass. The differences emerged in terms of biomass quality (i.e. dry matter and ash content) could be adopted as driving lines of crop management approaches depending on destination of harvested biomass. When the quantity is the main goal (e.g. biogas production, biochemical compound extraction, etc.), product lost, due to the fall of leaves and stalks usually observed in late harvest, is obviously to be considered as a negative aspect. On the contrary, when the objective to reach is a lower amount of ash for combustion purpose, the late harvest could be preferred solution.

4.2 Methodology

To analyse the fire and energetic properties of selected species of woody and herbaceous biomass to specify the rating of its suitability for energy production purposes, there were several standardized but also progressive analytical methods used.

In this sub-chapter, there are introduced the methodological approaches focusing the test samples pre-processing and further testing.

First, we introduce the samples pre-processing procedure, followed by description of particular methodological approaches applied to determine the spontaneous ignition temperature, gross calorific value, heating value, ash content, mass loss during thermal loading, chemical composition and activation energy.

The samples of woody species were represented by the blocks with dimensions of $50 \times 40 \times 20$ mm in case of mass loss testing; and $20 \times 20 \times 10$ mm in case of spontaneous ignition temperature testing. In case of herbaceous energy crop samples, the embankment of 3 ± 0.05 g was used.

4.2.1 Analysis of spontaneous ignition temperature and induction period of samples

The tests were carried out with all the samples. Each energy crop sample weighted 3.0 ± 0.05 g. The samples of woody biomass were cut to prisms with dimensions of $20 \times 20 \times 10$ mm to be used for spontaneous ignition temperature determination and $50 \times 40 \times 20$ mm for mass loss studies.

Before the test, all the samples were conditioned according to the STN EN ISO 291 standard requirements. Totally, three samples of each woody biomass and herbaceous energy crops undergone testing.

To determine the temperature of spontaneous ignition, the incendiary hot-air oven (Setchkin furnace) was used and the methodology for testing the spontaneous ignition temperature, according to the STN ISO 871 standard, was applied.

Those analyses were performed in the laboratories and using research infrastructure of the Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen.

4.2.2 Gross calorific value, heating value and ash content analysis

To calculate the heating value, it was necessary to determine the gross caloric value of the samples. The IKA C200 calorimeter was used to determine it. The procedure was conducted in correspondence with the standard STN ISO 1928:2003-07 Solid fuels.

Determination of gross calorific value and calculation of heating value. In the test, the sample is burnt in a calorimetric bomb, filled with oxygen under the pressure of 3 – 5 MPa.

Based on the mathematical equation (3) introduced in the same standard, there were further calculated the heating values ($\text{KJ}\cdot\text{kg}^{-1}$) of the samples:

$$q_{v,net,m} = [q_{v,gr,d} - 206.0 \cdot w(H)_d] \cdot (1 - 0.01 \cdot M_T) - 23.5 \cdot M_T \quad (3)$$

Where:

$q_{v,net,m}$ – Heating value at constant volume and containing with water ($\text{kJ}\cdot\text{kg}^{-1}$)

$q_{v,gr,d}$ – Gross calorific value at constant volume without water content ($\text{kJ}\cdot\text{kg}^{-1}$)

$w(H)_d$ – Percentage of hydrogen (%)

M_T – Total water content of the fuel for which conversion is required - relative moisture (%)

In the calculations of heating value, the relative moisture content of 10 % was used.

Before the testing the samples were dried at 103 ± 2 °C to reach the moisture content of 0 % and further conditioned in a desiccator at the temperature of 20 ± 1 °C for 24 hrs.

Three measurements were made for each sample. The results show the average value of those measurements.

The procedure for ash determination was based on the requirements of the standard STN ISO 1171: 2003 (44 1378) Solid mineral fuels. Determination of ash. The principle of the method is the incineration of the sample, which is heated in air at a temperature of $815 \text{ °C} \pm 10 \text{ °C}$, specified at a rate and maintained at that constant temperature. For this purpose, the Muffle furnace was used. The ash content was calculated from the weight of the residue after incineration.

Those analyses were performed at laboratories and using the research infrastructure of the Department of Forest Harvesting, Logistics and Ameliorations, Faculty of Forestry, Technical University in Zvolen.

4.2.3 Thermal analyses

To study the thermal degradation processes, the following thermal analysis techniques were deployed: thermogravimetry analysis (TG/DTG) and differential scanning calorimetry (DSC). The samples undergoing testing were prepared (melted to required fraction) and further analysed according to the requirements specified in the standards STN EN ISO 11358-1 and STN EN ISO 11357-1.

In the thermogravimetric analyses the samples with weight of 10.0 ± 0.3 mg were used. The samples were tested using the Mettler TA 3000, the TC 10A processor and TG 50 thermogravimetric weights, at an air flow rate of $200 \text{ ml}\cdot\text{min}^{-1}$, at heating rates of 10, 15, 20, 25 °C·min⁻¹ and under standard test room conditions at the Accredited Laboratory of the Fire Research Institute of the Ministry of Interior of the Slovak Republic.

During the analysis, the percent mass loss of a test sample was recorded while the samples were being heated at above specified rates in an appropriate environment. At the Accredited Laboratory of the Fire Research Institute were also performed the DSC analyses with the samples.

In the DSC analyses the samples with weight of 1.5 ± 0.15 mg were used. The samples were tested using the Mettler DSC analyser.

4.2.4 Analysis of mass loss during sample thermal loading with radiant heat source

To study the mass loss of the samples, two different methods of mass loss analysis were deployed: the non-standard method of solids thermal properties testing and thermogravimetry (TG).

Using the first method, the samples of woody biomass and energy crops undergone thermal loading by a radiant heater with power of 1,000 W for a specific time (Figure 23). Woody biomass samples for 10 min and short rotation woody crops for 5 min. The mass loss of the samples (g) was measured for each 10 s interval. Totally, three samples of each woody biomass and short rotation woody crops undergone testing.

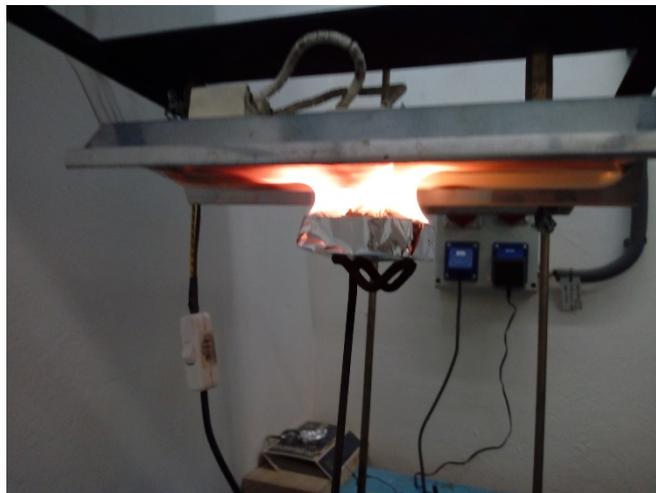


Figure 23 Thermal loading of samples with radiant heat source (Source: Authors)

Those analyses were performed in the laboratories and using research infrastructure of the Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen.

TG analyses was provided as a part of thermal analyses realised in the laboratories and with research infrastructure of the Fire Research Institute of the Ministry of Interior of the Slovak Republic. See the procedure description in sub-chapter 4.2.3.

4.2.5 Chemical analyses

The chemical analyses were focusing the elemental analysis and setting the content of extractives, lignin, holocellulose, hemicellulose and cellulose.

The elemental composition analysis of the fast-growing trees and energy crop samples was realized in the laboratories of the National Forest Centre, Zvolen, using the FLASH EA 1112 device. Using this device, there was analysed the content (mass) of carbon (C_{daf}), hydrogen (H_{daf}) and nitrogen (N_{daf}). The oxygen content (%) in the sample was calculated based on the formula (4):

$$O_{daf} = 100 - C_{daf} - H_{daf} - N_{daf} \quad (4)$$

For the purpose of chemical analysis focusing the content of extractives, lignin, holocellulose, hemicellulose and cellulose, first the samples were disintegrated and by grain size analysis arranged to fractions. A fractional piece of sample of 0.5 up to 1.0 mm was used for the chemical analysis. Extractive agents were determined in a Soxhlet apparatus by the mixture of ethanol and toluene (2:1) according to the standard ASTM D 1107-96. Lignin was determined according to the standard ASTM D 1106-96, and cellulose according to SEIFERT (1956). Measurements were performed on four replicates per sample.

Those analyses were performed in the laboratories and using research infrastructure of the Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology, Technical University in Zvolen.

4.2.6 Activation energy calculation

In general, the Arrhenius method for activation energy calculation belongs to the group of non-isothermal methods to calculate the reaction kinetics. Among the progressive methods recommended to be used for calculation of activation energy nowadays belong the iso-conversional methods like Ozawa-Flynn-Wall (OZAWA 1965; FLYNN ET AL. 1966), Kissinger (KISSINGER 1965), and Kissinger-Akahira-Sunose (AKAHIRA, SUNOSE (1971).

In the calculation of the activation energy according to Arrhenius, only the mean values of the spontaneous ignition temperature and induction period were involved.

The calculation of activation energy of spontaneous ignition was performed according to equation (5), which is an analogy to the equation of Arrhenius.

$$E = \ln\left(\frac{\tau}{A}\right) \times R \times T \quad (5)$$

Where:

- τ – Induction period of spontaneous ignition (s)
- A – Pre-exponential (frequency) factor (-)
- E – Activation energy of spontaneous ignition ($\text{J}\cdot\text{mol}^{-1}$)
- R – Gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
- T – Ignition thermodynamic temperature (K)

Further, kinetics of the combustion reaction for the biomass samples was described in terms of the activation energy ($\text{J}\cdot\text{mol}^{-1}$), calculated using three different iso-conversional kinetic methods: Ozawa-Flynn-Wall, Kissinger and ASTM-E698-05 (2018).

When using the Ozawa-Flynn-Wall method, the TG/DTG curves were used simultaneously to determine the activation energy values of biomass samples. At the same conversion levels, the following equation (6) was used, while the activation energy was obtained from the slope of the plot $\log(\beta)$ vs. $1/T$ at given conversion levels:

$$\left[\frac{d(\log \beta)}{d\left(\frac{1}{T}\right)} \right] = 0.4565 \left(\frac{E}{R} \right) \quad (6)$$

Where:

- E – activation energy ($\text{J}\cdot\text{mol}^{-1}$),
- R – ideal gas constant = $8.314 \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$,
- T – temperature (K) corresponding to the measured heating rate at same conversion,
- β – heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)

When applied the Kissinger method, the peak temperature from the DSC curve and heating rate for several thermal analysis curves were correlated and the activation energy was calculated based on the following equation (7).

$$\left[\frac{d\left(\frac{\ln \beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} \right] = - \left(\frac{E}{R} \right) \quad (7)$$

Where:

- E – activation energy ($\text{J}\cdot\text{mol}^{-1}$)
- R – ideal gas constant = $8.314 \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
- T_p – peak temperature (K)
- β – heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)

The activation energy was calculated from the slope of the plot $\ln(\beta/T_p^2)$ vs. $1/T_p$.

By ASTM method, there were plotted the reciprocal of temperatures at which the reaction peaks occur as a function of the logarithm (log) of respective heating rates. The activation energy was calculated based on the following equation (8):

$$E = -2.19R \left[\frac{d(\log_{10} \beta)}{d\frac{1}{T}} \right] \quad (8)$$

Where:

- E – activation energy ($\text{J}\cdot\text{mol}^{-1}$)
- R – ideal gas constant = $8.314 \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
- T – temperature (K) corresponding to the measured heating rate at same conversion
- β – heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)

4.3 Results and discussion

In this sub-chapter, we present and further discuss the results of the application of standardized and progressive analytical methods of fire engineering to determine selected fire and energy properties of selected woody and herbaceous biomass species.

4.3.1 Spontaneous ignition temperature and induction period analysis results

The measured data, together with the temperature recalculated values (inverse value of the temperature in °C to the thermodynamic temperature in K, necessary for the calculation of the activation energy), are shown in the Tables 3 – 9.

Table 3 shows an overview of the spontaneous ignition temperatures and induction periods reached by *Populus x euroamericana* clone MAX 4.

Table 3 Spontaneous ignition temperatures of *Populus x euroamericana* clone MAX 4

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t (°C) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K ⁻¹) |
|-----------------|-----------------------------|---|--|---|
| 1. | 339 | 425 | 698 | 0.001433 |
| 2. | 341 | 417 | 690 | 0.001449 |
| 3. | 309 | 420 | 693 | 0.001443 |
| Mean | 330 | 421 | 694 | 0.001442 |

Table 4 shows an overview of the temperatures reached of *Paulownia tomentosa*, completed with the induction period information.

Table 4 Spontaneous ignition temperatures of *Paulownia tomentosa*

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t (°C) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K ⁻¹) |
|-----------------|-----------------------------|---|--|---|
| 1. | 332 | 420 | 693 | 0.001442 |
| 2. | 292 | 411 | 684 | 0.001462 |
| 3. | 263 | 442 | 715 | 0.001399 |
| Mean | 296 | 424 | 697 | 0.001434 |

Table 5 shows an overview of the temperatures reached of *Salix viminalis* clone TORA, completed with the induction period information.

Table 5 Spontaneous ignition temperatures of *Salix viminalis* clone TORA

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t ($^{\circ}\text{C}$) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K^{-1}) |
|-----------------|-----------------------------|---|--|--|
| 1. | 338 | 413 | 686 | 0.001458 |
| 2. | 303 | 427 | 670 | 0.001429 |
| 3. | 345 | 419 | 692 | 0.001445 |
| Mean | 329 | 420 | 683 | 0.001444 |

Table 6 shows an overview of the spontaneous ignition temperatures and induction periods reached by *Sida hermaphrodita*.

Table 6 Spontaneous ignition temperatures of *Sida hermaphrodita*

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t ($^{\circ}\text{C}$) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K^{-1}) |
|-----------------|-----------------------------|---|--|--|
| 1. | 213 | 435 | 708 | 0.001413 |
| 2. | 222 | 431 | 704 | 0.001421 |
| 3. | 209 | 426 | 670 | 0.001429 |
| Mean | 215 | 431 | 694 | 0.001421 |

Table 7 shows an overview of the spontaneous ignition temperatures and induction periods reached by *Arundo donax*.

Table 7 Spontaneous ignition temperatures of *Arundo donax*

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t ($^{\circ}\text{C}$) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K^{-1}) |
|-----------------|-----------------------------|---|--|--|
| 1. | 215 | 432 | 705 | 0.001419 |
| 2. | 206 | 429 | 702 | 0.001425 |
| 3. | 213 | 433 | 706 | 0.001416 |
| Mean | 211 | 431 | 704 | 0.001420 |

Table 8 shows an overview of the spontaneous ignition temperatures and induction periods reached by *Miscanthus x giganteus*.

Table 8 Spontaneous ignition temperatures of *Miscanthus x giganteus*

| Measurement no. | Induction period τ (s) | Spontaneous ignition temperature t (°C) | Spontaneous ignition temperature T (K) | Temperature inverted value $1/T$ (K ⁻¹) |
|-----------------|-----------------------------|---|--|---|
| 1. | 235 | 427 | 670 | 0.001429 |
| 2. | 229 | 434 | 707 | 0.001415 |
| 3. | 231 | 416 | 689 | 0.001451 |
| Mean | 232 | 426 | 699 | 0.001431 |

The mean spontaneous ignition temperature values of all samples were in the range of 425 ± 8 °C (698 ± 8 K), see Table 9, where the mean spontaneous ignition temperature values are introduced together with the standard deviation values of individual temperatures measured Table 9 Summarized spontaneous ignition temperatures of the fast-growing tree species and energy crop samples

| Group | Sample | Spontaneous ignition temperature (°C) | Standard deviation |
|---------------------------|--|---------------------------------------|--------------------|
| Fast-growing tree species | <i>Populus x euroamericana</i> clone MAX 4 | 425 | 0.14 |
| | <i>Salix viminalis</i> clone TORA | 413 | 0.20 |
| | <i>Paulownia tomentosa</i> | 420 | 0.21 |
| Energy crops | <i>Sida Hermaphrodita</i> | 435 | 0.18 |
| | <i>Miscanthus x giganteus</i> | 427 | 0.09 |
| | <i>Arundo donax</i> | 432 | 0.11 |

The lowest mean spontaneous ignition temperature value was recorded by *Salix viminalis* clone TORA (413 °C, i. e. 686 K), which was reached in 338 s from the start of the test. The highest mean spontaneous ignition temperature value was recorded by *Sida hermaphrodita* (435 °C, i.e. 708 K), which showed the shortest mean induction period value, too.

The longest mean induction period was recorded by *Populus x euroamericana* clone MAX 4 (330 s).

The results showed also that the short rotation energy crops reached higher spontaneous ignition temperatures (429 ± 3 °C, i.e. 702 ± 3 K) and shorter induction periods (219 s on average) than the woody biomass (mean spontaneous ignition temperature of 422 ± 3 °C, i.e. 695 ± 3 K) and induction period of 318 s on average.

The results also showed, that with increasing thermal loading (and higher spontaneous ignition temperature value), the samples were resistant to fire for a shorter time. The results,

in general, confirmed the fact, that with increasing values of temperatures, the values of induction periods are decreasing.

4.3.2 Gross calorific value, heating value and ash content analysis results

The highest energy potential expressed in terms of the highest gross calorific values ($19.71 \pm 0.18 \text{ MJ}\cdot\text{kg}^{-1}$) as well as heating values were measured in case of *Paulownia tomentosa* and *Miscanthus x giganteus* ($19.60 \pm 0.14 \text{ MJ}\cdot\text{kg}^{-1}$), see the values introduced in Table 10. Those values are not very unlike. It confirms the suitability of energy crops to be used for energy production purposes together with the fast-growing tree species. Their only disadvantage is the stock which is necessary to plant to get the same yields as the wood of the fast-growing trees.

Table 10 Gross calorific value and heating value of the fast-growing tree species and energy crop samples

| Group | Sample | Gross calorific value ($\text{MJ}\cdot\text{kg}^{-1}$) | Heating value ($\text{MJ}\cdot\text{kg}^{-1}$) | Standard deviation |
|---------------------------|--|--|--|--------------------|
| Fast-growing tree species | <i>Populus x euroamericana</i> clone MAX 4 | 19.47 | 16.18 | 0.29 |
| | <i>Salix viminalis</i> clone Tora | 19.63 | 16.33 | 0.11 |
| | <i>Paulownia tomentosa</i> | 19.71 | 16.40 | 0.18 |
| Energy crops | <i>Sida Hermaphrodita</i> | 18.75 | 15.58 | 0.36 |
| | <i>Miscanthus x giganteus</i> | 19.60 | 16.29 | 0.14 |
| | <i>Arundo donax</i> | 18.85 | 15.66 | 0.09 |

The highest ash content was achieved by the energy crop samples, see Table 11.

Table 11 Ash content of the fast-growing tree species and energy crop samples

| Group | Sample | Ash content (w%) | Standard deviation |
|---------------------------|--|------------------|--------------------|
| Fast-growing tree species | <i>Populus x euroamericana</i> clone MAX 4 | 2.58 | 0.24 |
| | <i>Salix viminalis</i> clone Tora | 1.28 | 0.08 |
| | <i>Paulownia tomentosa</i> | 0.75 | 0.05 |
| Energy crops | <i>Sida Hermaphrodita</i> | 2.93 | 0.11 |
| | <i>Miscanthus x giganteus</i> | 2.67 | 0.08 |
| | <i>Arundo donax</i> | 3.46 | 0.11 |

The values of ash content were in the range of $2.67 \pm 0.08 \text{ w\%}$ (*Miscanthus x giganteus*) – $3.46 \pm 0.11 \text{ w\%}$ (*Arundo donax*). Lower values of ash content achieved the samples of wood from the fast-growing tree species, their values were in the range of $0.75 - 2.58 \text{ w\%}$. The lowest ash content was recorded by the *Paulownia tomentosa* samples ($0.75 \pm 0.05 \text{ w\%}$).

4.3.3 Thermal analyses results

The three pronounced regions (stages) of thermal degradation were detected through the DTG curves of all fast-growing tree species samples. In Figure 23 is introduced the course of the TG and DTG curves of the *Populus x euroamericana*, in Figure 24 of *Salix viminalis* sample and in Figure 25 for *Paulownia tomentosa* sample. All at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The other results at heating rates of 15, 20, 25 $^{\circ}\text{C}\cdot\text{min}^{-1}$ are introduced in Appendix 3.

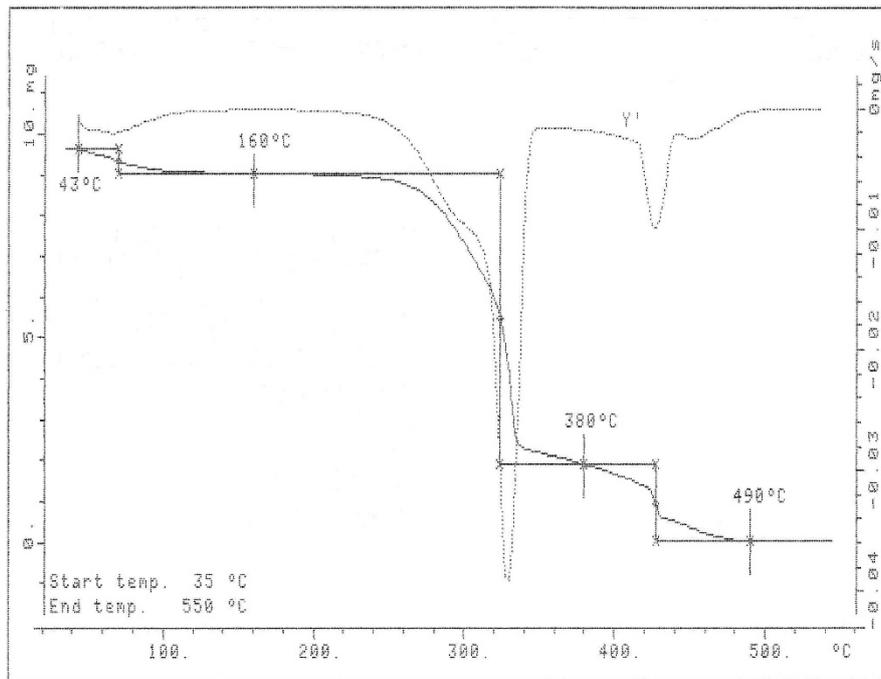


Figure 23 The TG/DTG curve of *Populus x euroamericana* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

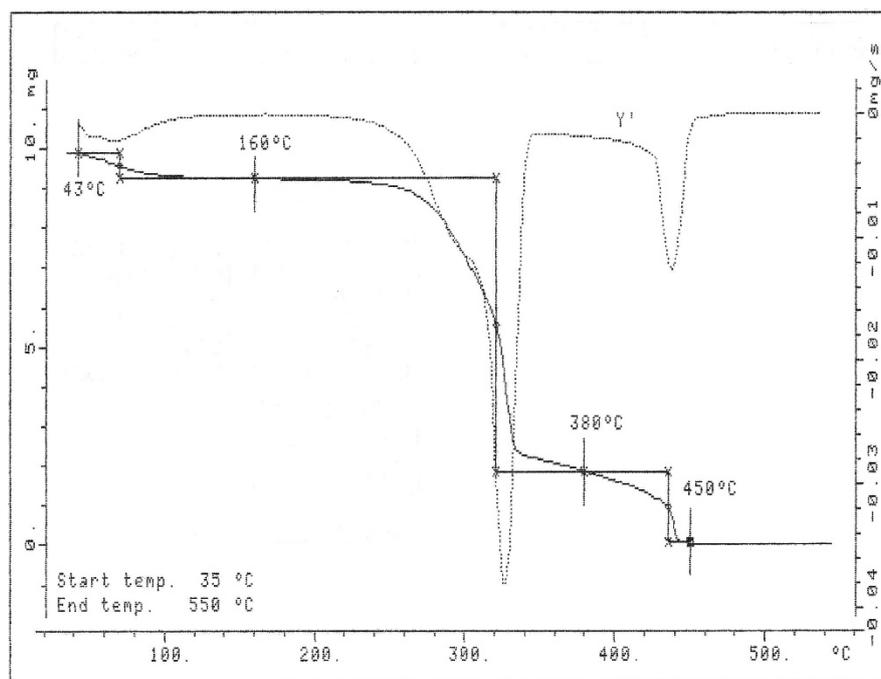


Figure 24 The TG/DTG curve of *Salix viminalis* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

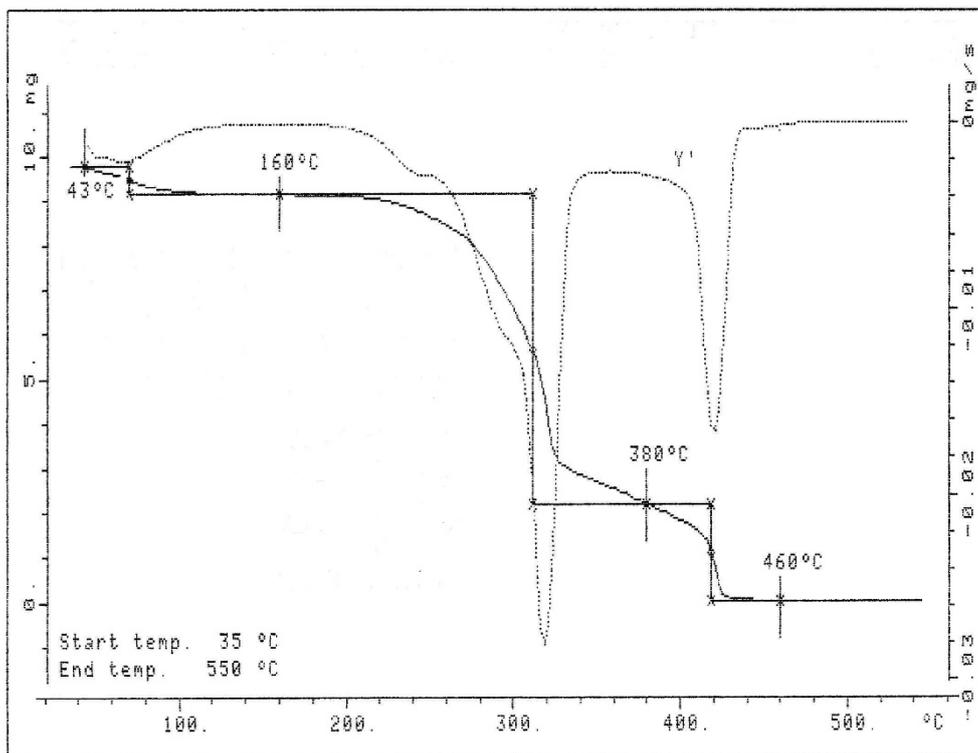


Figure 25 The TG/DTG curve of *Paulownia tomentosa* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

When evaluating the results of TG/DTG analysis of energy crop species, there were found three pronounced regions through the DTG curves in case of *Miscanthus x giganteus* (Figure 26) and *Arundo donax* (Figure 27). Only two regions were found by *Sida hermaphrodita* at heating rates of 10, 20 and $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (Figure 28).

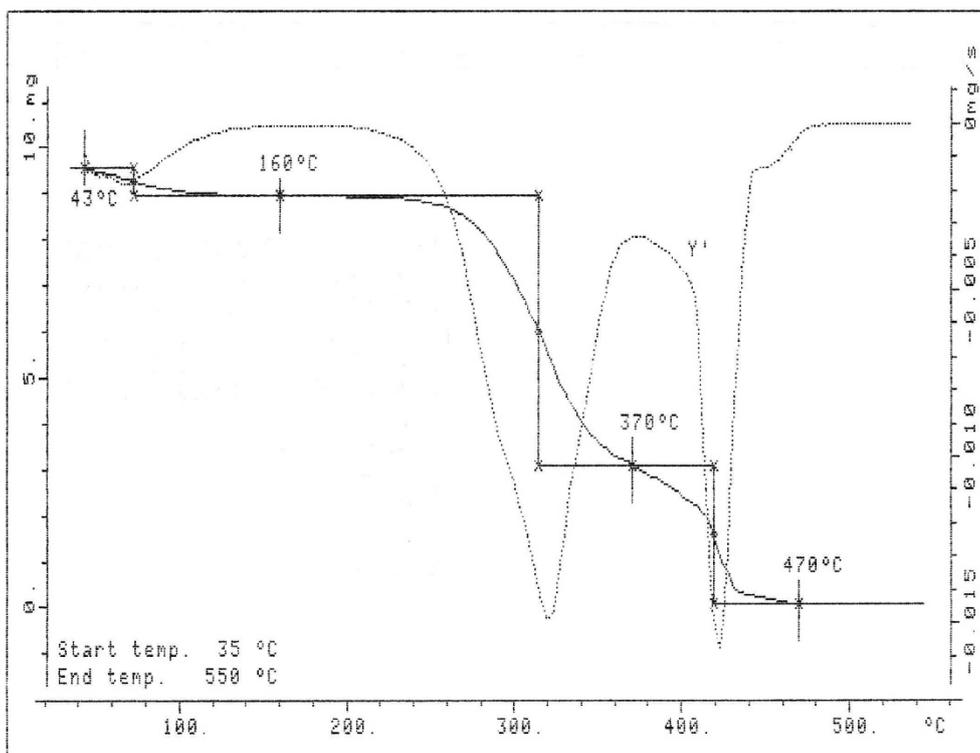


Figure 26 The TG/DTG curve of *Miscanthus x giganteus* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

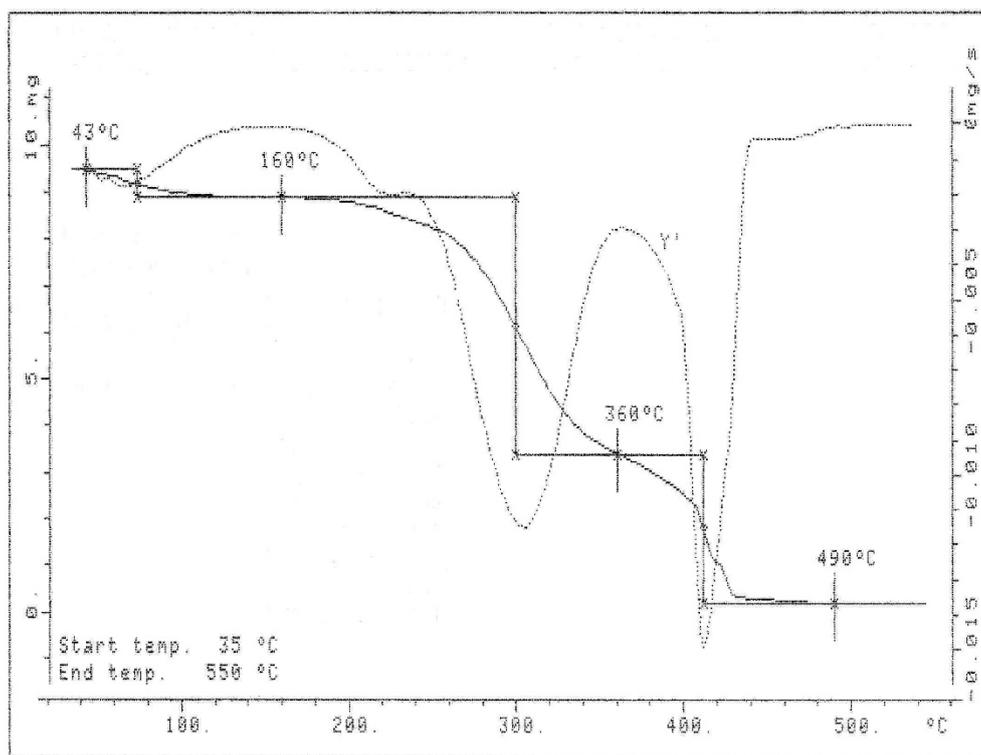


Figure 27 The TG/DTG curve of *Arundo donax* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

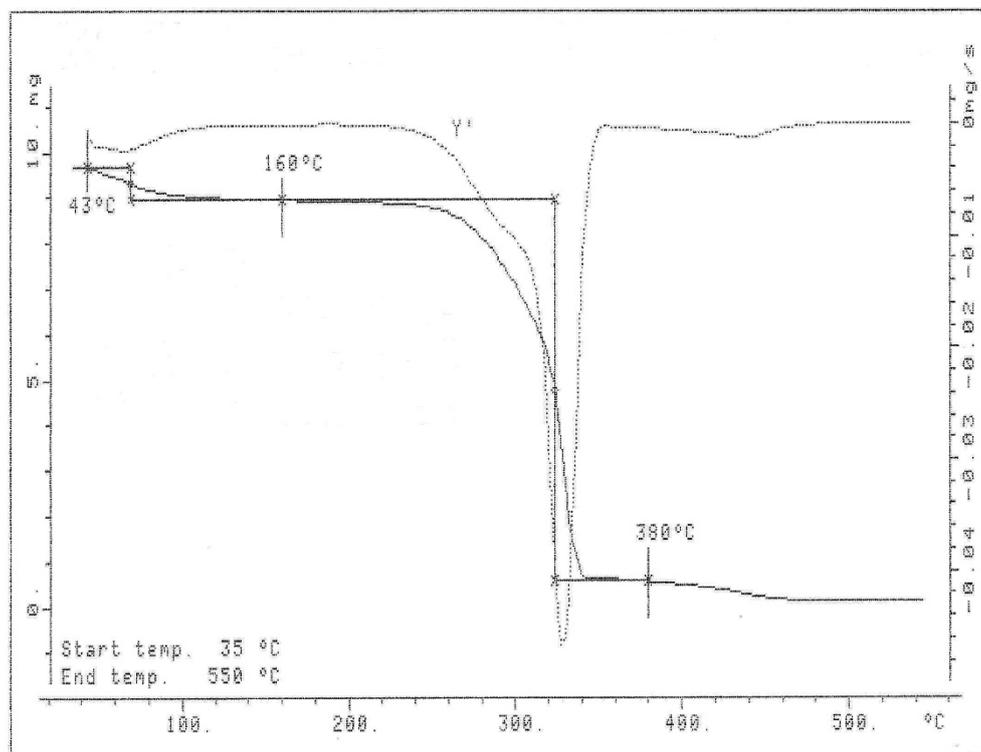


Figure 28 The TG/DTG curve of *Sida hermaphrodita* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

The pyrolysis took place exclusively in the second region (stage) of the thermal degradation process in case of all species and samples tested.

In Table 12, there are introduced the temperature intervals of detected DTG curves regions for the fast-growing tree species samples. Table 13 shows the temperature intervals of the detected DTG curves regions for the energy crop species samples

Table 12 Temperature intervals of detected regions of the fast-growing tree species samples

| Species Heating Rate (°C·min ⁻¹) | Region | Temperature interval (°C) | | | | |
|--|--------|---------------------------|-----------|-----------|-----------|-----------|
| | | 5 | 10 | 15 | 20 | 25 |
| <i>Populus x euroamericana</i> clone MAX 4 | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 |
| | Third | 380 – 470 | 380 – 490 | 380 – 490 | 380 – 500 | 380 – 480 |
| <i>Salix viminalis</i> clone Tora | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 |
| | Third | 380 – 450 | 380 – 450 | 380 – 450 | 380 – 590 | 380 – 450 |
| <i>Paulownia tomentosa</i> | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 |
| | Third | 380 – 460 | 380 – 460 | 380 – 440 | 380 – 460 | 380 – 460 |

Table 13 Temperature intervals of detected regions of the energy crop species samples

| Species Heating Rate (°C·min ⁻¹) | Region | Temperature interval (°C) | | | | |
|--|--------|---------------------------|-----------|-----------|-----------|-----------|
| | | 5 | 10 | 15 | 20 | 25 |
| <i>Sida Hermaphrodita</i> | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 | 160 – 380 |
| | Third | 380 – 430 | – | 380 – 460 | – | – |
| <i>Miscanthus x giganteus</i> | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 370 | 160 – 370 | 160 – 380 | 160 – 380 | 160 – 380 |
| | Third | 370 – 460 | 370 – 470 | 380 – 480 | 380 – 470 | 380 – 480 |
| <i>Arundo donax</i> | First | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 | 43 – 160 |
| | Second | 160 – 360 | 160 – 360 | 160 – 370 | 160 – 380 | 160 – 380 |
| | Third | 360 – 490 | 360 – 490 | 370 – 490 | 380 – 490 | 380 – 490 |

For all the samples, the first region was characterised by water evaporation and in all cases ranged from initial temperature (43 °C) up to 160 °C. The second region was characterised by combustion of pyrolytic volatiles, and the third region by combustion of fixed carbon.

DSC analyses of fast-growing tree species and energy crop species showed only exothermic reaction with two regions in case of all samples. In Figures 29 – 31, there are introduced the DSC curves of all fast-growing tree species samples at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

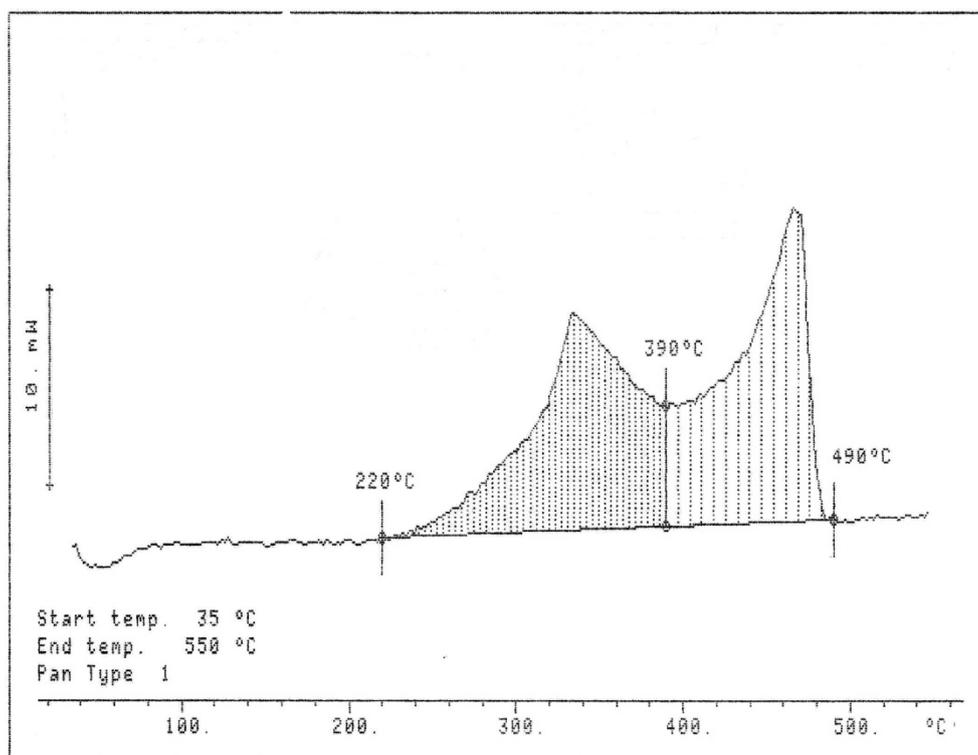


Figure 29 The DSC curve of *Populus x euroamericana* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

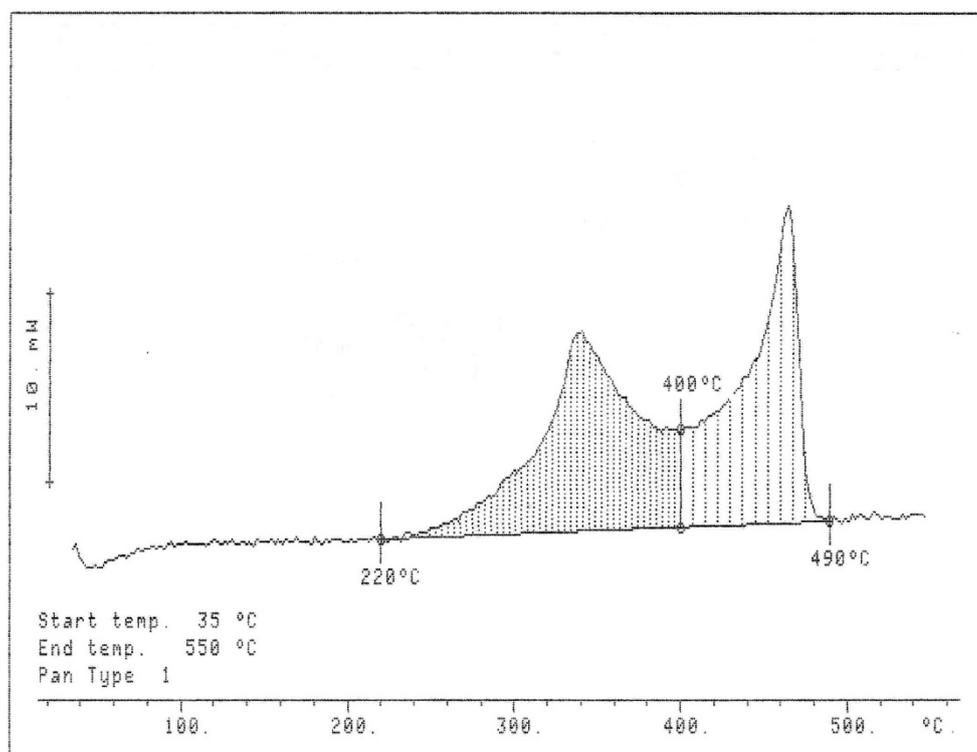


Figure 30 The DSC curve of *Salix viminalis* at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

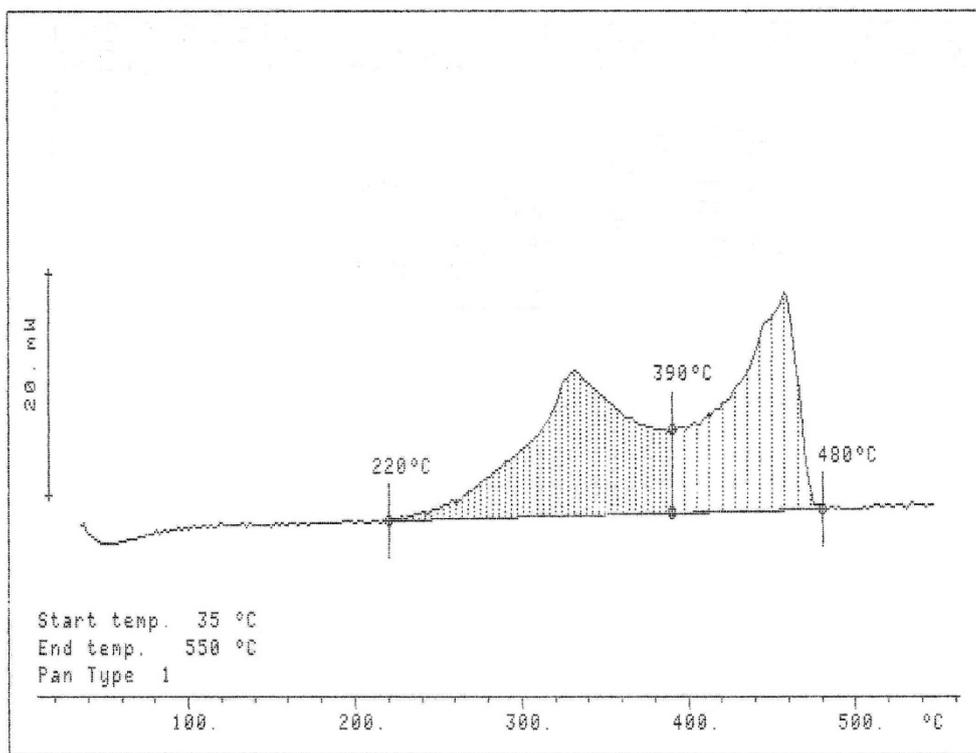


Figure 31 The DSC curve of *Paulownia tomentosa* at heating rate of 10 °C·min⁻¹

DSC curves of the energy crop species samples are introduced in Figures 32 – 34.

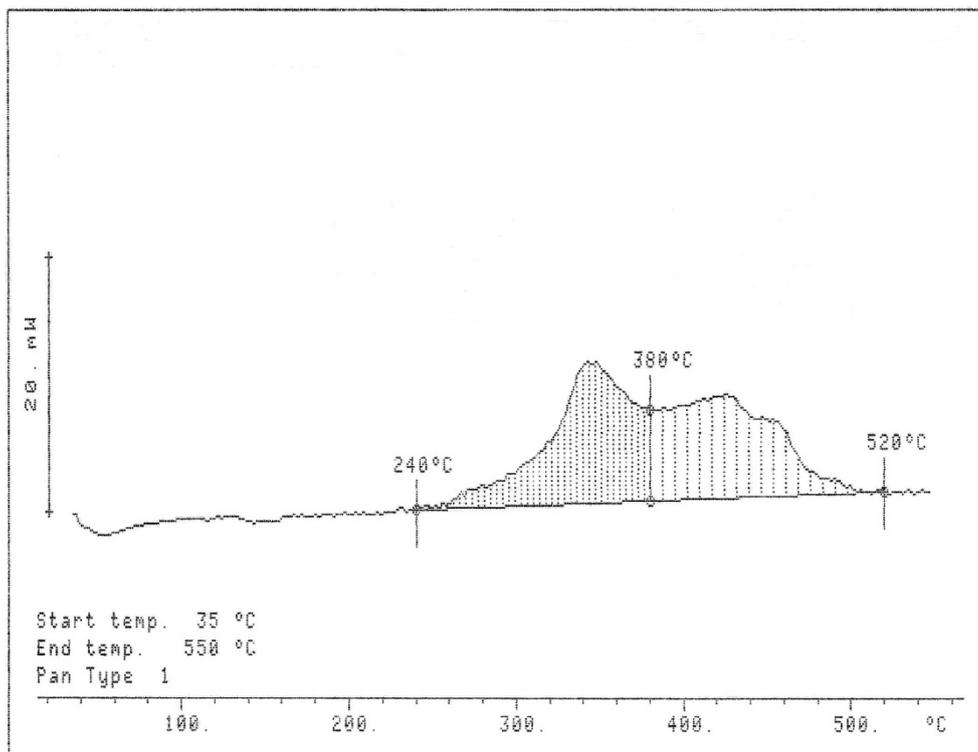


Figure 32 The DSC curve of *Sida hermaphrodita* at heating rate of 10 °C·min⁻¹

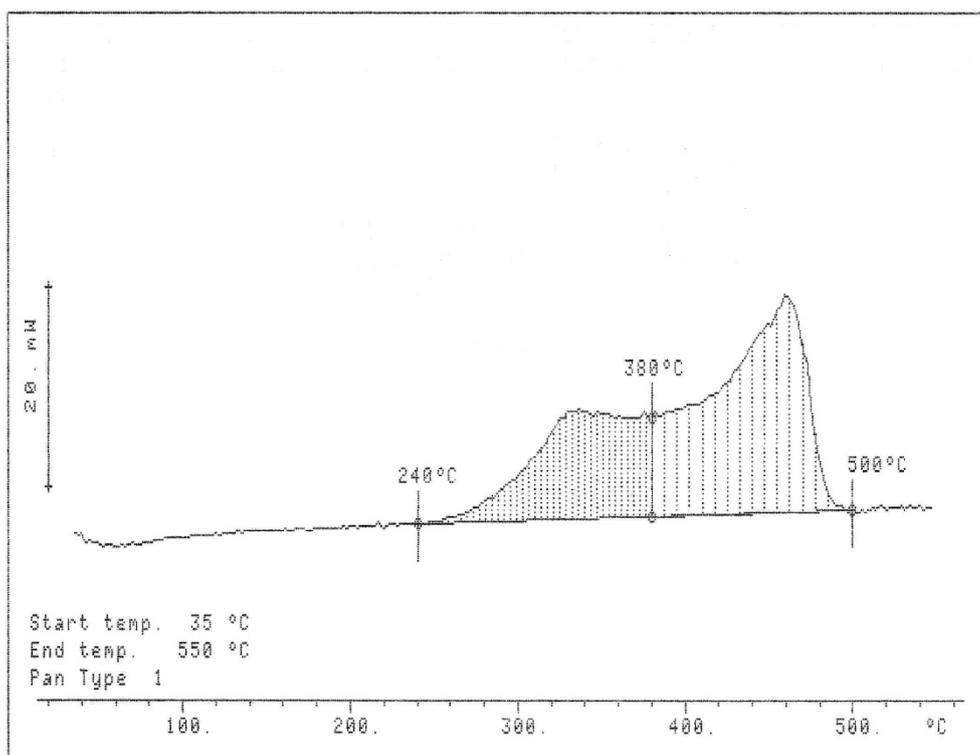


Figure 33 The DSC curve of *Miscanthus x giganteus* at heating rate of 10 °C·min⁻¹

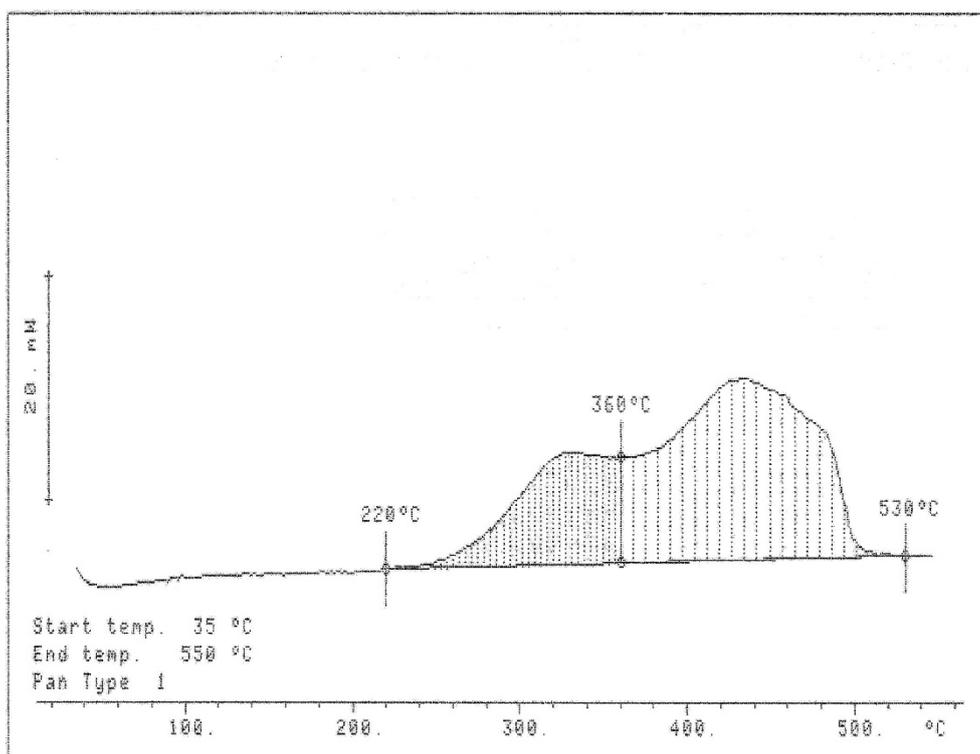


Figure 34 The DSC curve of *Arundo donax* at heating rate of 10 °C·min⁻¹

In Table 14 and Table 15, there are introduced the enthalpy change values (ΔH) determined for the peaks of the regions detected.

Table 14 Enthalpy change values (ΔH) of the fast-growing tree species samples

| Species | Region | Enthalpy change values (ΔH) | | | | | | | | | |
|------------------------------------|--------|---------------------------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) |
| <i>Populus x euroamericana</i> | Peak 1 | 323.8 | 3,478.0 | 335.1 | 3,273.1 | 344.6 | 3,216.7 | 351.8 | 3,501.2 | 353.8 | 3,353.0 |
| | Peak 2 | 451.8 | 3,066.4 | 467.5 | 3,324.1 | 480.2 | 3,272.2 | 485.5 | 3,494.5 | 491.7 | 3,656.1 |
| <i>Salix viminalis</i> | Peak 1 | 325.9 | 3,113.6 | 341.6 | 3,522.2 | 347.0 | 3,071.5 | 354.2 | 3,082.4 | 358.1 | 2,883.1 |
| | Peak 2 | 445.1 | 2,783.0 | 465.4 | 3,052.1 | 481.1 | 3,260.6 | 484.1 | 3,166.6 | 495.2 | 3,127.0 |
| <i>Paulownia tomentosa</i> | Peak 1 | 319.5 | 3,289.2 | 333.2 | 4,124.4 | 340.5 | 3,769.2 | 342.6 | 3,549.7 | 348.0 | 3,581.9 |
| | Peak 2 | 436.5 | 3,080.7 | 459.2 | 3,927.9 | 471.5 | 3,764.4 | 479.1 | 3,666.8 | 481.6 | 4,224.4 |

Table 15 Enthalpy change values (ΔH) of the energy crop species samples

| Species | Region | Enthalpy change values (ΔH) | | | | | | | | | |
|-----------------------------------|--------|---------------------------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) | T (°C) | (J·g ⁻¹) |
| <i>Sida Hermaphrodita</i> | Peak 1 | 332.5 | 2,702.5 | 343.9 | 2887.3 | 351.6 | 2,870.0 | 359.1 | 3,224.0 | 362.5 | 2,903.7 |
| | Peak 2 | 406.0 | 1,712.3 | 425.9 | 2798.3 | 434.4 | 2,734.9 | 435.4 | 2,597.0 | 443.1 | 2,734.6 |
| <i>Miscanthus x giganteus</i> | Peak 1 | 321.8 | 4,623.2 | 337.4 | 3366.9 | 340.2 | 2,678.8 | 347.1 | 2,572.0 | 344.3 | 2,099.8 |
| | Peak 2 | 432.4 | 4,780.4 | 461.6 | 5840.5 | 469.2 | 5,165.0 | 474.9 | 6,264.1 | 483.0 | 6,567.5 |
| <i>Arundo donax</i> | Peak 1 | 319.6 | 4,234.6 | 335.1 | 2915.9 | 333.4 | 2,448.4 | 344.7 | 2,494.9 | 345.5 | 2,655.0 |
| | Peak 1 | 319.6 | 4,234.6 | 335.1 | 2915.9 | 333.4 | 2,448.4 | 344.7 | 2,494.9 | 345.5 | 2,655.0 |

The heat flow values both for fast-growing tree species and energy crop species are introduced in Table 16.

Table 16 Heat flow values of the fast-growing tree species and energy crops samples

| Species | Heating Rate (°C·min ⁻¹) | Region | Heat flow | | | | | | | | | |
|--------------------------------|---|--------|-----------|------|-----------|------|-----------|-------|-----------|-------|-----------|-------|
| | | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | | T (°C) | (Mw) | T (°C) | mW | T (°C) | mW | T (°C) | mW | T (°C) | mW |
| <i>Populus x euroamericana</i> | | Peak 1 | 323.8 | 6.1 | 335.1 | 11.0 | 344.6 | 15.2 | 351.8 | 20.0 | 353.8 | 24.5 |
| | | Peak 2 | 451.8 | 7.9 | 467.5 | 16.0 | 480.2 | 25.2 | 485.5 | 33.3 | 491.7 | 173.8 |
| <i>Salix viminalis</i> | | Peak 1 | 325.9 | 4.7 | 341.6 | 10.7 | 347.0 | 16.1 | 354.2 | 20.4 | 358.1 | 25.5 |
| | | Peak 2 | 445.1 | 6.0 | 465.4 | 16.8 | 481.1 | 105.0 | 484.1 | 120.2 | 495.2 | 73.5 |
| <i>Paulownia tomentosa</i> | | Peak 1 | 319.5 | 5.7 | 333.2 | 13.1 | 340.5 | 17.6 | 342.6 | 21.2 | 348.0 | 28.3 |
| | | Peak 2 | 436.5 | 6.2 | 459.2 | 19.7 | 471.5 | 28.0 | 479.1 | 44.0 | 481.6 | 132.1 |
| <i>Sida Hermaphrodita</i> | | Peak 1 | 332.5 | 5.1 | 343.9 | 11.2 | 351.6 | 16.8 | 359.1 | 22.6 | 362.5 | 28.2 |
| | | Peak 2 | 406.0 | 3.3 | 425.9 | 8.2 | 434.4 | 12.8 | 435.4 | 16.4 | 443.1 | 21.6 |
| <i>Miscanthus x giganteus</i> | | Peak 1 | 321.8 | 6.8 | 337.4 | 10.9 | 340.2 | 14.3 | 347.1 | 18.5 | 344.3 | - |
| | | Peak 2 | 432.4 | 9.1 | 461.6 | 21.7 | 469.2 | 26.3 | 474.9 | 44.6 | 483.0 | 54.7 |
| <i>Arundo donax</i> | | Peak 1 | 319.6 | 6.9 | 335.1 | 10.1 | 333.4 | 13.7 | 344.7 | 17.4 | 345.5 | 23.2 |
| | | Peak 2 | 408.5 | 7.9 | 433.0 | 16.2 | 442.0 | 21.8 | 445.8 | 29.7 | 444.7 | 41.3 |

The results of DSC analysis considering the determined enthalpy change values showed that the highest energetic potential showed *Arundo donax*, *Miscanthus x giganteus* and from fast-growing tree species also *Paulownia tomentosa*.

The heat flow values confirmed the previous results. The highest heat flow values among the fast-growing tree species showed *Paulownia tomentosa*. Very good heat flow values achieved also the energy crop species, *Arundo donax* and *Miscanthus x giganteus*, followed by is clear, that higher energetic potential have fast-growing tree species,

Those results point out the suitability of energy crops to be used for energy production purposes together with the fast-growing tree species.

4.3.4 Mass loss analysis results

Better to understand the thermal decomposition process of all the samples tested during their burning, the implementation of thermal analyses, allowing the study the mass loss of the sample, is recommended. As mentioned in Introduction, the TG, DTG analyses are performed for this purpose.

However, in this study, we also used simplified approach, a non-standardized method which allow to study mass loss of the samples in time. The TG and DTG analyses allow to study the sample mass loss during its heating in ahead specified temperature interval.

The individual samples resulting courses of mass loss are introduced in Figures 35-40. Those are also completed with information on the samples time of auto ignition and flame dying out, when undergoing the thermal loading for 5 min (energy crops) – 10 min (fast-growing tree species), (Fig. 41).

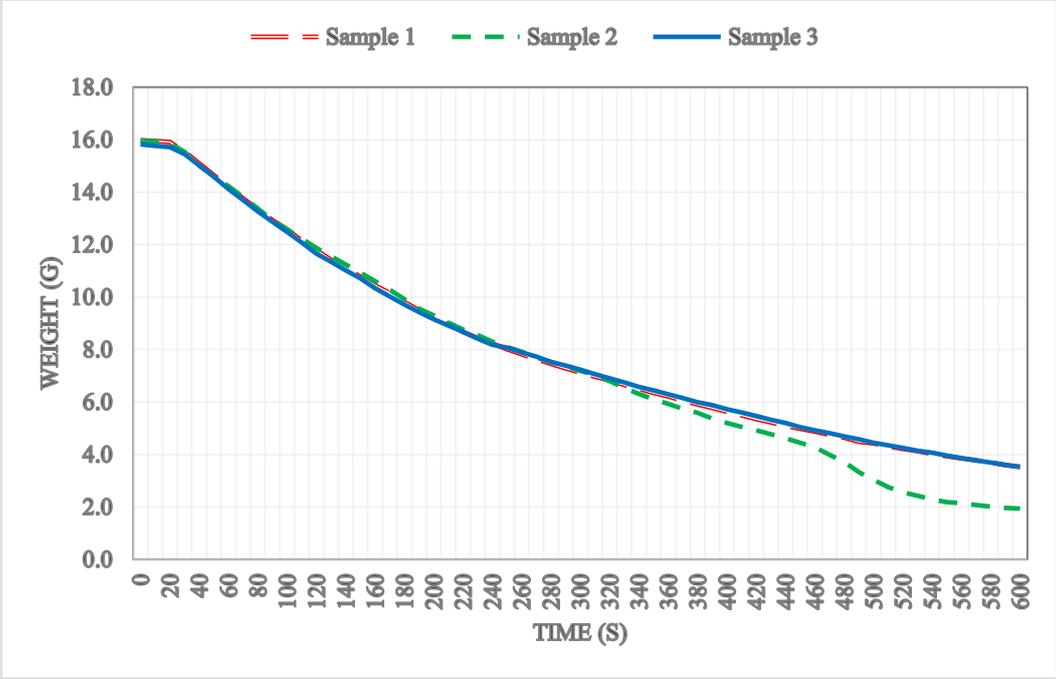


Figure 35 The mass loss course of *Populus x euroamericana* clone MAX 4 during the thermal loading

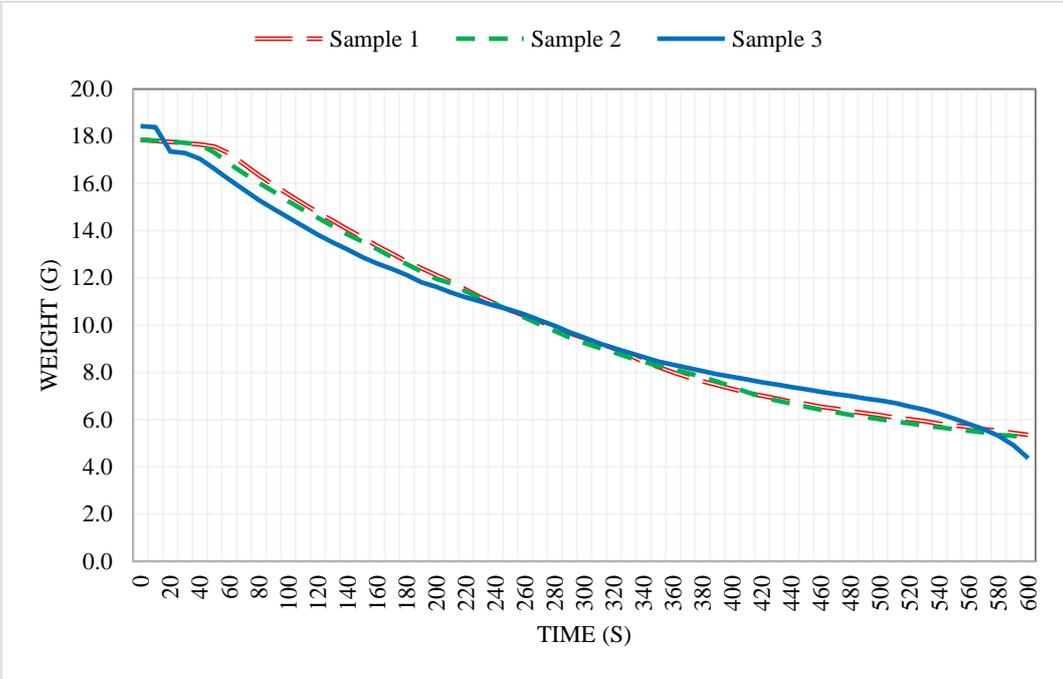


Figure 36 The mass loss course of *Salix viminalis* clone TORA during the thermal loading

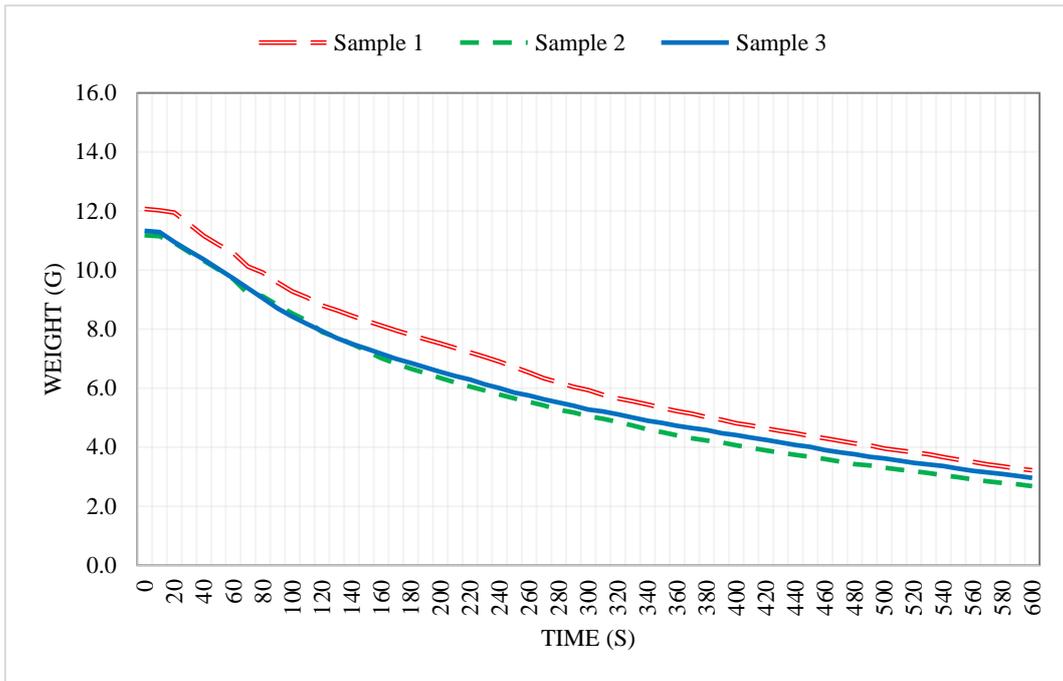


Figure 37 The mass loss course of *Paulownia tomentosa* during the thermal loading

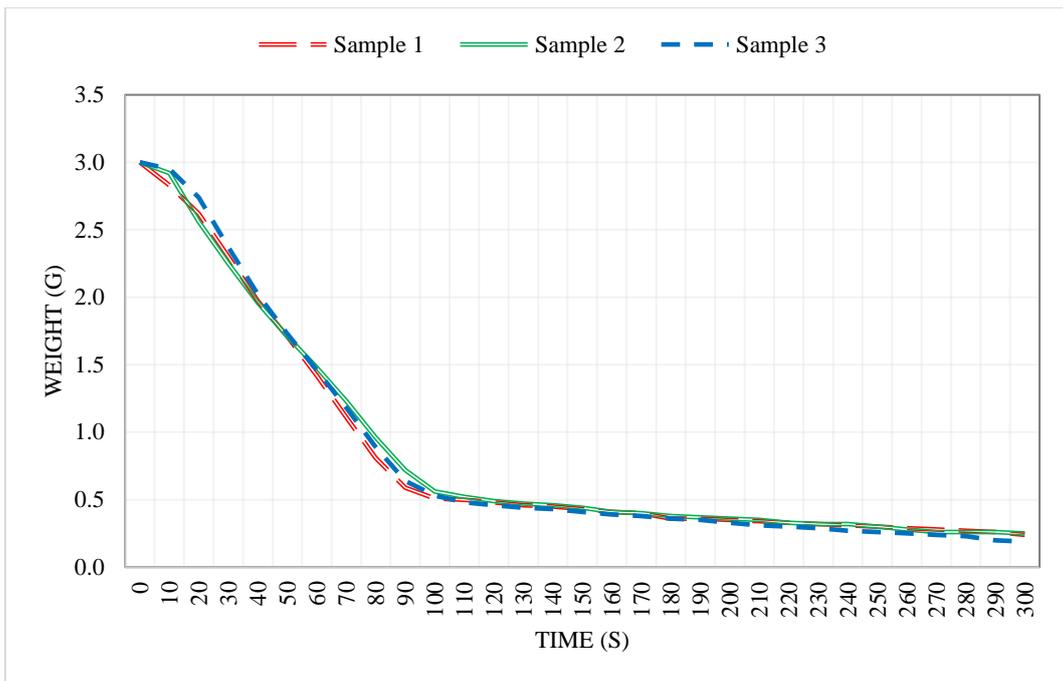


Figure 38 The mass loss course of *Sida hermaphrodita* during the thermal loading

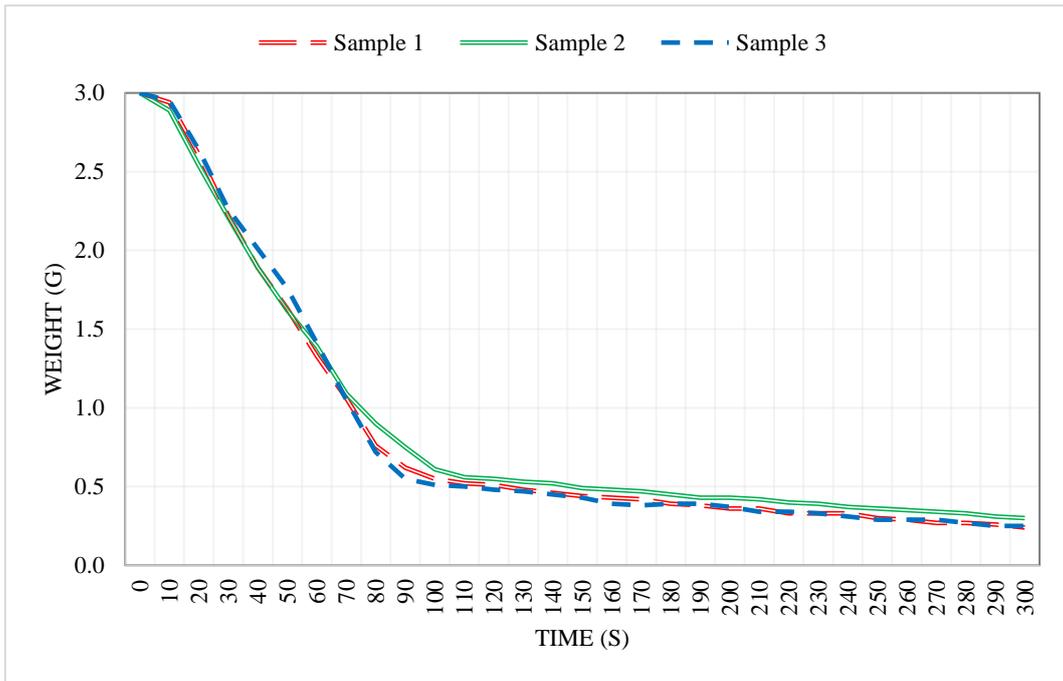


Figure 39 The mass loss course of *Miscanthus x giganteus* during the thermal loading

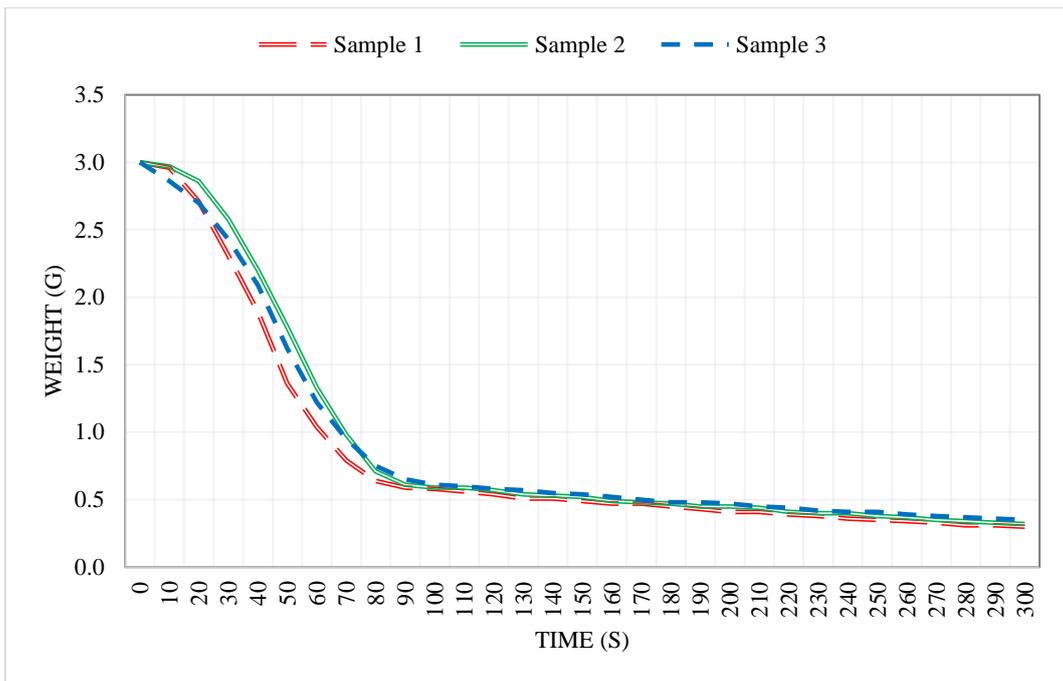


Figure 40 The mass loss course of *Arundo donax* during the thermal loading

From the mass loss courses are evident the differences in mass loss course of fast-growing tree species and energy crop species. The course of fast-growing tree species mass loss is more linear, meanwhile the course of the energy crops shows the rapid mass loss in interval 1–90 s, then the mass loss rate decreased and became linear, too. We can assume,

that in this first, and main, stage of thermal decomposition process, the active pyrolysis had place. Then, it was mostly the passive pyrolysis process.

In individual studies, only small differences during tested fast-growing tree and energy crop species samples could be distinguished.

Figure 41 shows the differences in time of ignition and time of flame dying out of the samples.

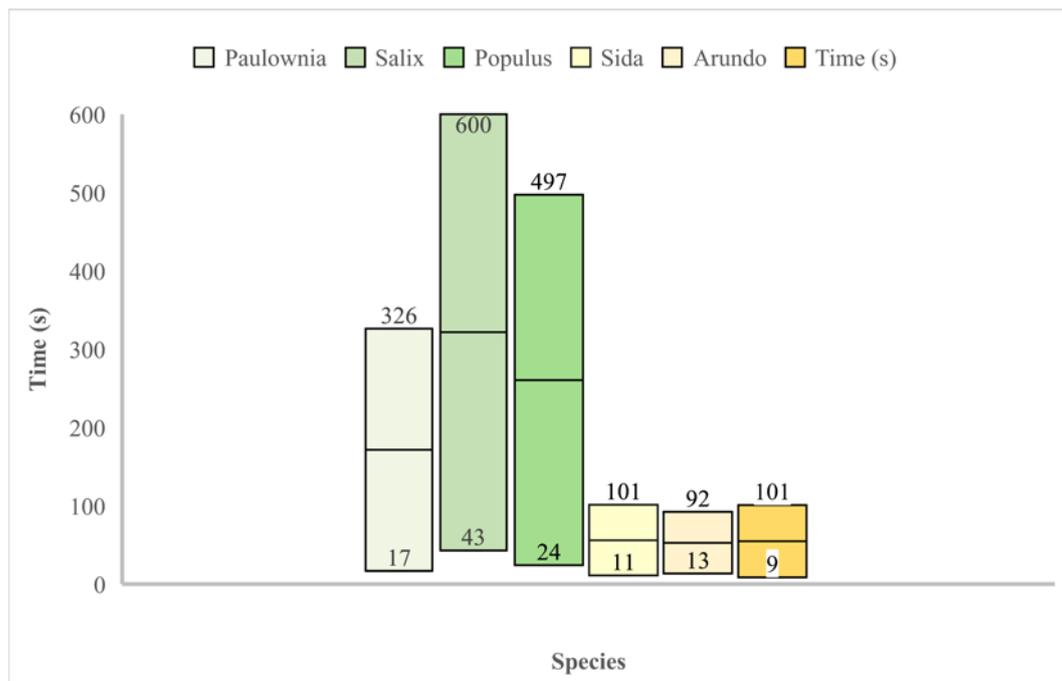


Figure 41 The samples tested time of ignition and time of flame dying out

The results introduced in Figure 41 shows evident differences in times of flame burning, when comparing the woody biomass and short rotation woody crops. The short rotation woody crops reached much shorter periods of flame burning. The results representing the mean length of flame burning of individual samples are as follows: *Populus x euroamericana* clone MAX 4 of 473 s, *Salix viminalis* clone TORA of 557 s (however the flames died out due to its manual extinguishing in 600 s), *Paulownia tomentosa* of 309.33 s, *Sida hermaphrodita* of 90.33 s, *Miscanthus x giganteus* of 92.33 s and *Arundo donax* of 79 s.

The mass loss of the sample is also possible to determine from the TG and DTG curves for the individual analysis steps (regions). Those values are introduced in Table 17 for fast-growing tree species and in Table 18 for energy crops species. The results showed that the highest mass loss occurred in the second region, where the pyrolysis occurred too.

Table 17 Mass loss of the fast-growing tree species samples

| Species Heating Rate (°C min ⁻¹) | Region | Mass loss (mg and %) | | | | | | | | | |
|--|--------|----------------------|--------|-------|--------|-------|--------|-------|--------|-------|--------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) |
| <i>Populus x euroamericana</i> clone MAX 4 | First | -0.59 | -5.96 | 0.60 | -6.26 | -0.65 | -6.55 | -0.66 | -6.82 | -0.60 | -6.30 |
| | Second | -7.20 | -73.32 | -7.13 | -74.01 | -7.25 | -73.28 | -6.95 | -71.73 | -7.02 | -73.24 |
| | Third | -1.95 | -19.89 | -1.88 | -19.50 | -1.98 | -19.99 | -2.04 | -21.01 | -1.89 | -19.75 |
| <i>Salix viminalis</i> clone TORA | First | -0.55 | -5.57 | -0.64 | -6.51 | -0.68 | -6.80 | -0.65 | -6.95 | -0.68 | -7.38 |
| | Second | -7.32 | -74.71 | -7.38 | -74.71 | -7.19 | -72.39 | -6.84 | -72.66 | -6.84 | -73.02 |
| | Third | -1.89 | -19.30 | -1.82 | -18.37 | -1.96 | -19.79 | -1.89 | -20.06 | -1.67 | -17.78 |
| <i>Paulownia tomentosa</i> | First | -0.55 | -5.61 | -0.64 | -6.50 | -0.60 | -6.21 | -0.63 | -6.33 | -0.61 | -6.22 |
| | Second | -7.2 | -73.29 | -6.93 | -70.90 | -6.93 | -72.28 | -7.05 | -70.63 | -6.90 | -70.72 |
| | Third | -2.01 | -20.48 | -2.19 | -22.35 | -2.09 | -21.77 | -2.26 | -22.63 | -2.25 | -23.10 |

Table 18 Mass loss of the energy crop species samples

| Species Heating Rate (°C min ⁻¹) | Region | Mass loss (mg and %) | | | | | | | | | |
|--|--------|----------------------|--------|-------|--------|-------|--------|-------|--------|-------|--------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) |
| <i>Sida Hermaphrodita</i> | First | -0.69 | -7.20 | -0.71 | -7.31 | -0.76 | -7.78 | 0.76 | -7.92 | -0.78 | -7.95 |
| | Second | -7.06 | -73.94 | -8.40 | -86.83 | -8.41 | -85.57 | -8.59 | -88.99 | -8.87 | -90.19 |
| | Third | -1.39 | -14.58 | - | - | -0.60 | -6.08 | - | - | - | - |
| <i>Miscanthus x giganteus</i> | First | -0.57 | -5.98 | -0.60 | -6.32 | -0.61 | -6.38 | -0.62 | -6.44 | -0.63 | -6.35 |
| | Second | -6.07 | -63.40 | -5.87 | -61.47 | -5.65 | -59.56 | -5.83 | -60.59 | -6.06 | -61.35 |
| | Third | -2.80 | -29.24 | -3.01 | -31.48 | -3.16 | -33.29 | -3.10 | -32.25 | -3.13 | -31.67 |
| <i>Arundo donax</i> | First | -0.53 | -5.45 | -0.60 | -6.33 | -0.63 | -6.59 | -0.59 | -5.91 | -0.62 | -6.20 |
| | Second | -5.74 | -59.22 | -5.74 | -57.77 | -5.67 | -59.55 | -5.99 | -60.14 | -6.03 | -60.38 |
| | Third | -3.24 | -33.44 | -3.21 | -33.90 | -3.02 | -31.72 | -3.18 | -31.90 | -3.11 | -31.19 |

Further, we introduce also the information on carbon residue. The data were obtained from TG analyses of the samples, see Tables 19 and 20.

Table 19 Carbon residue of the fast-growing tree species samples

| Species Heating Rate (°C min ⁻¹) | Region | Carbon residue (mg and %) | | | | | | | | | |
|--|--------|---------------------------|-------|------|-------|------|-------|------|-------|------|-------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) |
| <i>Populus x euroamericana</i> clone MAX 4 | First | 9.19 | 93.57 | 9.03 | 93.80 | 9.27 | 93.69 | 9.05 | 93.37 | 8.99 | 93.80 |
| | Second | 1.99 | 20.25 | 1.91 | 19.79 | 2.02 | 20.41 | 2.10 | 21.64 | 1.91 | 20.57 |
| | Third | 0.04 | 0.36 | 0.03 | 0.29 | 0.04 | 0.42 | 0.06 | 0.63 | 0.08 | 0.82 |
| <i>Salix viminalis</i> clone TORA | First | 9.21 | 94.05 | 9.25 | 93.60 | 9.27 | 93.42 | 8.78 | 93.20 | 8.69 | 92.80 |
| | Second | 1.89 | 19.34 | 1.87 | 18.89 | 2.09 | 21.03 | 1.94 | 20.54 | 1.85 | 19.78 |
| | Third | 0.00 | 0.00 | 0.05 | 0.51 | 0.12 | 1.24 | 0.05 | 0.49 | 0.19 | 1.99 |
| <i>Paulownia tomentosa</i> | First | 9.22 | 93.92 | 9.15 | 93.56 | 9.01 | 94.02 | 9.37 | 93.83 | 9.16 | 93.87 |
| | Second | 2.03 | 20.63 | 2.22 | 22.67 | 2.08 | 21.73 | 2.32 | 23.20 | 2.26 | 23.15 |
| | Third | 0.01 | 0.15 | 0.03 | 0.32 | 0.00 | 0.00 | 0.06 | 0.57 | 0.00 | 0.00 |

Table 20 Carbon residue of the energy crop species samples

| Species Heating Rate (°C min ⁻¹) | Region | Carbon residue (mg and %) | | | | | | | | | |
|--|--------|---------------------------|-------|------|-------|------|-------|------|-------|------|-------|
| | | 5 | | 10 | | 15 | | 20 | | 25 | |
| | | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) | (mg) | (%) |
| <i>Sida hermaphrodita</i> | First | 8.80 | 92.25 | 8.96 | 92.67 | 9.09 | 92.45 | 8.91 | 92.25 | 9.06 | 92.16 |
| | Second | 1.75 | 18.31 | 0.56 | 5.84 | 0.68 | 6.88 | 0.32 | 3.26 | 0.19 | 1.97 |
| | Third | 0.36 | 3.74 | – | – | 0.08 | 0.81 | – | – | – | – |
| <i>Miscanthus x giganteus</i> | First | 8.98 | 93.77 | 9.59 | 94.67 | 8.90 | 93.88 | 9.02 | 93.74 | 9.26 | 93.76 |
| | Second | 2.91 | 30.37 | 3.58 | 35.28 | 3.25 | 34.32 | 3.19 | 33.15 | 3.20 | 32.40 |
| | Third | 0.11 | 1.13 | 0.34 | 3.38 | 0.10 | 1.03 | 0.09 | 0.91 | 0.07 | 0.73 |
| <i>Arundo donax</i> | First | 9.13 | 94.15 | 8.88 | 93.72 | 8.92 | 93.65 | 9.39 | 94.26 | 9.38 | 93.90 |
| | Second | 3.39 | 34.93 | 3.41 | 35.95 | 3.25 | 34.10 | 3.40 | 34.12 | 3.35 | 33.53 |
| | Third | 0.14 | 1.49 | 0.19 | 2.05 | 0.23 | 2.38 | 0.22 | 2.22 | 0.23 | 2.34 |

According to results achieved, we can state that the fast-growing tree species achieved very similar values of mass loss rate. Higher differences we found in case of energy crop samples. The most rapid rate of thermal degradation showed *Sida hermaphrodita*. The rate of thermal degradation of other energy crop samples was very similar. All of them (besides *Sida hermaphrodita* at heating rates of 10, 20, 25 °C·min⁻¹) showed three stage thermal degradation process. The most rapid thermal degradation, i.e. mass loss, was observed in the second stage. This stage is characterised by sample pyrolysis.

From the carbon residue point of view the least carbon residue was recorded by *Paulownia tomentosa* and the highest carbon residue was recorded by *Populus x euroamericana*.

From the energy crop species, the lowest carbon residue was recorded by *Sida hermaphrodita* and the highest residue was found by *Arundo donax*.

The fast-growing tree species samples showed lower carbon residues at second stage of thermal degradation than the energy crop species, in general.

4.3.5 Chemical analyses results

The best elemental composition from the energy potential point of view showed the *Populus x euroamericana* from the group of fast-growing species and *Miscanthus x giganteus* from the group of energy crop species (see results in Table 21).

Table 21 Carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) content (w%) in the fast-growing tree species and energy crop samples

| Group | Sample | C (w%) | H (w%) | N (w%) | O (w%) |
|---------------------------|--|--------|--------|--------|--------|
| Fast-growing tree species | <i>Populus x euroamericana</i> clone MAX 4 | 50.14 | 5.97 | 0.60 | 43.29 |
| | <i>Salix viminalis</i> clone TORA | 49.29 | 6.41 | 0.61 | 43.69 |
| | <i>Paulownia tomentosa</i> | 48.91 | 5.91 | 0.61 | 44.57 |
| Energy crops | <i>Sida hermaphrodita</i> | 43.74 | 5.68 | 0.77 | 49.81 |
| | <i>Miscanthus x giganteus</i> | 45.28 | 5.74 | 0.29 | 48.69 |
| | <i>Arundo donax</i> | 44.19 | 5.70 | 1.29 | 48.82 |

The highest carbon (C) mass was recorded by *Populus x euroamericana* (50.14 w%) and *Miscanthus x giganteus* (45.28 w%), the lowest values were recorded by *Paulownia tomentosa* (48.91 w%) and *Arundo donax* (44.19 w%).

The highest values of hydrogen (H) mass were found by *Salix viminalis* (6.41 w%) and *Miscanthus x giganteus* (5.74 w%). The lowest values of hydrogen mass were found by *Paulownia tomentosa* (5.91 w%) and *Arundo donax* (5.70 w%).

The highest values of nitrogen (N) mass were found by *Salix viminalis* (0.61 w%), *Paulownia tomentosa* (0.61 w%) and *Arundo donax* (1.29 w%). The lowest values of nitrogen mass were found by *Populus x euroamericana* (0.60 w%) and *Miscanthus x giganteus* (0.29 w%).

The highest values of oxygen (O) mass were found by *Paulownia tomentosa* (44.57 w%) and *Sida hermaphrodita* (49.81 w%). The lowest values of oxygen mass were found by *Populus x euroamericana* (43.29 w%) and *Miscanthus x giganteus* (48.69 w%).

In Table 22, there are introduced the results of lignin, cellulose, holocellulose, hemicellulose and extractives analyses.

Table 22 Lignin, cellulose, holocellulose, hemicellulose and extractives content (%) in the fast-growing tree species and energy crop samples

| Species | Lignin (%) | Cellulose (%) | Holocellulose (%) | Hemicellulose (%) | Extractives (%) |
|--------------------------------|------------|---------------|-------------------|-------------------|-----------------|
| <i>Populus x euroamericana</i> | 24.69 | 36.80 | 76.49 | 39.69 | 6.67 |
| <i>Salix viminalis</i> | 21.65 | 38.65 | 71.18 | 32.53 | 11.25 |
| <i>Paulownia tomentosa</i> | 19.26 | 36.44 | 69.18 | 32.74 | 12.38 |
| <i>Sida hermaphrodita</i> | 19.92 | 38.30 | 84.41 | 46.11 | 1.78 |
| <i>Miscanthus x giganteus</i> | 21.20 | 40.63 | 80.52 | 39.89 | 2.71 |
| <i>Arundo donax</i> | 21.49 | 35.95 | 69.76 | 33.81 | 12.27 |

The highest content of lignin was found by *Populus x euroamericana* (24.69 %) and *Arundo donax* (21.49 %). The lowest values were found by *Paulownia tomentosa* (19.26 %) and *Sida hermaphrodita* (19.92 %).

The highest content of cellulose was found by *Salix viminalis* (38.65 %) and *Miscanthus x giganteus* (40.63 %). The lowest values were found by *Paulownia tomentosa* (36.44 %) and *Arundo donax* (35.95 %).

Holocellulose highest content was found by *Populus x euroamericana* (76.49 %) and *Sida hermaphrodita* (84.41 %). The lowest values were found by *Paulownia tomentosa* (69.18 %) and *Arundo donax* (69.76 %).

The highest content of hemicellulose had *Populus x euroamericana* (39.69 %) and *Sida hermaphrodita* (46.11 %). The lowest values were found by *Salix viminalis* (32.53 %) and *Arundo donax* (33.81 %).

Highest extractives content was found by *Paulownia tomentosa* (12.38 %) and *Arundo donax* (12.27 %). The lowest values were found by *Populus x euroamericana* (6.67 %) and *Sida hermaphrodita* (1.78 %).

4.3.6 Activation energy calculation results

First, we introduce the results of activation energy calculation using the equation of Arrhenius. In Table 21, there are introduced the values of pre-exponential factor (A), which represents the regression coefficient in the correlation equation calculated between the spontaneous ignition temperature and induction period values of individual samples. Those data were used in calculation of the activation energy of individual samples, together with the mean values of spontaneous ignition temperature and induction periods. The calculated activation energy values are introduced in Table 23.

Table 23 Activation energy values of individual samples tested calculated by Arrhenius equation

| Sample | Pre-exponential factor (A) | Activation energy of spontaneous ignition (kJ·mol ⁻¹) |
|--|----------------------------|---|
| <i>Paulownia tomentosa</i> | 0.00647 | 127.90 |
| <i>Salix viminalis</i> clone TORA | 0.00368 | 136.90 |
| <i>Populus x euroamericana</i> clone MAX 4 | 0.00175 | 145.60 |
| <i>Sida hermaphrodita</i> | 0.00215 | 136.00 |
| <i>Arundo donax</i> | 0.00104 | 144.30 |
| <i>Miscanthus x giganteus</i> | 0.00433 | 129.60 |
| Mean | - | 136.72 |

The Arrhenius activation energies of the fast-growing tree species and energy crop species were very similar. The mean value for all of them was of 136.72 ± 7.28 kJ·mol⁻¹.

Further, we introduce also the activation energy values of the tested samples of fast-growing tree species and energy crop species obtained by application of three different iso-conversional methods, see Table 24. In the table, there are also included the activation energy values calculated by Arrhenius and in accordance to ASTM standard.

Table 24 Activation energy values calculated for the fast-growing tree species and energy crops using the iso-conversional methods

| Method/Species | Activation energy (kJ·mol ⁻¹) | | | | | |
|-------------------------|---|--------------|------------------|-------------|-------------------|---------------|
| | <i>Populus</i> | <i>Salix</i> | <i>Paulownia</i> | <i>Sida</i> | <i>Miscanthus</i> | <i>Arundo</i> |
| Ozawa-Flynn-Wall | 209.70 | 193.16 | 187.64 | 196.17 | 191.50 | 201.75 |
| Kissinger-Akahira-Sunos | 119.72 | 113.36 | 101.66 | 114.54 | 102.80 | 115.35 |
| ASTM | 128.63 | 122.27 | 110.57 | 123.45 | 112.01 | 124.17 |
| Arrhenius | 145.60 | 136.90 | 127.90 | 136.00 | 129.60 | 144.30 |
| St Dev | ± 40.64 | ± 35.83 | ± 38.70 | ± 36.82 | ± 39.93 | ± 38.84 |

From the activation energy point of view the best results were obtained by *Miscanthus x giganteus* and *Paulownia tomentosa*.

The activation energies calculated by different methods show significant differences, which are caused by application of different approaches to determination of thermal degradation process and different equations for setting the activation energy. Those are still developing to find an approach which will be more appropriate and precise and will exclude the known errors which present methods include.

The overall difference of activation energy calculation results was of $\mp 38.46 \text{ kJ}\cdot\text{mol}^{-1}$ on average.

Those results confirm the suitability of energy crops to be used as a renewable energy source. Their advantage, compared to woody biomass, are their higher and mostly annual yields with very similar energetic properties.

4.3.7 Discussion

In the experiment, we focused on the investigation of the selected fire and thermal properties of totally six species of woody biomass and energy crops (*Paulownia tomentosa*, *Salix viminalis* clone TORA, *Populus x euroamericana* clone MAX 4 and *Sida hermaphrodita*, *Arundo donax*, *Miscanthus x giganteus*), which are mostly planted and harvested on energetic plantations in Slovakia.

When comparing the fire and thermal properties of woody and herbaceous biomass for energy purposes, the basic requirements specified by MCKENDRY (2002) shall be considered.

Very important property to assess the suitability of a biomass for energy purposes is the moisture content of the sample. In the analyses, all tested samples were in the range of 0 % (dry mass) to 50 ± 5 % according to requirement of the methodological approaches, standards used.

The moisture content value needs to be stated when quoting a calorific value or heating value. It reduces the available energy from the biomass.

The calorific value of biomass samples was expressed in form of gross calorific value. In the analysis the dry mass of samples was used.

The highest energy potential expressed in terms of the highest gross calorific values as well as heating values (at 10 % moisture content) were recorded in case of *Paulownia tomentosa* ($19.71 \pm 0.18 \text{ MJ}\cdot\text{kg}^{-1}$; $16.40 \pm 0.18 \text{ MJ}\cdot\text{kg}^{-1}$) and *Miscanthus x giganteus* ($19.60 \pm 0.14 \text{ MJ}\cdot\text{kg}^{-1}$; $16.29 \pm 0.14 \text{ MJ}\cdot\text{kg}^{-1}$). The lowest values of gross calorific values and heating were recorded by *Populus x euroamericana* clone MAX 4 ($19.47 \pm 0.29 \text{ MJ}\cdot\text{kg}^{-1}$; $16.18 \pm 0.29 \text{ MJ}\cdot\text{kg}^{-1}$) and *Sida hermaphrodita* ($18.75 \pm 0.36 \text{ MJ}\cdot\text{kg}^{-1}$; $15.58 \pm 0.36 \text{ MJ}\cdot\text{kg}^{-1}$).

The differences in values recorded by the tested samples of fast-growing tree species and energy crop species were very low. According to these finding, all the tested biomass species were considered suitable to be used for further energy use. However, *Paulownia tomentosa* and *Miscanthus x giganteus* seems to be the most suitable from calorific value and heating value point of view.

Heating value should be tightly connected also with elemental composition and affected by the variation in cell wall composition and ash. This fact was confirmed also by ash content analysis using the muffle furnace for ashing. The highest ash content was achieved by the energy crop samples. The values of ash content were in the range of 2.67 w% (*Miscanthus x giganteus*) – 3.46 w% (*Arundo donax*). Lower values of ash content achieved the samples of wood from the fast-growing tree species, their values were in the range of 0.75 – 2.58 w%. The lowest values of ash content were recorded right by *Paulownia tomentosa* (0.75 ± 0.05 w%) and *Miscanthus x giganteus* (2.67 ± 0.08 w%).

Thermal analyses methods are also often applied to assess the proportions of fixed carbon, i.e. carbon residue (ash). From the thermogravimetric analysis and results related to the carbon residue study is evident that the least carbon residue was recorded by *Paulownia tomentosa* () and the highest carbon residue was recorded by *Populus x euroamericana* (2.58 ± 0.24 w%), which reached the lowest heating value. From the energy crop species, the highest residue was found by *Arundo donax* (3.46 ± 0.11 w%), which heating value was very close to *Sida hermaphrodita* value (2.93 ± 0.11 w%) that reached the lowest heating value.

This information confirmed the best suitability of *Paulownia tomentosa* and *Miscanthus x giganteus* for further energy use due to lower ash content, which is required.

Elemental analysis of a biomass samples showed that the highest carbon mass was recorded by *Populus x euroamericana* and *Miscanthus x giganteus*, while the lowest ones by *Paulownia tomentosa* and *Arundo donax*. The highest values of hydrogen mass were found by *Salix viminalis* and *Miscanthus x giganteus*, the lowest ones by *Paulownia tomentosa* and *Arundo donax*. The highest values of nitrogen mass were found by *Salix viminalis*, *Paulownia tomentosa* and *Arundo donax*, and the lowest values by *Populus x euroamericana* and *Miscanthus x giganteus*. The highest values of oxygen mass were found by *Paulownia tomentosa* and *Sida hermaphrodita*. The lowest values of oxygen mass were found by *Populus x euroamericana* and *Miscanthus x giganteus*.

The relative proportions of cellulose and lignin is one of the determining factors in identifying the suitability of plants species for subsequent processing as energy trees or energy crops. The proportions of cellulose and lignin in biomass are important in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon-containing plant material present as cellulose is greater than for plants with a higher proportion of lignin, a determining factor when selecting biomass species for biochemical processing. To produce ethanol, a biomass feedstock

with a high, cellulose / hemicellulose content is needed to provide a high yield. Lignin content represents a potentially large energy source. (MCKENDRY 2002)

In this study, the highest content of lignin was found in case of fast-growing tree species by *Populus x euroamericana* (24.69 %) and considering the energy crops species by *Arundo donax* (21.49 %). The lowest values were found by *Paulownia tomentosa* (19.26 %) and *Sida hermaphrodita* (19.92 %). The *Paulownia tomentosa* had the lowest lignin content, at all.

From lignin content point of view, the most suitable for energy production (including biochemical processes) use are *Populus x euroamericana* and *Arundo donax*. However, the difference in lignin content value between *Arundo donax* and *Miscanthus x giganteus* is not very large. Based on this fact, *Miscanthus x giganteus* shall be very suitable for energy purposes, also for biochemical processes, from lignin content point of view.

For production bioethanol, due to high cellulose / holocellulose content as the most suitable seem to be *Populus x euroamericana* and *Miscanthus x giganteus*.

According to TG / DTG analyses results, we can state that for all the samples, the first region was characterised by water evaporation and in all cases ranged from initial temperature (43 °C) up to 160 °C. The second region was characterised by combustion of pyrolytic volatiles, and the third region by combustion of fixed carbon.

Mass loss analysis results based on TG / DTG analysis showed, that the fast-growing tree species achieved very similar values of mass loss rate. Higher differences we found in case of energy crop samples. The rapidest rate of thermal degradation showed *Sida Hermaphrodita*. The rate of thermal degradation of other energy crop samples was very similar.

From the mass loss analysis results obtained by application of non-standardized method of sample thermal loading by radiant heater are clear the differences in mass loss course of fast-growing tree species and energy crop species. The course of fast-growing tree species mass loss was more linear, meanwhile the course of the energy crops showed rapid mass loss in interval 1 – 90 s, then the mass loss rate decreased and became linear, too. We can assume, that in this first, and main, stage of thermal decomposition process, the active pyrolysis had place. Then, it was mostly the passive pyrolysis process. In individual tests, only small differences during tested fast-growing tree and energy crop species samples could be distinguished.

DSC analyses of fast-growing tree species and energy crop species showed only exothermic reaction with two regions in case of all samples. The results of DSC analysis considering the determined enthalpy change values showed that the highest energetic potential was found by *Arundo donax*, *Miscanthus x giganteus* and from fast-growing tree species by *Paulownia*

tomentosa. The heat flow values confirmed these results. The highest heat flow values among the fast-growing tree species was found by *Paulownia tomentosa*. Very good heat flow values achieved also the energy crop species, *Arundo donax* and *Miscanthus giganteus*. From the DSC results is also clear, that higher energetic potential has fast-growing tree species

The results focusing the activation energies of samples showed the very similar values for both fast-growing tree species and energy crop species. From the activation energy point of view the best results were obtained by *Paulownia tomentosa* and *Miscanthus x giganteus*. But there remains the problem with activation energy calculation results, when different kinetics methods are used for calculation. To only compare the thermal / energy properties of biomass samples is better to use only one method for evaluation.

The spontaneous ignition temperature analysis results showed the mean spontaneous ignition temperature values of all samples in the range of 425 ± 8 °C (698 ± 8 K). The lowest mean spontaneous ignition temperature value was recorded by *Salix viminalis* which was reached in 338 s from the start of the test. The highest mean spontaneous ignition temperature value was recorded by *Sida hermaphrodita*, which showed the shortest mean induction period value, too. The longest mean induction period was recorded by *Populus x euroamericana*. In general, the results showed also that the energy crops reached higher spontaneous ignition temperatures and shorter induction periods than the fast-growing tree species (mean spontaneous ignition temperature of 429 ± 3 °C, i.e. 695 ± 3 K) and induction period of 318 s on average.

Further we introduce the comparison of our results with the results of other authors dealing with similar issues.

YAVOROV ET AL. (2015) were engaged in determination the potential of fast-growing hardwood species from Bulgaria: *Paulownia elongata*, *Populus alba* and *Salix viminalis* RUBRA based on chemical analyses. The highest cellulose content they found in *Populus alba*, while the amount of lignin was the lowest in *Paulownia elongata*. They obtained the lowest calorific value for *Paulownia elongata*. This fact they accounted the determined lower content of lignin. The authors also confirmed, based on the calorific value of the fast-growing tree species tested, that the *Populus alba*, *Salix viminalis* RUBRA and *Paulownia elongata* are perspective and suitable for bioenergy production.

Our results confirmed the findings published in study of YAVOROV ET AL. (2015) *Populus x euroamericana* showed the highest content of lignin and *Paulownia tomentosa* the lowest content of all tested fast-growing tree species. However, as in the abovementioned study, *Paulownia tomentosa* reached the highest gross calorific (19.71 ± 0.18 MJ·kg⁻¹) and heating values (16.40 ± 0.18 MJ·kg⁻¹).

The calorific value and fire risk of selected fast-growing hardwood species, especially of *Populus nigra x Populus maximowiczii*, *Salix alba* L. and *Robinia pseudoacacia* L. were studied by MARTINKA ET AL. (2018). The average heat of combustion (gross calorific value) of the wood species tested was of $19.20 \pm 0.10 \text{ MJ}\cdot\text{kg}^{-1}$. This value is similar to results achieved in the framework of our study, where the average gross calorific value for fast-growing tree species was $19.60 \pm 0.12 \text{ MJ}\cdot\text{kg}^{-1}$.

As stated MORALES ET AL. (2017), the gross calorific value of dry matter of whole plants is about $19.0 \text{ MJ}\cdot\text{kg}^{-1}$. In our study the gross calorific values of tested energy crop species were in range from 18.75 to $19.60 \text{ MJ}\cdot\text{kg}^{-1}$. Those results shall be similar.

It should be also noted that this value is more than brown coal commonly used for domestic heating, which gross calorific values ranges from 12.00 to $14.00 \text{ MJ}\cdot\text{kg}^{-1}$. That is why the wood and plant-based biomass sources are very valuable not only from the efficiency and economy point of view, but also from environment protection point of view.

MOYA AND TENORIO (2013) studied the fuel characteristics (gross calorific value and fuel value index) of ten fast-growing species in plantations in Costa Rica. The results related to the gross calorific value varied from 16.5 to $20.6 \text{ MJ}\cdot\text{kg}^{-1}$ for sapwood, and from 16.3 to $20.1 \text{ MJ}\cdot\text{kg}^{-1}$ for heartwood. No consistency was observed with regard to which type of wood (sapwood or heartwood) had the highest gross calorific value. The gross calorific values of the fast-growing tree species found in our study varied in range of $19.47 - 19.71 \text{ MJ}\cdot\text{kg}^{-1}$, which corresponds with results published by above mentioned authors.

The major elemental composition based on dry matter in *Miscanthus* includes 47.1 to 49.7 % of carbon, 5.38 to 5.92 % of hydrogen and 41.4 to 44.6 % of oxygen, which reflects the variation of three major lignocellulosic components to some extent, stated LEWANDOWSKI AND KIRCHERER (1997); HODGSON ET AL. (2011); LYGIN ET AL. (2011). Our results showed that *Miscanthus x giganteus* elemental composition was very similar: 45.28 % of carbon, 5.74 % of hydrogen, and 48.69 % of oxygen.

Thermal analysis of biomass samples focused number of investigators. They used the results to study the reaction kinetics and calculate the activation energy of the reaction.

Thermal analysis was utilized by WONGSIRIAMNUAY AND TIPPAYAWONG (2010) to study the thermal degradation of giant sensitive plants (*Mimosa pigra* L.) under oxidative environment. Thermogravimetric (TG) method was used under air sweeping in dynamic conditions at the heating rates of 10, 30, and $50 \text{ }^\circ\text{C min}$, from room temperature to about $725 \text{ }^\circ\text{C}$. Starting with dehydration step between 30 and $150 \text{ }^\circ\text{C}$, the main thermal decomposition process under air showed two distinct degradation zones, corresponding

to devolatilization step between 200 and 375 °C and combustion step around 375 – 500 °C. Kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined, too. Comparison was made against other biomass materials. Mass loss and mass loss rates were strongly affected by heating rate. It was found that an increase in heating rate resulted in a shift of thermograms to higher temperatures. As the heating rates increased, average devolatilization and combustion rates were observed to increase while the activation energy showed slight increase.

Natural and treated hemp hurds thermal degradation process under air and nitrogen atmosphere studied STEVULOVA ET AL. (2017). To study the thermal decomposition of the samples TGA and DSC analyses were performed. Thermal decomposition of hemp hurds involved several parallel reactions related to heat and mass transfer processes. A comparison of DSC and TG/DTG results of hemp hurds samples before and after treatments demonstrated a better thermal stability for treated samples. It was caused by changes in chemical composition due to a partial removal of non-cellulosic components from hemp hurds structure, an increase in cellulose content and decrease in its degree of polymerization. The results showed different thermal behaviour of the hurds samples heated under nitrogen and air atmosphere. Based on DTG records, several-stage process of mass loss was found for the samples under air, whereas only two-stage process under nitrogen.

Pyrolysis characteristics of cellulose derived from moso bamboo and poplar described LIANG ET AL. (2018). To compare the pyrolysis characteristics of cellulose from moso bamboo and poplar, the samples were pyrolyzed with different heating rates through TG analysis. The kinetics was calculated by Kissinger-Akahitra-Sunose method. The results showed that pyrolysis process of moso bamboo and poplar fiber included three stages, and the main pyrolysis occurred in the second step. Moso bamboo fiber had higher start temperature, lower end temperature higher mass loss at each heating rate in the main pyrolysis stage. With increase in heating rate, the temperature corresponding to the maximum of mass loss increased and the DTG curve shifted to the higher temperature. The reaction rates varied at different heating rates. The activation energy of cellulose from moso bamboo was lower than poplar cellulose, indicating cellulose of moso bamboo to be pyrolyzed easier.

According to our TG / DTG results, we can state that we observed very similar course of thermal degradation process, which was divided to three stage, besides the *Sida hermaphrodita* samples, which in majority of heating rates showd only two stage thermal degradation process. Main pyrolysis process was recorded in the second stage of thermal degradation process by all species and their samples.

KOK AND ÖZGÜR (2013) used thermal analysis techniques (TG/DTG and DSC) for investigation *Miscanthus*, poplar wood and rice husk combustion behaviour. The combustion experiments were performed at five different heating rates (5, 10, 15, 25 and 50 °C·min⁻¹). Activation energy of the biomass samples were calculated using iso-conversional methods: Ozawa-Flynn-Wall, Kissinger and ASTM. They found that the biomass samples have two-stage of combustion. In the first stage, the combustion of the light volatiles occurred in the region of 250 °C to 400 °C and in the second stage; the combustion of fixed carbon took place in the region between 400 °C and 500 °C, depending on the biomass sample and heating rate. Ignition temperature and burnout temperature of biomass samples were found to increase with increasing heating rate. It was observed that the reactivity of biomass fuels is due to the combustion of light volatiles, however the energy release of biomass fuels is mainly due to the combustion of fixed carbon.

Our results of TG / DTG analyses point out the three-stage thermal degradation process. In the first stage combustion of the light volatiles occurred in the region of 43 °C to 160 °C, in the second stage the pyrolysis took place in the region 160 °C to 380 °C and in the third stage combustion of fixed carbon took place in the range between 360 °C and 490 °C.

Thermal behaviour of *Miscanthus x giganteus* and *Arundo donax* studied JEGUIRIM ET AL. (2010). Thermogravimetric analyses were performed at temperature of 5 °C·min⁻¹ under air atmosphere. The thermal degradation rates in devolatilization and combustion steps, the initial degradation temperature, and the residual weight were determined. Results showed that the initial degradation temperature for *Arundo donax* under air atmosphere was lower than for *Miscanthus x giganteus*. However, the thermal degradation rate was higher for *Miscanthus x giganteus*. Apparent activation energy was calculated as for devolatilization as for char oxidation phase. In the devolatilization phase *Arundo donax* apparent activation energy was of 107.2 kJ·mol⁻¹ and of 253.6 kJ·mol⁻¹ in the char oxidation phase. Apparent activation energy value for *Miscanthus x giganteus* was of 96.4 kJ·mol⁻¹ in the devolatilization phase and of 279.9 kJ·mol⁻¹ in the char oxidation phase.

Our results showed that the degradation temperature for *Arundo donax* under air atmosphere was lower than for *Miscanthus x giganteus* only in the second stage of thermal degradation process, i.e. pyrolysis. The activation energies were calculated for second stage of thermal degradation process. The activation energy of *Arundo donax* was calculated to 115.35 kJ·mol⁻¹ and of *Miscanthus x giganteus* to 102.80 kJ·mol⁻¹, using the Kissinger-Akahira-Sunos method.

The activation energy of the *Populus sp.* cellulose studied also LIANG ET AL. (2018). For its determination, they applied the Kissinger-Akahira-Sunose method. The mean activation energy

value of poplar in their experiments was calculated to $176.20 \text{ kJ}\cdot\text{mol}^{-1}$. The activation energy values of *Populus x euroamericana* calculated by the means of four different methods ranged from $119.72 \text{ kJ}\cdot\text{mol}^{-1}$ (Kissinger-Akahira-Sunose method) to $209.70 \text{ kJ}\cdot\text{mol}^{-1}$ (Ozawa-Flynn-Wall method).

Kinetic parameters (activation energy E_a , pre-exponential coefficient A , rate constant k) of thermolysis in torrefied and raw willow wood (*Salix viminalis L.*), as well as the effect of thermal modification conditions on the kinetics process was studied by WALKOWIAK AND BARTKOWIAK (2012). Samples of raw and torrefied willow wood in a steam atmosphere were analysed. The samples were subjected to thermogravimetric analysis under isothermal conditions. Analyses were conducted in an atmosphere of helium at $270 - 330^\circ\text{C}$. TG and DTG curves were recorded. The thermal characteristics of the samples were based on thermogravimetric analysis under dynamic conditions at a temperature of up to 600°C . Based on the data obtained from the TGA analyses, the kinetic parameters were calculated. The process of the thermal decomposition of raw and torrefied willow wood takes place within one temperature range of active thermolysis. In the areas of the active thermolysis of the experimental material, two temperatures each were established for the maximum decomposition rate. One, contained within the range of $260 - 269^\circ\text{C}$, may be related to the pyrolysis of the carbohydrate compounds of the lignocellulosic materials, while the other, covering the range of $333 - 334^\circ\text{C}$, to the thermolysis of the aromatic compounds of the raw material. Moreover, at the above-mentioned temperatures, maximum decomposition rates and percentage mass loss were also established. The kinetics of the thermal decomposition of the willow wood (*Salix viminalis L.*) the raw willow wood lost 77.5% of its initial mass. Under identical conditions, the mass loss in the torrefied willow wood was in range 72.6 – 76.1%. The calculated values of activation energy for the tested material (raw and torrefied willow wood) with respect to selected kinetic models were in the range from $138.1 \text{ kJ}\cdot\text{mol}^{-1}$ to $227.3 \text{ kJ}\cdot\text{mol}^{-1}$. The highest activation energy values were calculated for raw and torrefied willow wood at a temperature of 200°C in 24 hrs.

In our study, the thermal degradation process of *Salix viminalis* was divided to three stage. The second stage of thermal degradation process, i.e. pyrolysis, took place in the temperature region from 160°C to 380°C . In this stage the ash content was 1.9 w% on average, considering the different heating rate used in the thermal analyses. The mass loss values were in range 72.39 – 74.71 %. The activation energy values were in range $113.96 - 193.16 \text{ kJ}\cdot\text{mol}^{-1}$, in dependence on the calculation method used.

JEGUIRIM AND TROUVÉ (2010) studied the activation energy of two energy crops: *Arundo donax* and *Miscanthus x giganteus*, in the devotalisation and char oxidation steps. Activation energy for the *Arundo donax* was set to 107.20 kJ·mol⁻¹ and to 96.40 kJ·mol⁻¹ for *Miscanthus x giganteus*.

Quite different results achieved KOK AND ÖZGÜR (2013), who applied the Ozawa-Flynn-Wall, Kissinger and ASTM methods to calculate the activation energies of *Populus sp.* and *Miscanthus x giganteus* samples. Those methods require to perform the TG/DTG and DSC analyses to calculate it. The activation energy values for *Populus* were calculated as follows: by the Ozawa-Flynn-Wall method was of 219.20 kJ·mol⁻¹, by the Kissinger method of 129.20 kJ·mol⁻¹ and by the ASTM method was of 138.1 kJ·mol⁻¹. The *Miscanthus x giganteus* activation energies: by the Ozawa-Flynn-Wall method was of 229.40 kJ·mol⁻¹, by the Kissinger method of 135.80 kJ·mol⁻¹ and by the ASTM method was of 143.2 kJ·mol⁻¹.

In our study the *Arundo donax* reached the activation energy values ranging from 115.35 kJ·mol⁻¹ (Kissinger-Akahira-Sunose method) to 201.75 kJ·mol⁻¹ (Ozawa-Flynn-Wall method). The activation energy values of *Miscanthus x giganteus* were in range 102.80 kJ·mol⁻¹ (Kissinger-Akahira-Sunose method) – 191.50 kJ·mol⁻¹ (Ozawa-Flynn-Wall method).

Sida hermaphrodita was studied by JABLONOWSKI ET AL. (2016). They found the calorific value of *Sida hermaphrodita* of 16.96 MJ·kg⁻¹ and the ash content of 2.69 % w. Carbon contents of *Sida* biomass ca. 49 % of dm stated STOLARSKI ET AL. (2014a). Values for the carbon content in two other studies (WRÓBLEWSKA ET AL. 2009; MICHALSKA ET AL. 2015) amounted to 45.9 % and 47 %, and the nitrogen content to 0.3 % and 0.2 %, respectively. Results of our study point out the gross calorific value of *Sida hermaphrodita* of 18.75 ± 0.36 MJ·kg⁻¹ and heating value of 15.58 ± 0.36 MJ·kg⁻¹, ash content of 2.93 % w, carbon content of 43.74 % and nitrogen content of 0.77 %. In our study we reached higher calorific value and the content of nitrogen was much higher. These differences could have been caused by multiple factors such as different plant age, different methodological approaches, etc.

CONCLUSIONS

In recent years, renewable energy resources have become widely accepted to help solve the world's potential energy crisis. Developments are progressing rapidly, and new materials employed in the field of renewable energy require adequate quality control.

Perspective of the exhaustion of fossil fuels has accelerated the search for new alternative sources of raw materials for industrial and energy use. Another stimulus is also indicative targets set by the EU's renewable sources of energy (RES) that, among other things, assume that RES will provide 20 % of the total energy needs of the EU. These renewable sources should have irreplaceable share of energy from biomass (fast-growing trees and energy crop).

Forest biomass accounts for about 2 % of the total direct energy consumption currently, with 20% share of total direct energy consumption in 2020, with the forest biomass share of 12 %. The balance of available forest biomass can realistically increase the potential for energy crops production based on the regionalization of the area suitable for the cultivation of energy forests.

At present, in most Western European countries, the energy crop is mainly used for energy purposes to produce heat (direct burning or pyrolysis). Nowadays, it is possible to mix it with the coal, they can be burned together. Replacing a part of coal leads to a reduction in CO₂, NO_x, SO_x emissions, because biomass contains a small amount of nitrogen and sulphur in comparison to coal. If the phytomass is used for energy purposes, it is necessary to know its fire and energetic properties.

To analyse the fire and energetic properties of selected species of woody and herbaceous biomass to specify the rating of its suitability for energy production purposes was the aim of this study. We studied those properties using the samples of selected fast-growing tree species (*Populus x euroamericana* clone MAX 4, *Salix viminalis* clone TORA and *Pawlonia tomentosa*) and energy crop species (*Sida hermaphrodita*, *Miscanthus x giganteus* and *Arundo donax*).

To reach the objective several standardized and progressive analytical methods were applied to determine, e.g. the spontaneous ignition temperature and induction period which were further applied in the calculation of the activation energy according to Arrhenius. Then, there were provided the thermogravimetric analysis and differential scanning calorimetry to study the mass loss of samples in process of thermal degradation and to determine the carbon residue. Those results were further applied in calculation of activation energies according to selected iso-conversional methods: Ozawa-Flynn-Wall, Kissinger and ASTM-E698-05 (2018).

Those analyses were supplemented with calorific value, heating value analyses and ash content analysis as well as chemical analyses focusing the elemental composition and cellulose, hemicellulose, holocellulose, lignin and extractives content.

According to the provided analyses results, we can state that all the tested species of fast-growing trees and energy crop are the suitable to be used as a source of energy, as was stated in several work of other experts in this field. We found, that from majority of the properties (high calorific and heating value, high enthalpy values, and low ash content), the most suitable species for energy purposes are *Paulownia tomentosa* and *Miscanthus x giganteus*. From lignin content and activation energy point of view among the most suitable for further energy use belong *Populus x euroamericana* and *Arundo donax*. These results also point out the fact that energy crop species could be consider to be more suitable to be used as a renewable energy source, not only from the energetic properties point of view, but mostly due to the yields, which can be harvested each year, in comparison to woody biomass.

Besides the experiment results, an important part of this monography is also its theoretical introduction which provides very good background to be informed about the state-of-the-art related to the renewable energy source use, which is focused particularly on biomass use for energy purposes. It provides also a good base for planning further research activities in this field.

SUMMARY IN SLOVAK

Predkladaná monografia sa zaoberá problematikou využívania obnoviteľných zdrojov energie, konkrétne biomasy, na zaistenie nepretržitých dodávok energie do budúcnosti. Táto problematika priamo súvisí aj s potrebou zaistenia energetickej bezpečnosti ako Európskej únie, tak aj samotnej Slovenskej republiky.

Teoretické poznatky o obnoviteľných zdrojoch energie (štatistické ukazovatele využívania obnoviteľných zdrojov energie a legislatívne pozadie), samotnej biomase ako zdroja energie sú doplnené o experimentálnu časť, ktorá je venovaná popisu pestovných potrieb a produkčných vlastností vybraných druhov rýchlorastúcich drevín (*Paulownia tomentosa*, *Salix viminalis* clone TORA, *Populus x euroamericana* clone MAX 4) a energetických plodín (*Sida hermaphrodita*, *Arundo donax*, *Miscanthus x giganteus*) a zisťovaniu ich požiarnotechnických a energetických vlastností s cieľom posúdenia ich vhodnosti pre využitie ako obnoviteľného zdroja pre produkciu tepla a elektriny.

Pri získavaní experimentálnych výsledkov boli využité progresívne analytické metódy stanovenia dôležitých materiálových a požiarno-technických charakteristík. Výsledky boli diskutované s podporou poznatkou z medzinárodnej spolupráce a s využitím najnovších trendov v danej oblasti v zahraničí.

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GLOSSARY

| | |
|---|--|
| Activation energy | Minimum quantity of energy which the reacting species must possess in order to undergo a specified reaction. |
| Agricultural biomass | Subset of biomass produced directly from agricultural activities, including cereal grains, sugar crops, oilseeds, other arable crops and crop by-products such as straw, vegetative grasses, farm forestry (e.g. willow and poplar), and livestock by-products, e.g. manure and animal fats. |
| Bioenergy | Renewable energy produced from biomass when used to produce heat and / or power and transport fuels. |
| Biogas | Mixture of gases produced by the breakdown of organic matter in the absence of oxygen. |
| Biomass | Biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste. |
| C₄ carbon fixation | Photosynthetic process in some plants. It is the first step in extracting carbon from carbon dioxide to be able to use it in sugar and other biomolecules. |
| Combustion | Decomposition of organic material by the action of heat, while generating flammable gases, followed by subsequent oxidation and release of energy. |
| Dendromass | Organic matter of woody and shrubby plants consisting of wood, bark and green matter. |
| Electricity produced from renewable energy sources | Electricity produced by plants using only renewable energy sources, as well as the proportion of electricity produced from renewable energy sources in hybrid plants also using conventional energy sources and including renewable electricity used for filling storage systems, and excluding electricity produced as a result of storage systems. |
| Gross calorific value | Heat released by the perfect combustion (by oxidation of the active elements of the fuel) of 1 kg of fuel and cooling of the flue gas and the ash to the initial temperature (i.e. 20 °C), while the water vapour condenses and changes to the water. |

| | |
|---|---|
| Heating value | Heat released by the perfect combustion of 1 kg of fuel, when the combustion is cooled to its original ambient temperature ($t = 20\text{ }^{\circ}\text{C}$), while the water (evaporated from the fuel produced by the oxidation of hydrogen contained in fuel and supplied with humid air) remains in the gaseous state. |
| Herbaceous energy crop | Grassy or forage energy crops. |
| Induction period | Initial slow stage of a chemical reaction; after the induction period, the reaction accelerates. |
| Phytomass | Biomass of herbaceous origin. |
| Plantation | Large-scale estate meant for farming that specializes in cash crops. |
| Renewable energy source | Renewable non-fossil energy sources (wind, solar, geothermal, wave, tidal, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases). |
| Spontaneous combustion | Ignition of organic matter (e.g. hay or coal) without apparent cause, typically through heat generated internally by rapid oxidation. |
| Spontaneous ignition temperature | Lowest temperature at which a substance will ignite itself without the presence of a spark or flame. |
| Thermogravimetry | Metóda termickej analýzy, pri ktorej sa meria kontinuálne hmotnosť vzorky v čase, za súčasného rastu teploty. |
| Thermal analysis | Group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. |
| Thermal degradation | Molecular deterioration as a result of overheating. |
| Zoomass | Total mass of a living animal. |
| Pyrolysis | Thermochemical decomposition of organic materials in the absence of oxygen. |

LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|--|
| A | Pre-exponential (frequency) factor |
| APVV | Slovak Research and Development Agency / Agentúra pre podporu vedy a výskumu |
| ASTM | American Society for Testing and Materials |
| C | Carbon |
| C₄ | C ₄ carbon fixation |
| C₆H₁₂O₆ | Glucose |
| CaCO₃ | Calcium carbonate |
| CHP | Combined heat and power |
| Cl | Chlorine |
| CN | China |
| CO₂ | Carbon dioxide |
| Coll. | Collection of Laws / Z. z. |
| COM | Communication from the Commission to the European Parliament |
| Cu | Copper |
| CV | Calorific value |
| dm | Dry mass |
| <i>dm</i> | Mass difference |
| DMA | Dynamic Mechanical Analysis |
| DSC | Differential scanning calorimetry |
| <i>dt</i> | Time or temperature difference |
| DTA | Differential Thermal Analysis |
| DTG | Derivation thermogravimetry |
| <i>E</i> | Activation energy |
| EC | European Commission |
| EU | European Union |
| EU-28 | 28 member countries of the European Union |
| Fe | Iron |
| GC-MS | Gas Chromatography - Mass Spectroscopy |
| GCV | Gross calorific value |
| HHV | Higher heating value |
| HV | Heating value |
| K | Potassium |
| <i>K</i> | Kelvin |
| KEGA | Cultural and Educational Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic / Kultúrna a edukačná grantová agentúra MŠVVaŠ SR |
| Kt | Thousand tons |

| | |
|-----------------------------|---|
| LHV | Lower heating value |
| LZ | Forest enterprise / Lesný závod |
| MMT | Million tons |
| MPSR | 9,10-dihydro-9-oxa-10-fosfafenantrén-10-oxid |
| N | Nitrogen |
| NCV | Net calorific value |
| Ni | Nickel |
| NLC | National Forest Centre / Národné lesnícke centrum |
| NO_x | Nitrogen oxides |
| Pb | Lead |
| PSL | Forest management plan / Program starostlivosti o les |
| Py-GC-MS | Pyrolysis - Gas Chromatography - Mass Spectroscopy |
| <i>qv</i> | Airflow rate |
| <i>R</i> | Ideal gas constant |
| RES | Renewable energy sources |
| S | Sulphur |
| S.E. | State Enterprise |
| SES | Slovak power engineering plant / Slovenské energetické strojárne |
| SK | Slovakia |
| SO₂ | Sulphur dioxide |
| SO_x | Sulphur oxides |
| SR | Slovak Republic |
| SRC | Short rotation coppice |
| STN | Slovak Technical Standard |
| SWD | European Commission Staff Working Document |
| SZVT | Slovak Association of Heat Producers / Slovenský zväz výrobcov tepla |
| <i>T</i> | Thermodynamic temperature |
| <i>T</i> | Ignition thermodynamic temperature |
| TA | Thermal analysis |
| TDE | Total direct energy consumption |
| TG | Thermogravimetry |
| TGA | Thermogravimetric analysis |
| TMA | Thermomechanical Analysis |
| TOA | Thermo Optical Analysis |
| <i>T_p</i> | Peak temperature |
| U.S. | United States |
| URSO | Regulatory Office for Network Industries |
| VEGA | Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and Slovak Academy of Sciences / Vedecká grantová agentúra Ministerstva školstva, vedy, výskumu a športu Slovenskej republiky a Slovenskej akadémie vied |

| | |
|------------------------------|--|
| W | Watt |
| Zn | Zinc |
| β | Heating rate |
| ΔH | Enthalpy change |
| τ | Induction period of spontaneous ignition |

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zariadenie alebo zrekonštruované plynárenské zariadenie / Decree of the Regulatory Office for Network Industries laying down details of the request and the list of documents for exemption from the obligation to provide third party access to networks and storage capacity for new significant gas facility or refurbished gas facility.
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APPENDIX

Appendix 1: Primary production of energy from renewable sources (2008-2017)

Appendix 2: Share of energy from renewable sources in heating and cooling

Appendix 3: TG / DTG and DSC analysis results

**Appendix 1: Primary production of energy from renewable sources in EU-28 in period
2008-2017 (thousand tonnes of oil equivalent - TOE)**

(Source: EUROSTAT 2019)

| Country/Year | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| European Union (28 countries) | 1,863,562 | 1,749,493 | 1,817,609 | 1,757,302 | 1,738,117 | 1,717,327 | 1,655,884 | 1,680,744 | 1,692,907 | 1,719,424 |
| Euro area (19 countries) | 1,325,692 | 1,249,927 | 1,291,610 | 1,248,226 | 1,233,630 | 1,221,669 | 1,177,628 | 1,195,795 | 1,203,642 | 1,223,145 |
| Belgium | 68,737 | 63,881 | 68,769 | 64,173 | 60,836 | 62,901 | 59,139 | 59,576 | 63,520 | 64,116 |
| Bulgaria | 20,165 | 17,741 | 17,969 | 19,210 | 18,431 | 17,122 | 17,925 | 18,732 | 18,338 | 18,978 |
| Czechia | 45,592 | 42,823 | 45,599 | 43,785 | 43,461 | 43,707 | 42,183 | 42,346 | 41,935 | 43,432 |
| Denmark | 21,197 | 19,790 | 21,099 | 19,666 | 18,781 | 18,933 | 18,111 | 18,138 | 18,512 | 18,743 |
| Germany (until 1990 former territory of the FRG) | 342,695 | 321,206 | 337,327 | 320,346 | 321,946 | 328,833 | 316,813 | 318,941 | 321,927 | 324,473 |
| Estonia | 5,818 | 5,064 | 5,873 | 5,849 | 5,893 | 6,543 | 6,119 | 5,712 | 6,261 | 6,071 |
| Ireland | 16,011 | 15,274 | 15,185 | 13,941 | 14,105 | 13,525 | 13,586 | 14,301 | 15,038 | 14,805 |
| Greece | 34,339 | 32,770 | 30,868 | 30,125 | 29,308 | 25,992 | 25,648 | 25,649 | 25,150 | 26,365 |
| Spain | 150,966 | 139,329 | 138,852 | 138,404 | 137,828 | 128,347 | 126,460 | 130,824 | 132,223 | 137,828 |
| France | 274,498 | 263,901 | 271,993 | 266,978 | 267,086 | 268,099 | 257,620 | 261,756 | 257,378 | 257,619 |
| Croatia | 9,928 | 9,563 | 9,464 | 9,269 | 8,716 | 8,545 | 8,144 | 8,493 | 8,570 | 8,873 |
| Italy | 187,549 | 174,924 | 179,819 | 173,688 | 166,908 | 160,570 | 151,759 | 157,630 | 156,490 | 161,815 |
| Cyprus | 3,170 | 3,057 | 2,941 | 2,905 | 2,730 | 2,435 | 2,473 | 2,533 | 2,741 | 2,815 |
| Latvia | 4,899 | 4,783 | 4,881 | 4,592 | 4,778 | 4,706 | 4,684 | 4,634 | 4,707 | 4,812 |
| Lithuania | 9,478 | 8,707 | 6,968 | 7,198 | 7,264 | 6,839 | 6,771 | 6,985 | 7,246 | 7,547 |
| Luxembourg | 4,639 | 4,369 | 4,646 | 4,570 | 4,461 | 4,337 | 4,224 | 4,180 | 4,194 | 4,338 |
| Hungary | 27,170 | 25,840 | 26,592 | 26,063 | 24,771 | 23,920 | 23,823 | 25,203 | 25,585 | 26,679 |
| Malta | 1,889 | 2,027 | 2,388 | 2,271 | 2,166 | 2,054 | 2,101 | 2,294 | 2,470 | 2,939 |
| Netherlands | 98,559 | 95,189 | 100,014 | 95,475 | 94,449 | 92,261 | 87,969 | 88,096 | 89,605 | 89,937 |
| Austria | 33,995 | 32,258 | 34,371 | 33,389 | 33,186 | 33,973 | 32,899 | 33,512 | 33,779 | 34,445 |
| Poland | 98,536 | 94,482 | 101,774 | 101,770 | 98,175 | 98,680 | 94,853 | 95,932 | 100,641 | 105,347 |
| Portugal | 26,110 | 25,641 | 24,828 | 24,317 | 22,964 | 23,035 | 22,722 | 23,621 | 23,687 | 24,767 |
| Romania | 39,689 | 34,820 | 35,041 | 35,784 | 34,999 | 31,910 | 31,647 | 31,899 | 31,789 | 33,473 |
| Slovenia | 7,845 | 7,061 | 7,235 | 7,237 | 6,978 | 6,813 | 6,568 | 6,508 | 6,793 | 6,935 |

Continuation of the table

| Country/Year | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Slovakia | 18,262 | 16,690 | 17,711 | 17,195 | 16,551 | 16,756 | 15,757 | 16,265 | 16,346 | 17,248 |
| Finland | 36,232 | 33,796 | 36,939 | 35,573 | 34,194 | 33,649 | 34,316 | 32,779 | 34,085 | 34,271 |
| Sweden | 51,878 | 47,197 | 52,666 | 52,643 | 52,548 | 51,519 | 51,217 | 50,136 | 52,662 | 52,848 |
| United Kingdom | 223,715 | 207,309 | 215,795 | 200,886 | 204,604 | 201,321 | 190,352 | 194,070 | 191,233 | 187,906 |
| Iceland | 5,734 | 5,890 | 5,602 | 6,000 | 5,864 | 6,091 | 6,089 | 5,871 | 5,663 | 5,934 |
| Norway | 33,145 | 32,503 | 33,781 | 29,258 | 31,869 | 33,822 | 29,370 | 30,031 | 28,318 | 30,775 |
| Montenegro | 1,233 | 965 | 1,129 | 1,134 | 1,071 | 996 | 975 | 1,030 | 988 | 1,038 |
| North Macedonia | 3,032 | 2,817 | 2,881 | 3,122 | 3,004 | 2,783 | 2,707 | 2,656 | 2,696 | 2,762 |
| Albania | 2,140 | 2,171 | 2,152 | 2,245 | 2,023 | 2,386 | 2,376 | 2,220 | 2,285 | 2,405 |
| Serbia | 16,874 | 15,230 | 15,608 | 16,325 | 14,610 | 14,950 | 13,374 | 14,833 | 15,452 | 15,763 |
| Turkey | 100,120 | 99,986 | 105,737 | 112,981 | 118,045 | 114,832 | 123,245 | 133,178 | 140,511 | 151,259 |
| Bosnia and Herzegovina | no data | 6,003 | 6,183 | 6,767 | 6,754 |
| Kosovo (under United Nations Security Council Resolution 1244/99) | 2,219 | 2,459 | 2,517 | 2,541 | 2,384 | 2,312 | 2,217 | 2,524 | 2,704 | 2,569 |
| Ukraine | 134,982 | 114,625 | 132,573 | 126,644 | 122,650 | 115,114 | 104,909 | 92,247 | 93,751 | 89,196 |
| Georgia | no data | 3,986 | 4,472 | 4,703 | 4,860 | 4,896 |

Appendix 2: Share of energy from renewable sources in heating and cooling

Share of renewable energy sources in heating and cooling, 2004-2017

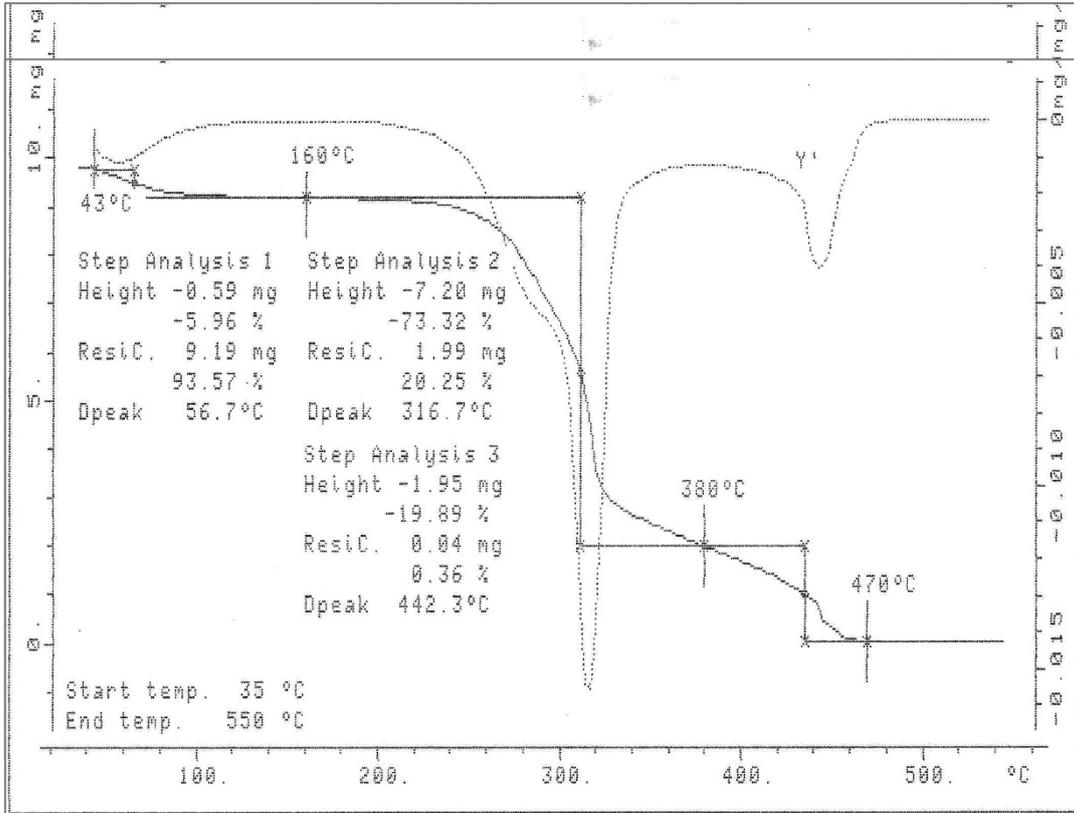
(%)

| | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| EU-28 | 10.4 | 11.1 | 11.8 | 13.2 | 13.8 | 15.2 | 15.4 | 16.0 | 17.0 | 17.5 | 18.4 | 18.8 | 19.0 | 19.5 |
| Belgium | 2.8 | 3.4 | 3.7 | 4.6 | 5.0 | 5.9 | 6.1 | 6.6 | 7.3 | 7.4 | 7.7 | 7.7 | 8.1 | 8.0 |
| Bulgaria | 14.1 | 14.3 | 14.8 | 13.9 | 17.3 | 21.7 | 24.4 | 24.9 | 27.5 | 29.2 | 28.3 | 28.6 | 30.0 | 29.9 |
| Czechia | 9.9 | 10.9 | 11.2 | 12.4 | 12.9 | 14.3 | 14.1 | 15.4 | 16.3 | 17.7 | 19.5 | 19.7 | 19.8 | 19.7 |
| Denmark | 20.6 | 22.8 | 23.8 | 26.9 | 28.1 | 29.5 | 31.0 | 32.3 | 33.6 | 35.1 | 38.5 | 40.7 | 42.2 | 46.5 |
| Germany | 7.1 | 7.7 | 8.4 | 10.2 | 10.3 | 11.2 | 12.1 | 12.6 | 13.5 | 13.5 | 13.5 | 13.5 | 13.1 | 13.4 |
| Estonia | 33.2 | 32.2 | 30.7 | 32.7 | 35.5 | 41.8 | 43.3 | 44.1 | 43.1 | 43.2 | 45.2 | 49.6 | 51.2 | 51.6 |
| Ireland | 2.9 | 3.4 | 3.7 | 3.8 | 3.5 | 4.2 | 4.3 | 4.7 | 4.9 | 5.2 | 6.3 | 6.3 | 6.3 | 6.9 |
| Greece | 12.8 | 12.8 | 12.4 | 14.4 | 14.2 | 16.5 | 17.9 | 19.4 | 23.4 | 26.5 | 27.0 | 25.8 | 24.6 | 26.6 |
| Spain | 9.5 | 9.4 | 11.3 | 11.2 | 11.6 | 13.3 | 12.6 | 13.6 | 14.1 | 14.1 | 15.7 | 17.0 | 17.1 | 17.5 |
| France | 12.5 | 12.4 | 11.7 | 12.8 | 13.3 | 15.0 | 16.1 | 16.0 | 17.5 | 18.6 | 19.1 | 19.9 | 21.1 | 21.3 |
| Croatia | 29.4 | 30.0 | 29.1 | 29.2 | 28.6 | 31.2 | 32.8 | 33.7 | 36.5 | 37.2 | 36.1 | 38.5 | 37.6 | 36.5 |
| Italy | 5.7 | 8.2 | 10.1 | 13.3 | 15.3 | 16.4 | 15.6 | 13.8 | 17.0 | 18.1 | 18.9 | 19.3 | 18.9 | 20.1 |
| Cyprus | 9.3 | 10.0 | 10.4 | 13.1 | 14.5 | 16.3 | 18.2 | 19.2 | 20.7 | 21.6 | 21.6 | 22.5 | 23.0 | 24.5 |
| Latvia | 42.5 | 42.7 | 42.6 | 42.4 | 42.9 | 47.9 | 40.7 | 44.7 | 47.3 | 49.7 | 52.2 | 51.7 | 51.8 | 54.6 |
| Lithuania | 30.4 | 29.3 | 29.2 | 29.1 | 32.0 | 33.7 | 32.5 | 32.8 | 34.5 | 36.9 | 40.6 | 46.1 | 46.6 | 46.5 |
| Luxembourg | 1.8 | 3.6 | 3.6 | 4.4 | 4.6 | 4.7 | 4.7 | 4.8 | 5.0 | 5.5 | 7.2 | 7.1 | 7.3 | 8.1 |
| Hungary | 6.4 | 9.9 | 11.4 | 13.5 | 12.0 | 17.0 | 18.1 | 20.0 | 23.3 | 23.7 | 21.2 | 21.2 | 20.9 | 19.6 |
| Malta | 1.0 | 1.0 | 1.4 | 1.5 | 1.7 | 2.0 | 3.1 | 3.7 | 3.8 | 4.1 | 5.1 | 5.4 | 5.4 | 5.9 |
| Netherlands | 2.2 | 2.4 | 2.7 | 3.0 | 3.1 | 3.4 | 3.1 | 3.7 | 3.8 | 4.1 | 5.1 | 5.4 | 5.4 | 5.9 |
| Austria | 20.2 | 21.9 | 22.9 | 25.1 | 25.1 | 27.4 | 28.7 | 28.9 | 30.0 | 31.9 | 32.9 | 32.0 | 32.2 | 32.0 |
| Poland | 10.2 | 10.2 | 10.2 | 10.5 | 10.8 | 11.5 | 11.7 | 13.1 | 13.4 | 14.1 | 14.0 | 14.5 | 14.7 | 14.5 |
| Portugal | 32.5 | 32.1 | 34.2 | 35.0 | 37.5 | 38.0 | 33.9 | 35.2 | 33.2 | 34.6 | 34.0 | 33.5 | 35.1 | 34.4 |
| Romania | 17.3 | 17.9 | 17.6 | 19.5 | 23.2 | 26.4 | 27.2 | 24.3 | 25.7 | 26.2 | 26.7 | 25.9 | 26.9 | 26.6 |
| Slovenia | 18.4 | 18.9 | 18.5 | 20.4 | 19.2 | 27.6 | 28.1 | 30.3 | 31.5 | 33.4 | 32.4 | 33.9 | 34.0 | 33.2 |
| Slovakia | 5.1 | 5.0 | 4.5 | 6.2 | 6.1 | 8.2 | 7.9 | 9.3 | 8.8 | 7.9 | 8.9 | 10.8 | 9.9 | 9.8 |
| Finland | 39.5 | 39.1 | 41.4 | 41.4 | 43.3 | 43.1 | 44.2 | 45.9 | 48.4 | 50.8 | 52.0 | 52.6 | 53.7 | 54.8 |
| Sweden | 46.6 | 51.8 | 56.3 | 58.7 | 61.0 | 63.6 | 60.9 | 62.2 | 65.8 | 67.1 | 67.9 | 68.6 | 68.5 | 69.1 |
| United Kingdom | 0.7 | 0.8 | 0.9 | 1.0 | 1.9 | 2.3 | 2.6 | 3.0 | 3.2 | 4.0 | 4.7 | 6.1 | 7.0 | 7.5 |
| Montenegro | . | 52.9 | 51.4 | 49.1 | 46.0 | 62.1 | 76.5 | 81.3 | 79.8 | 68.5 | 67.6 | 68.5 | 69.2 | 67.5 |
| North Macedonia | 23.3 | 24.7 | 24.9 | 22.5 | 24.6 | 29.2 | 26.5 | 27.3 | 29.6 | 31.8 | 35.0 | 34.5 | 30.9 | 36.4 |
| Albania | 33.1 | 37.8 | 31.0 | 33.1 | 37.1 | 34.7 | 31.3 | 31.4 | 39.1 | 37.8 | 31.0 | 34.6 | 33.8 | 24.9 |
| Serbia | 14.0 | 15.6 | 15.8 | 13.2 | 16.7 | 26.5 | 23.2 | 21.1 | 23.2 | 25.1 | 28.8 | 26.5 | 24.7 | 24.4 |
| Turkey | 17.6 | 17.0 | 15.2 | 14.6 | 15.0 | 15.4 | 14.4 | 12.0 | 12.1 | 12.6 | 12.3 | 12.1 | 11.7 | 10.3 |
| Kosovo (*) | 51.9 | 49.5 | 48.9 | 49.2 | 47.8 | 47.8 | 45.5 | 44.7 | 49.3 | 49.7 | 51.8 | 46.7 | 51.8 | 50.5 |

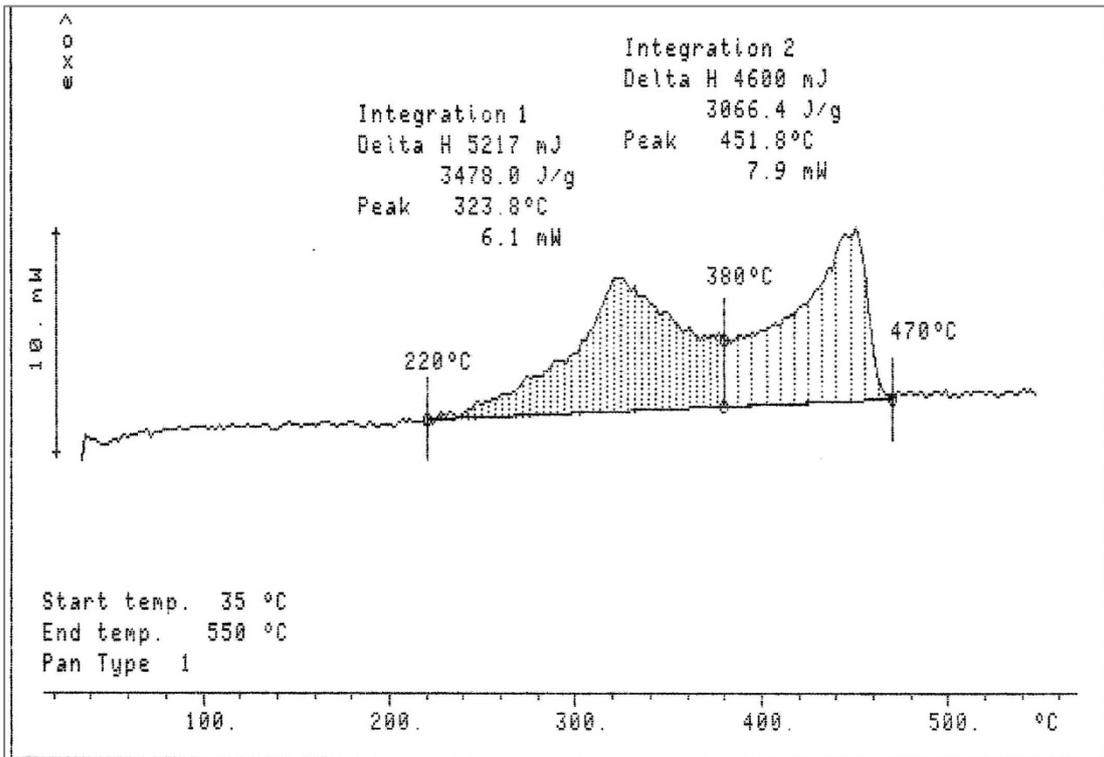
(*) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo declaration of independence.
Source: SHARES_summary_results in <http://ec.europa.eu/eurostatweb/energy/data/shares>

Appendix 3: TG / DTG and DSC analysis results

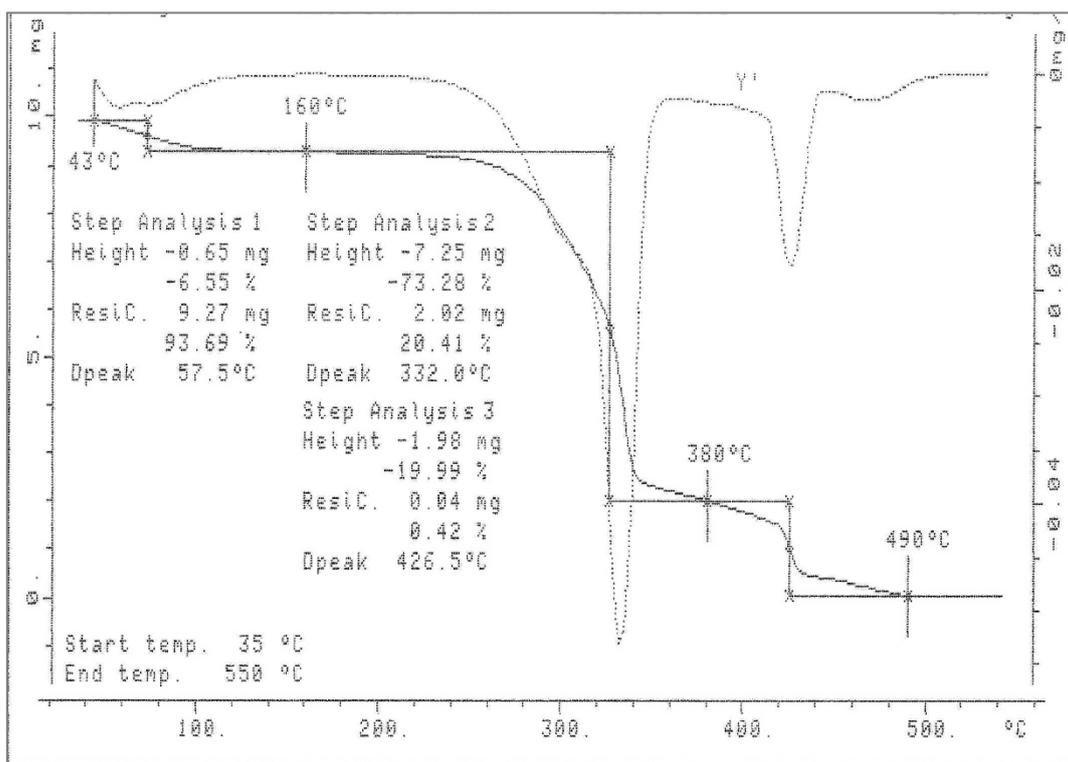
Populus x euroamericana MAX 4 – TG / DT analysis (heating rate 5 °C·min⁻¹)



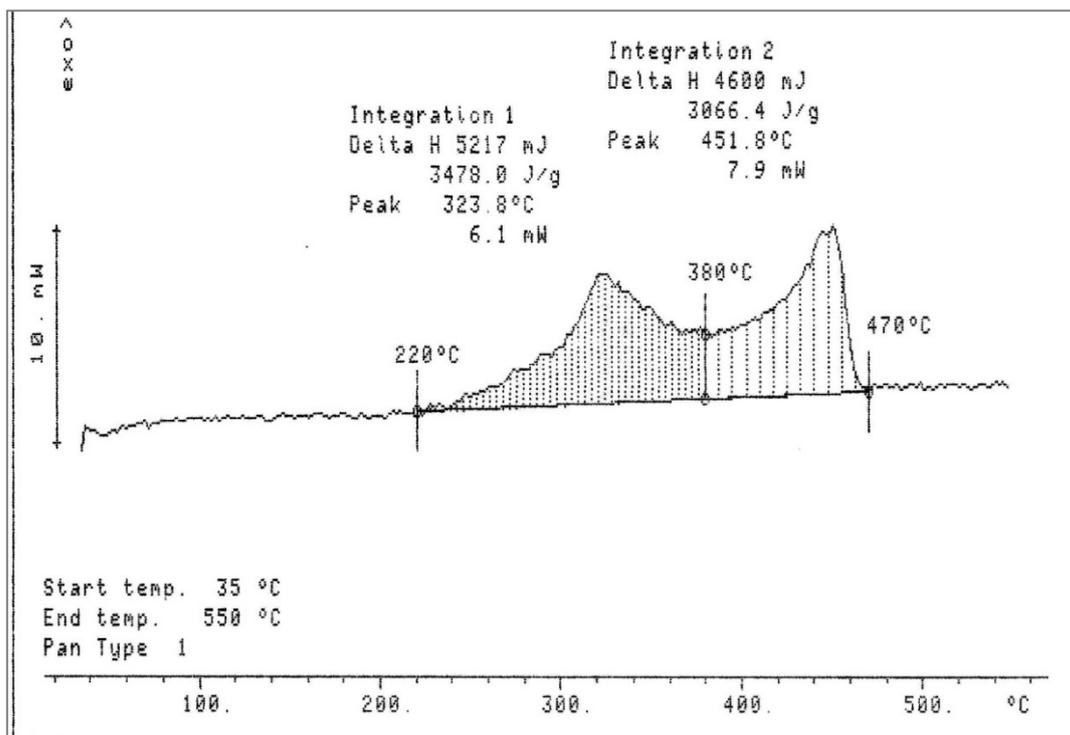
Populus x euroamericana MAX 4 – DSC analysis (heating rate 5 °C·min⁻¹)



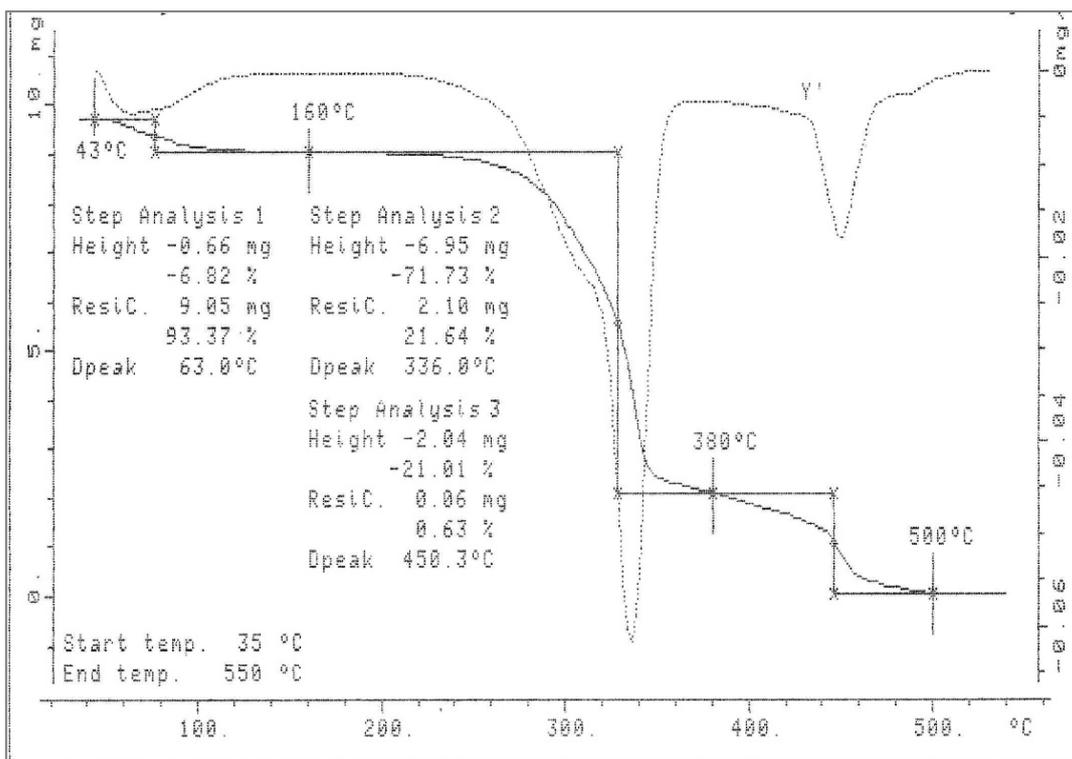
Populus x euroamericana MAX 4 – TG / DT analysis (heating rate 15 °C·min⁻¹)



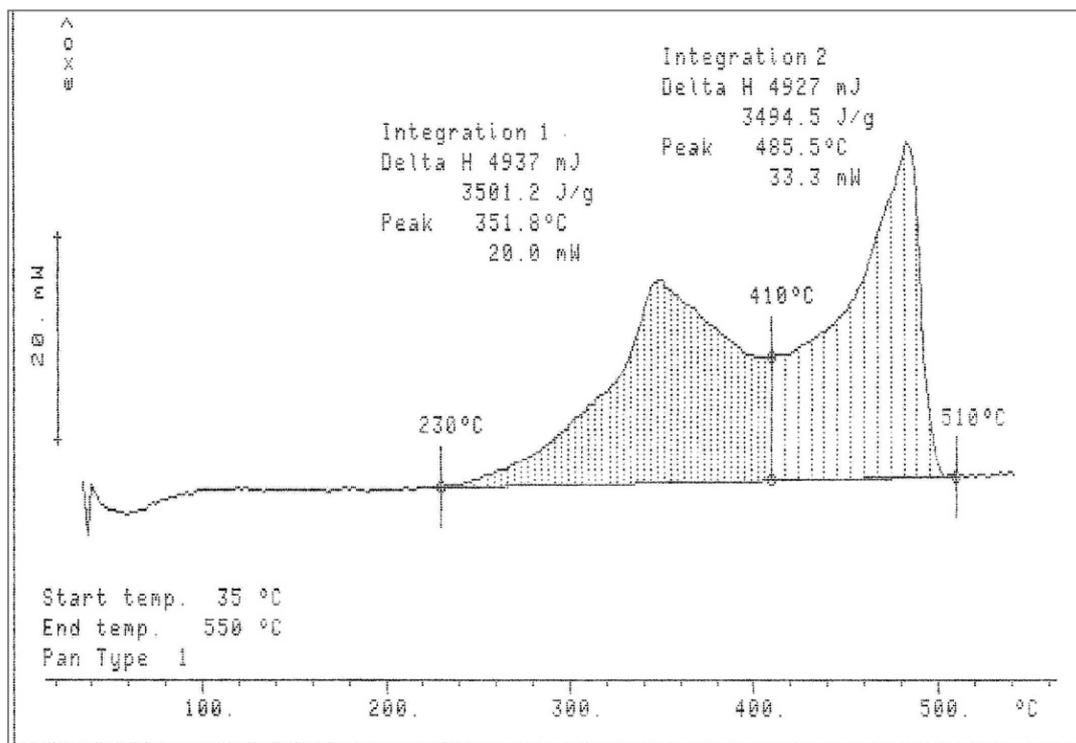
Populus x euroamericana MAX 4 – DSC analysis (heating rate 15 °C·min⁻¹)



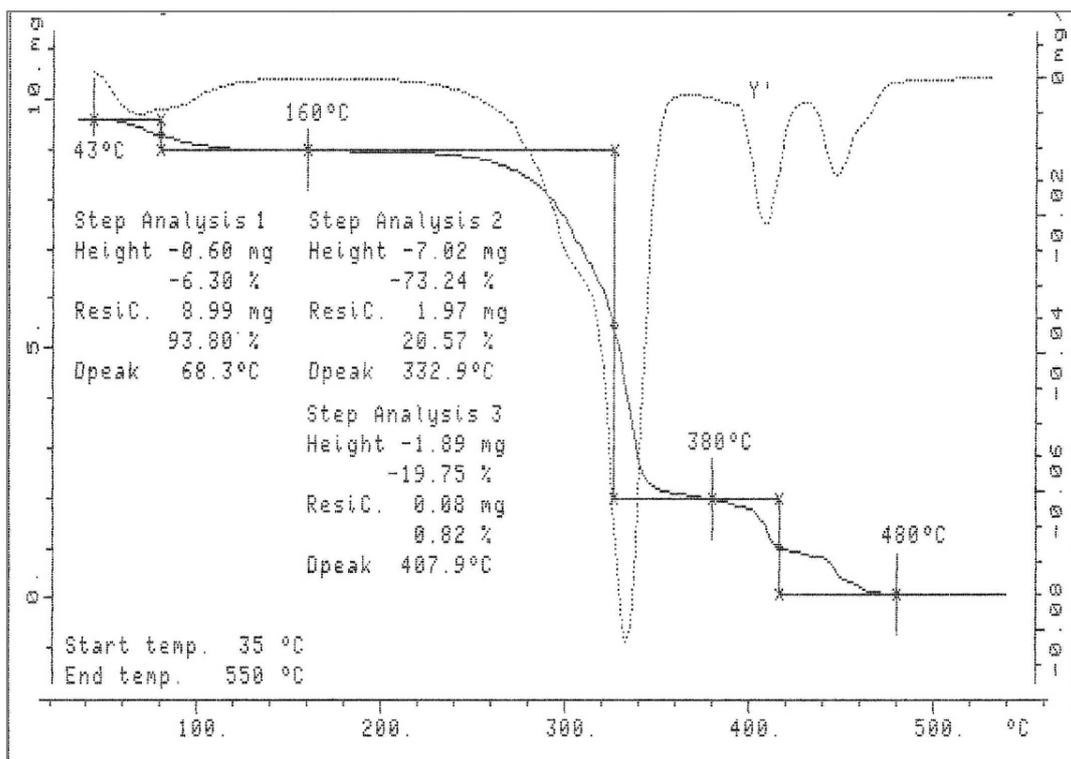
Populus x euroamericana MAX 4 – TG / DTG analysis (heating rate 20 °C·min⁻¹)



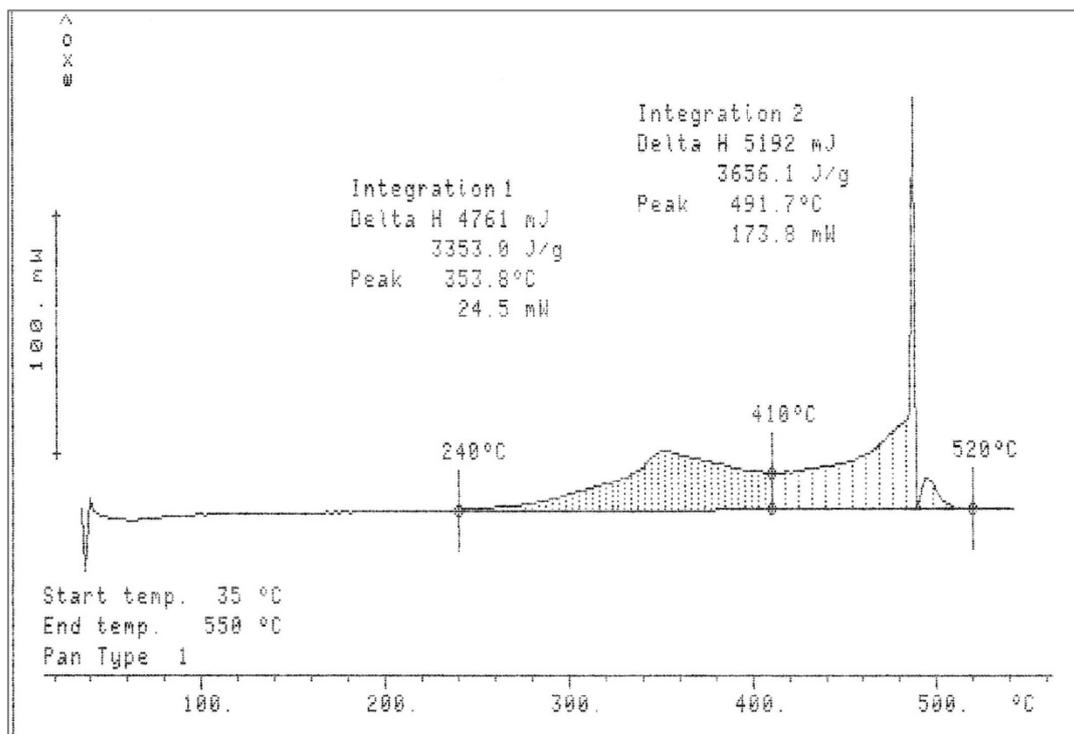
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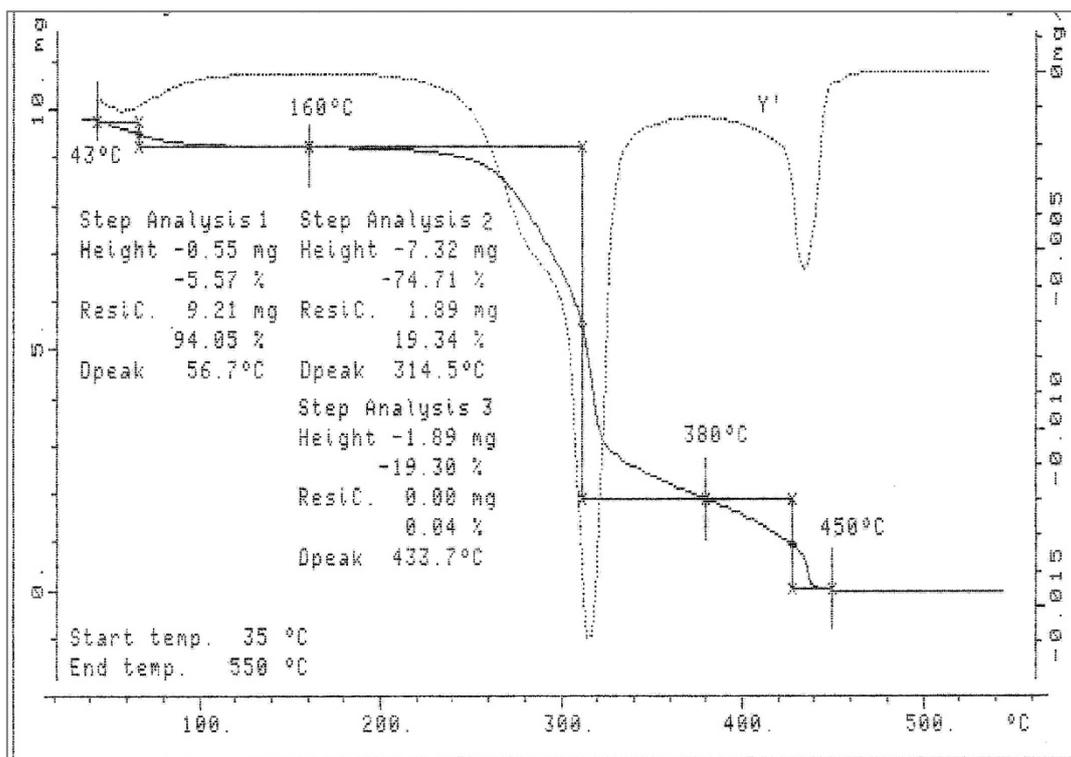
Populus x euroamericana MAX 4 – TG / DTG analysis (heating rate 25 °C·min⁻¹)



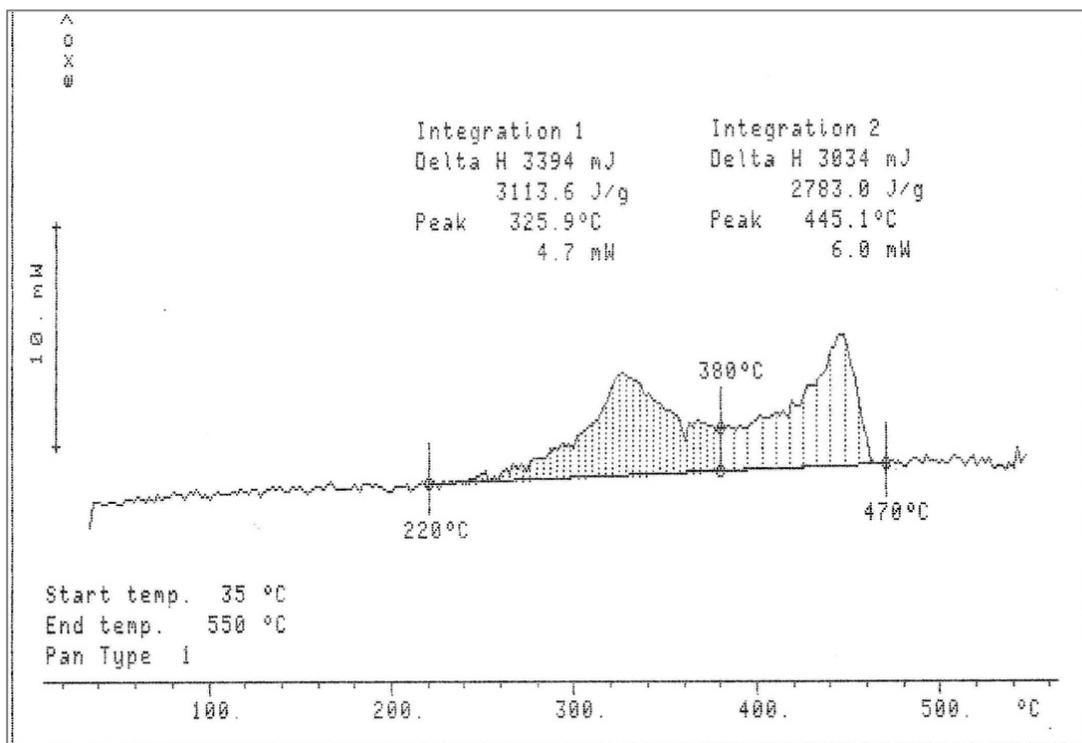
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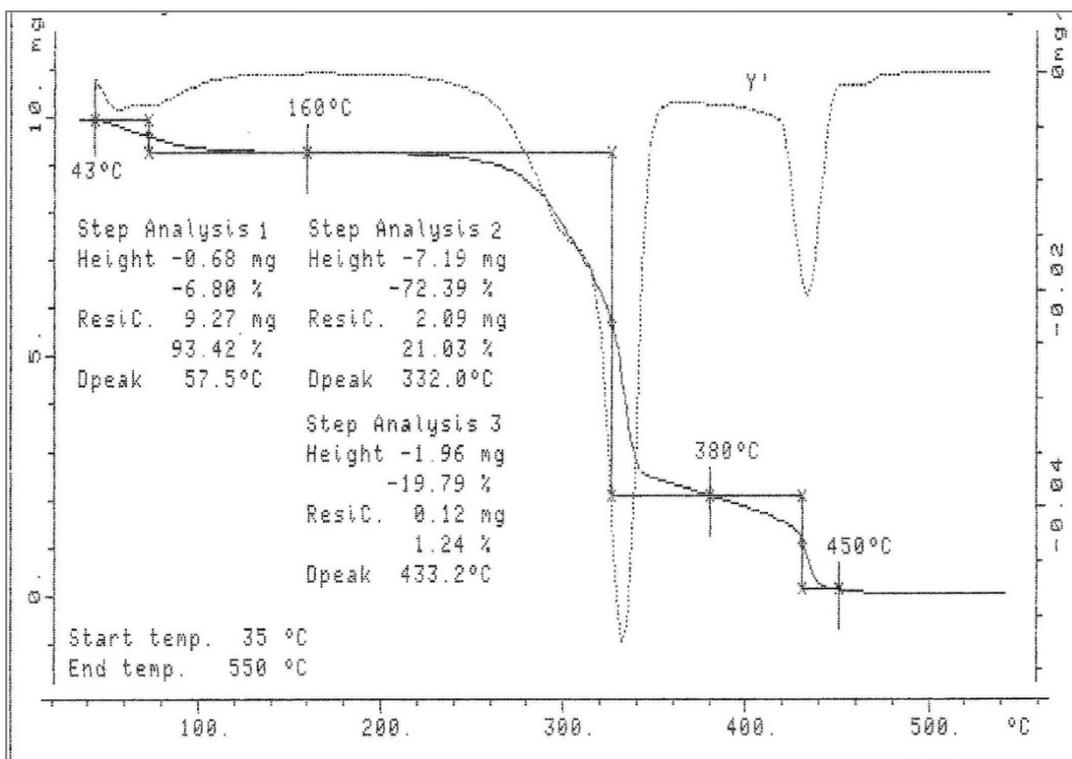
Salix viminalis TORA – TG / DTG analysis (heating rate 5 °C·min⁻¹)



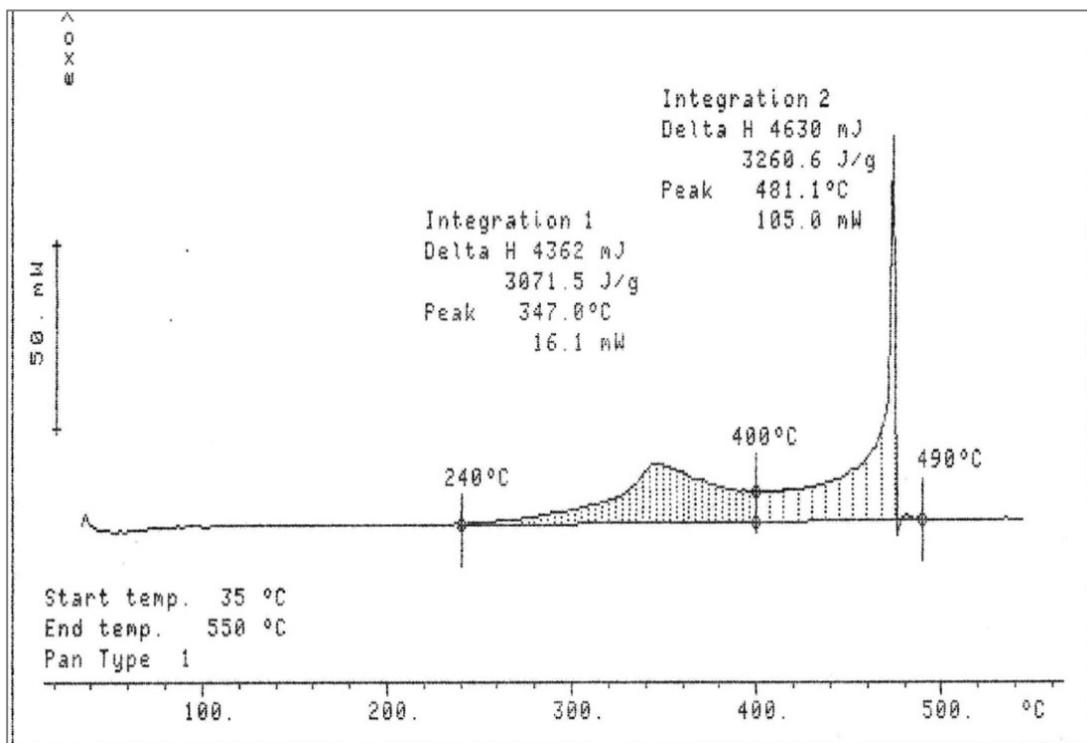
Salix viminalis TORA – DSC analysis (heating rate 5 °C·min⁻¹)



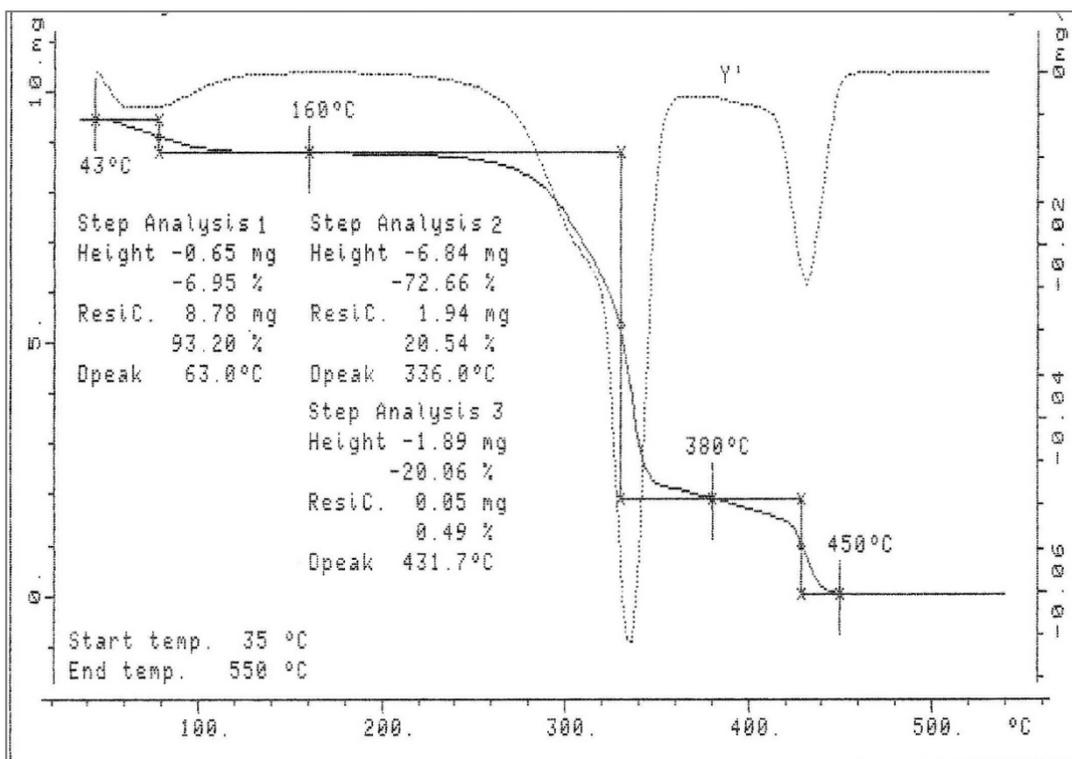
Salix viminalis TORA – TG / DTG analysis (heating rate 15 °C·min⁻¹)



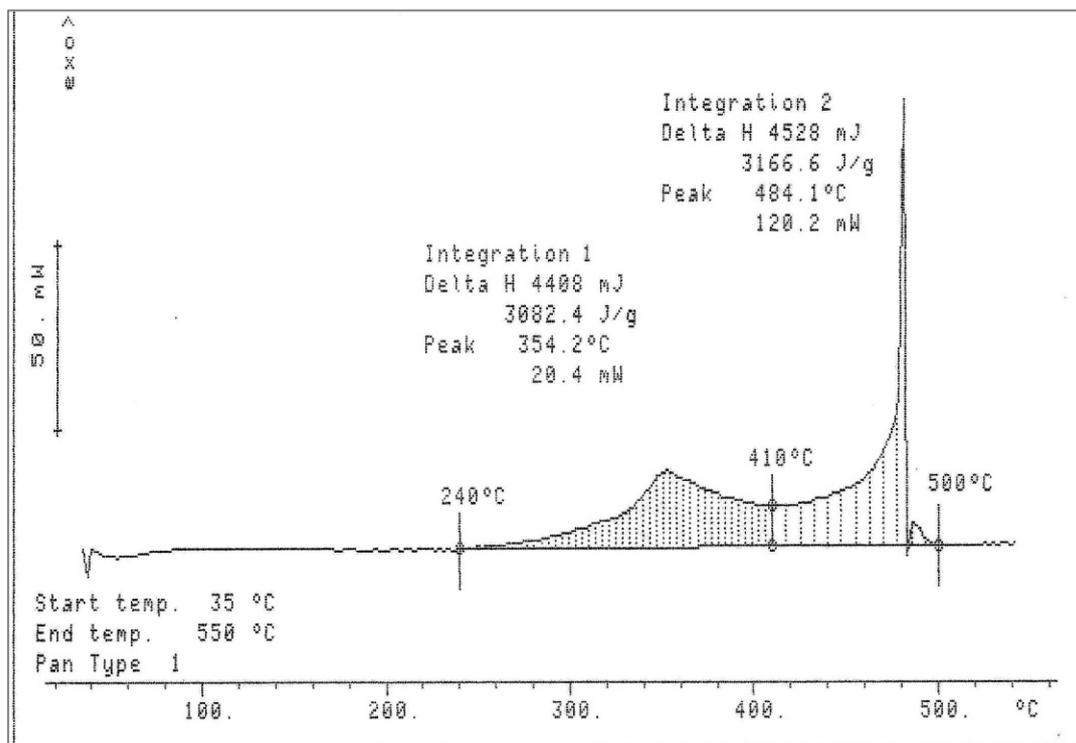
Salix viminalis TORA – DSC analysis (heating rate 15 °C·min⁻¹)



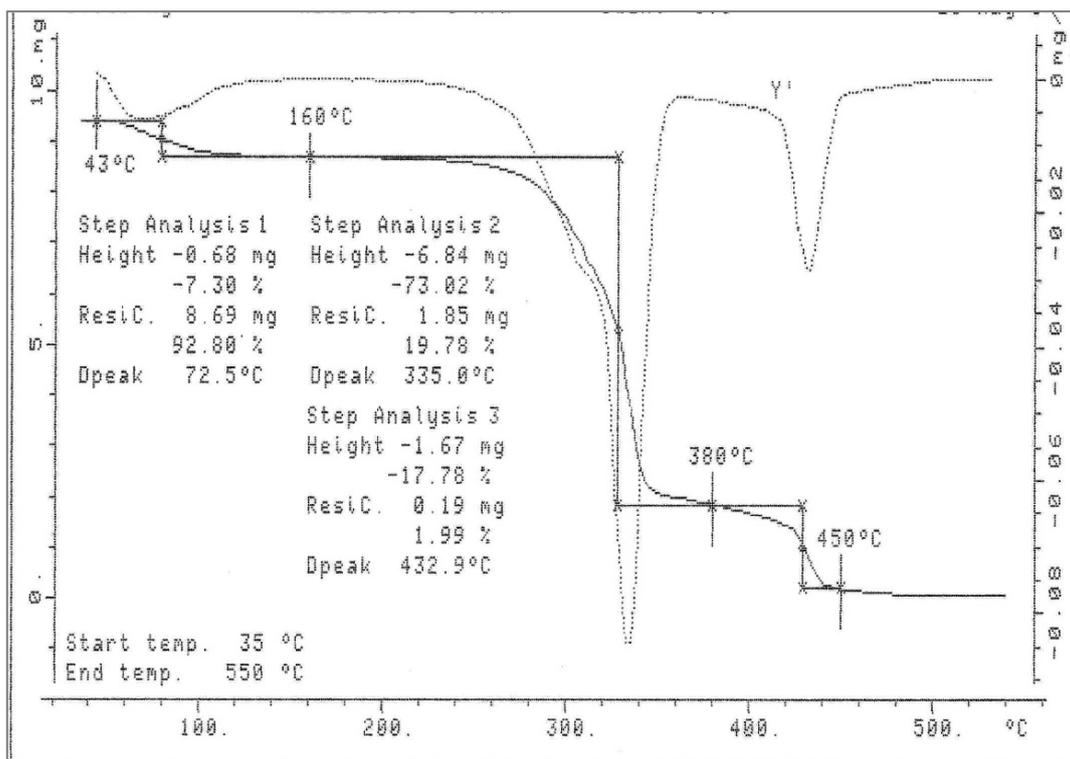
Salix viminalis TORA – TG / DTG analysis (heating rate 20 °C·min⁻¹)



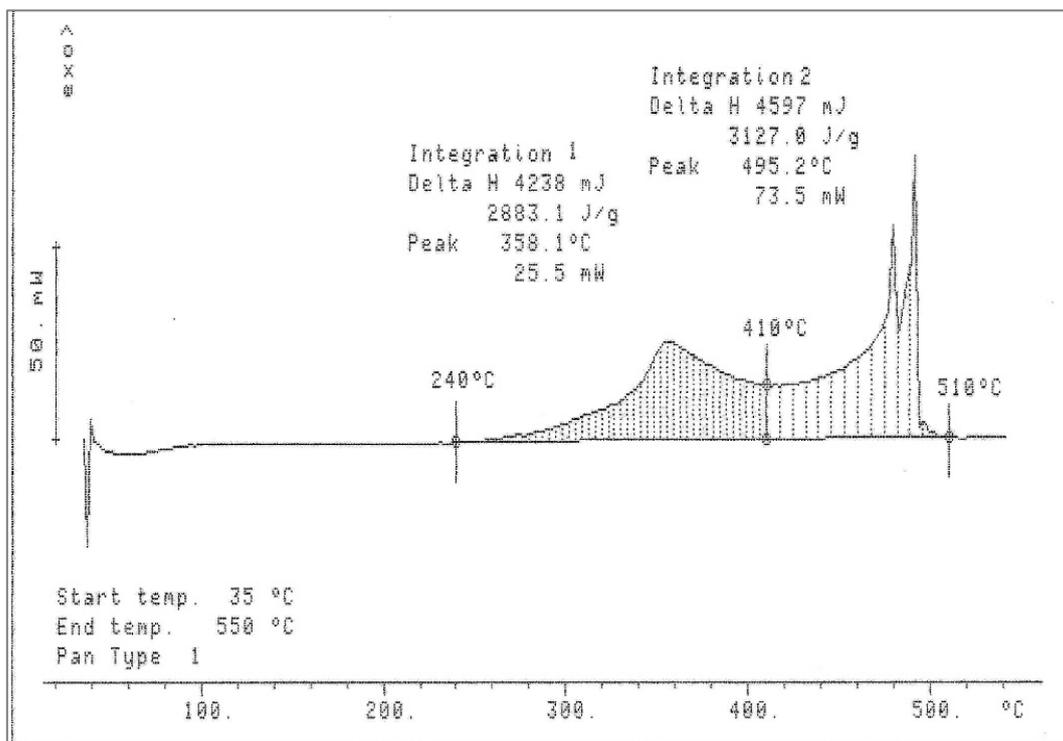
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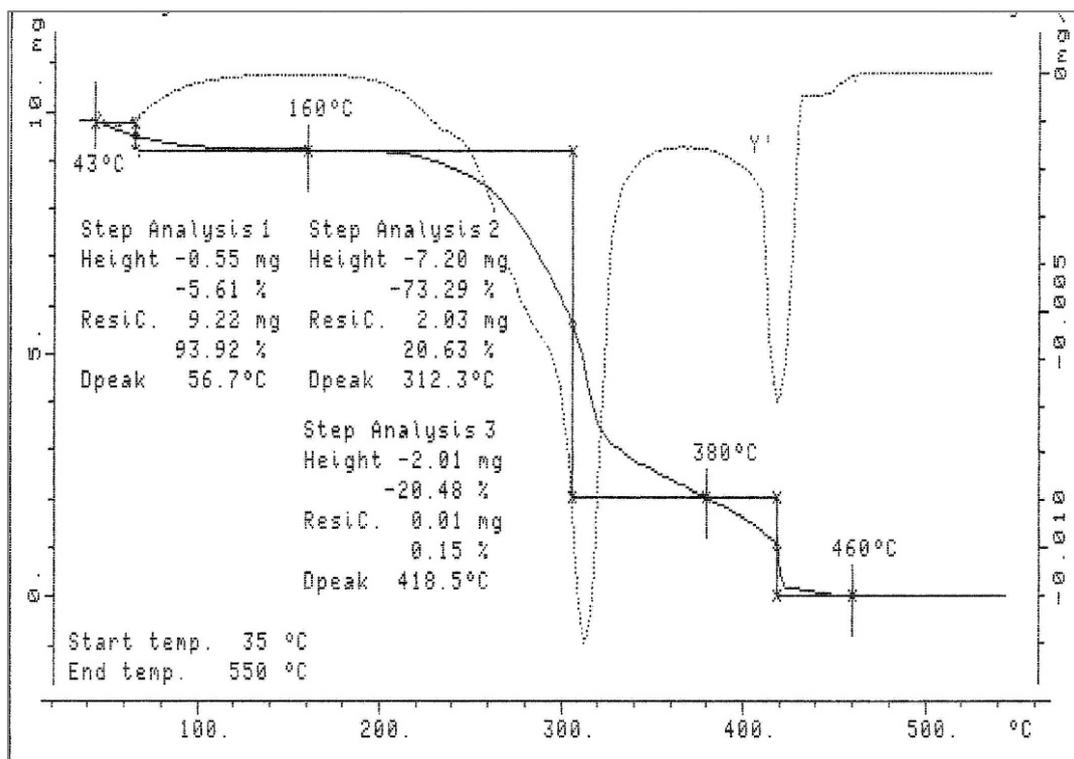
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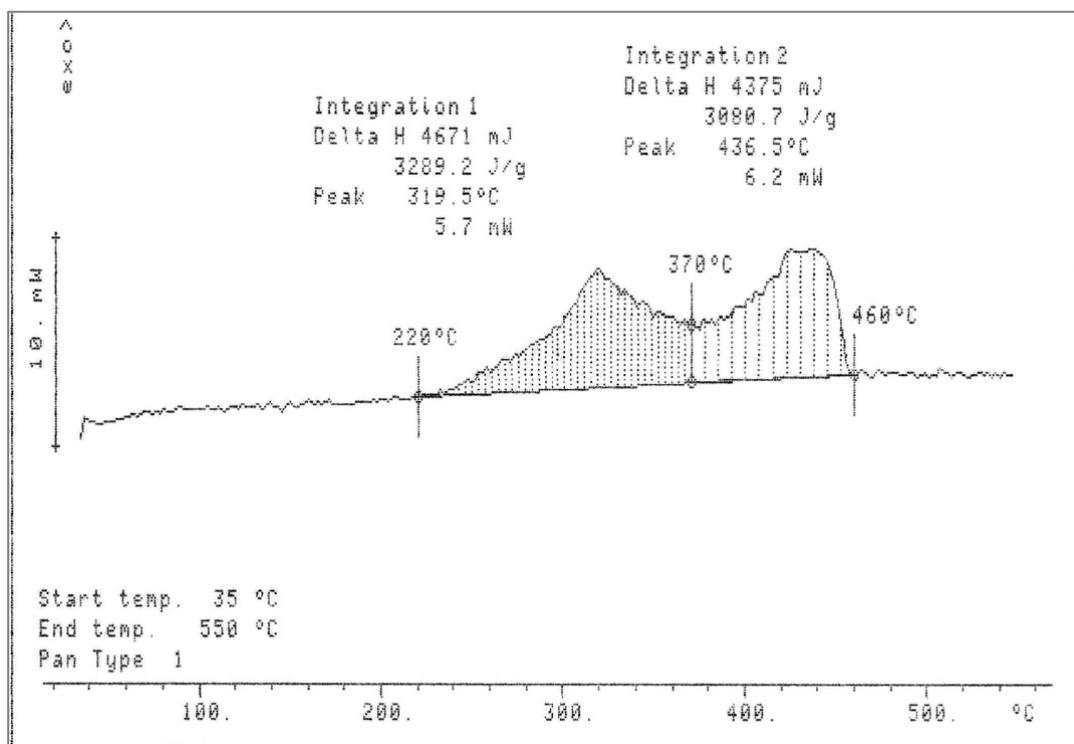
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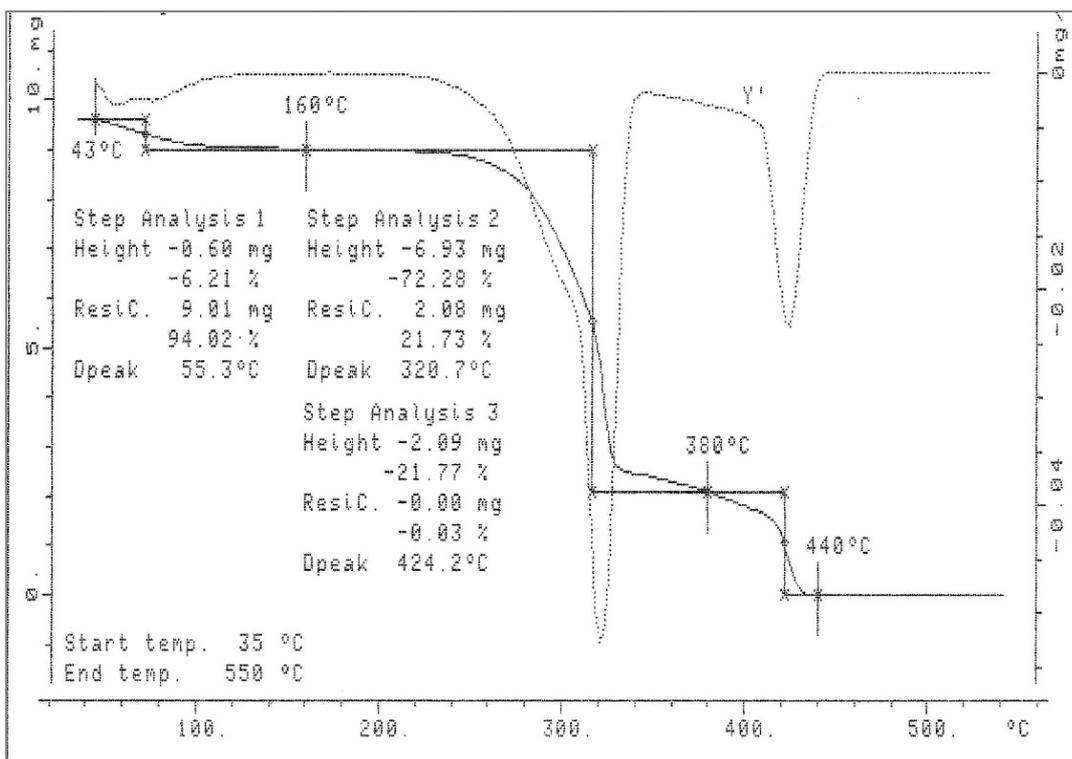
Paulownia tomentosa – TG / DTG analysis (heating rate 5 °C·min⁻¹)



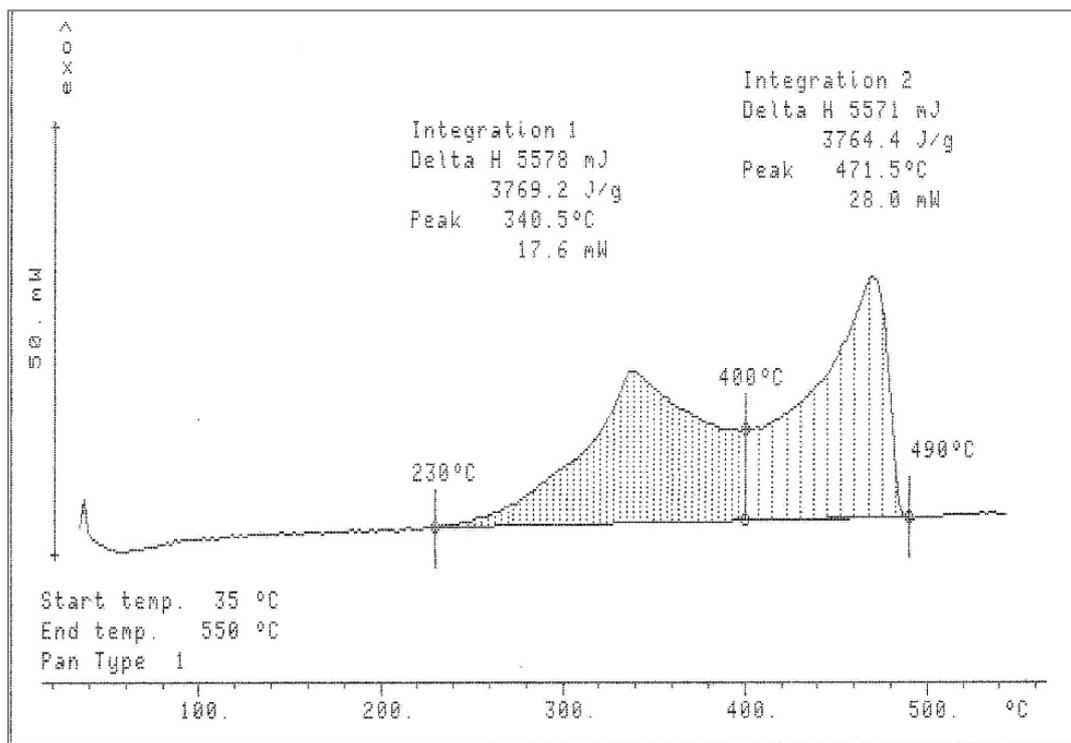
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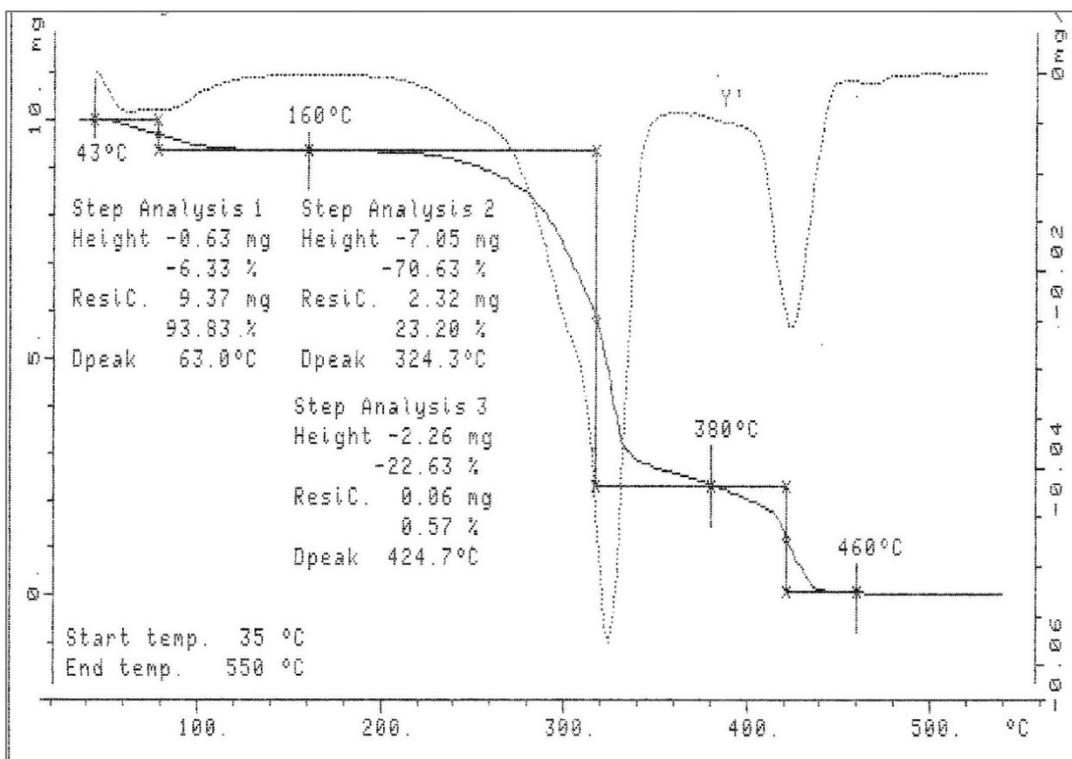
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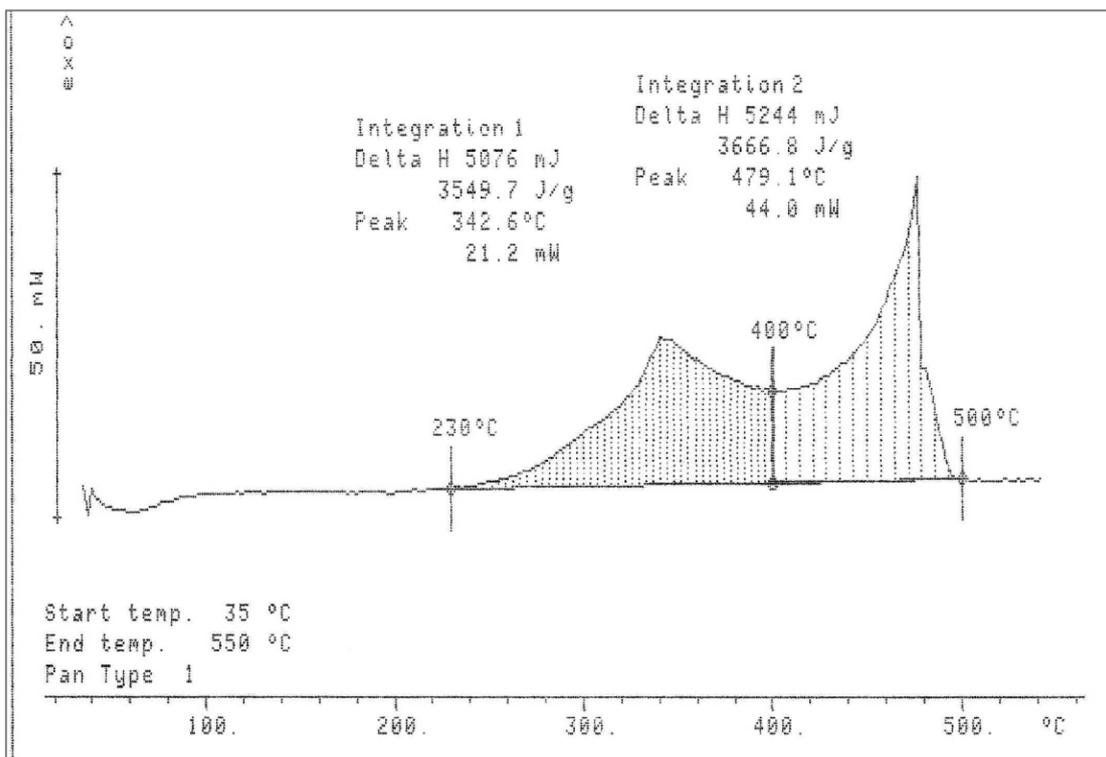
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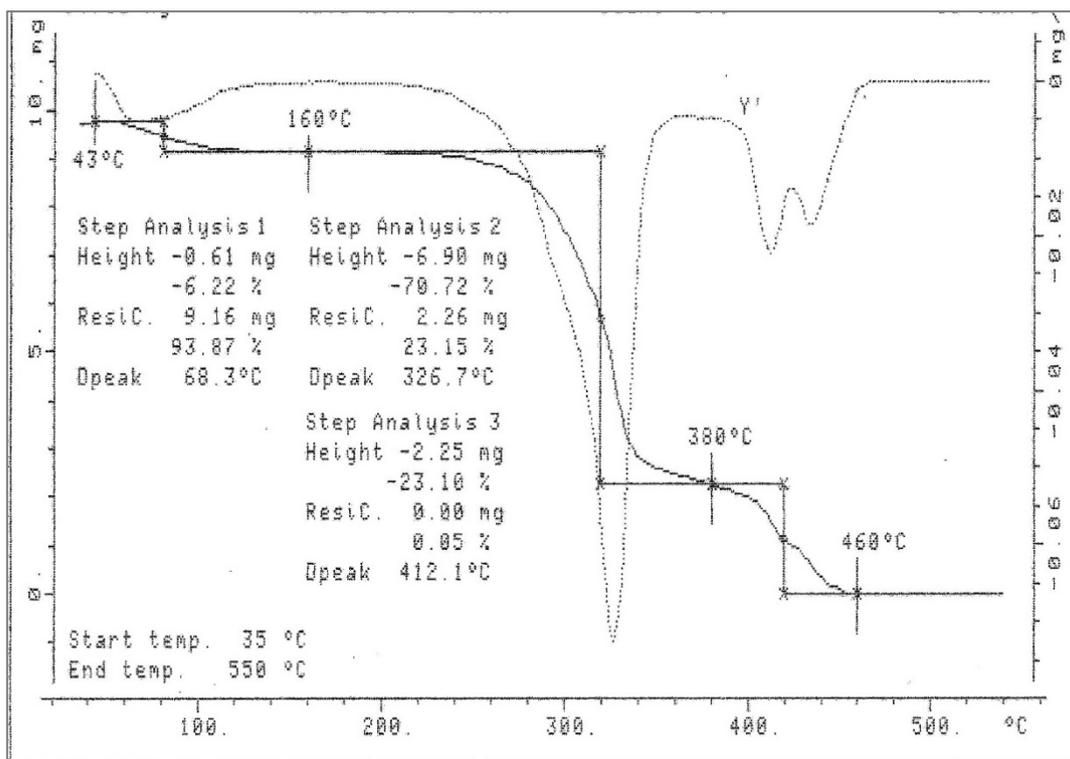
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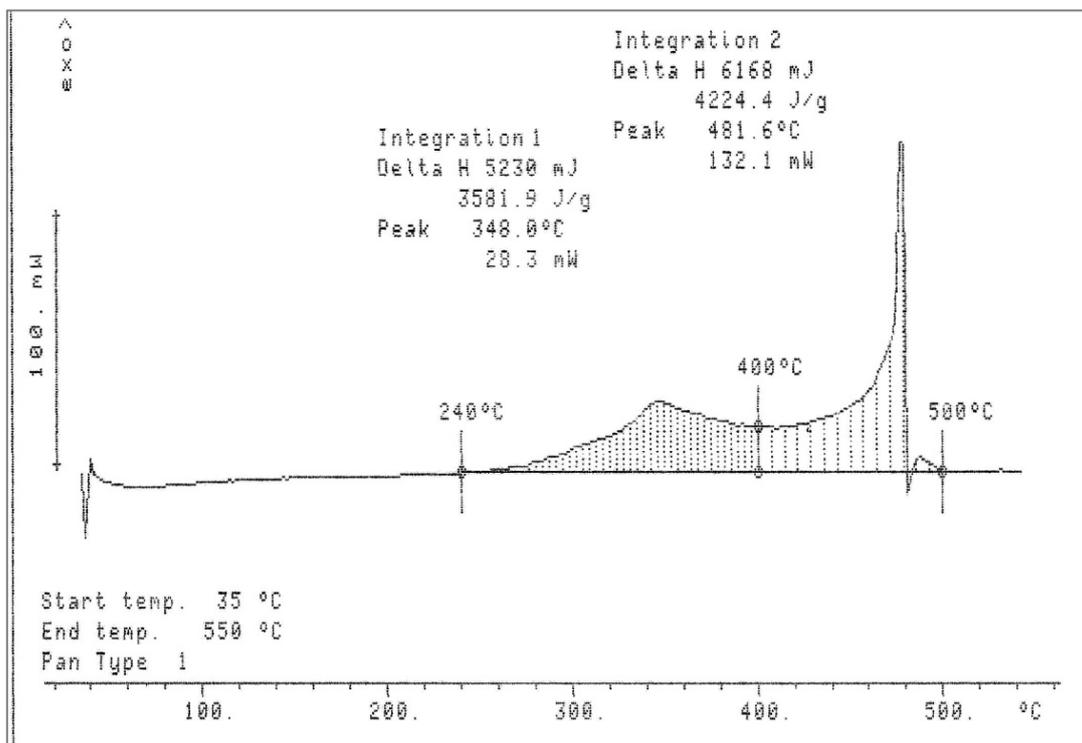
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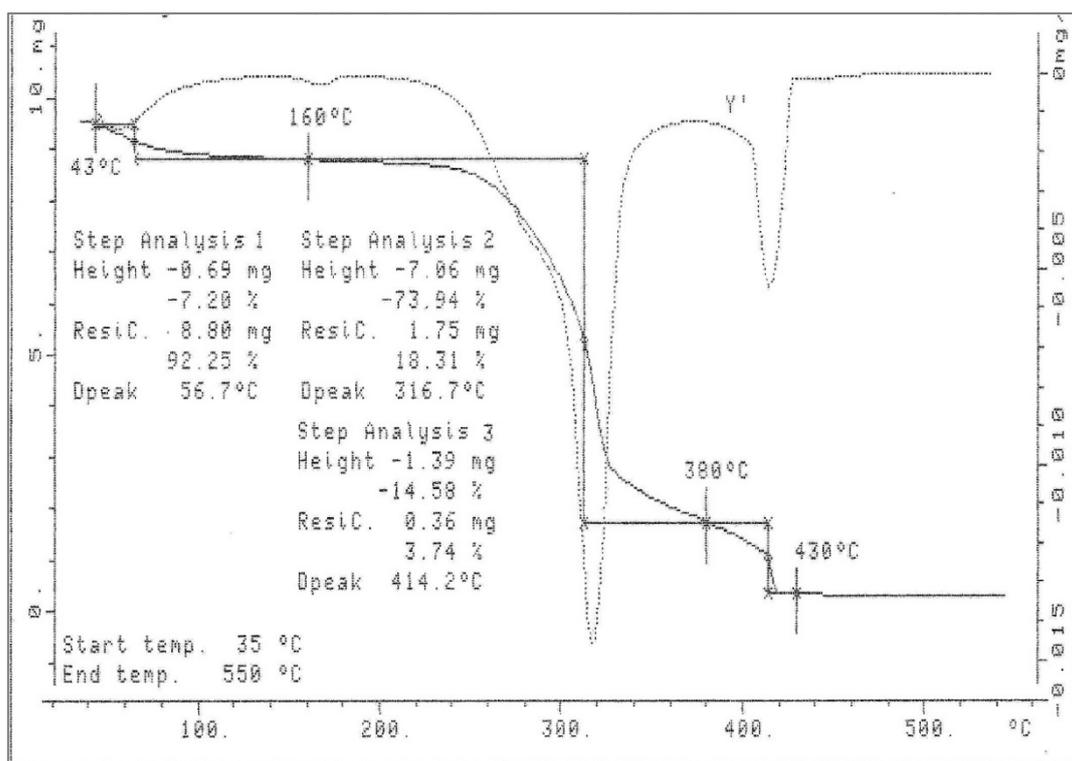
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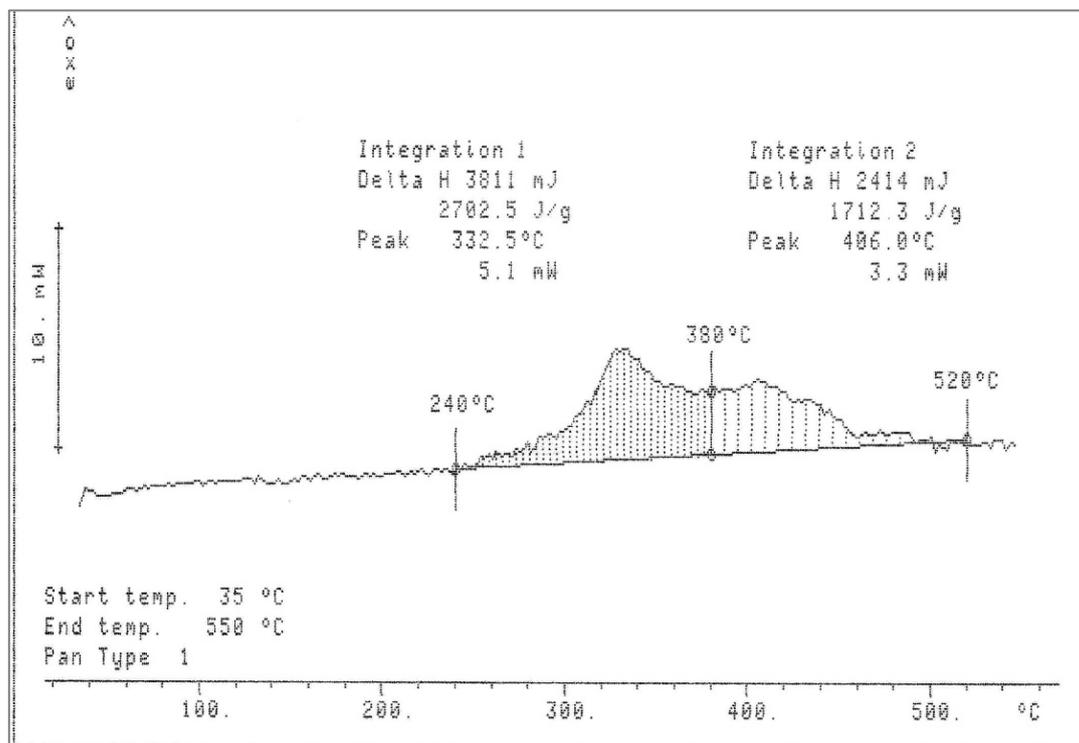
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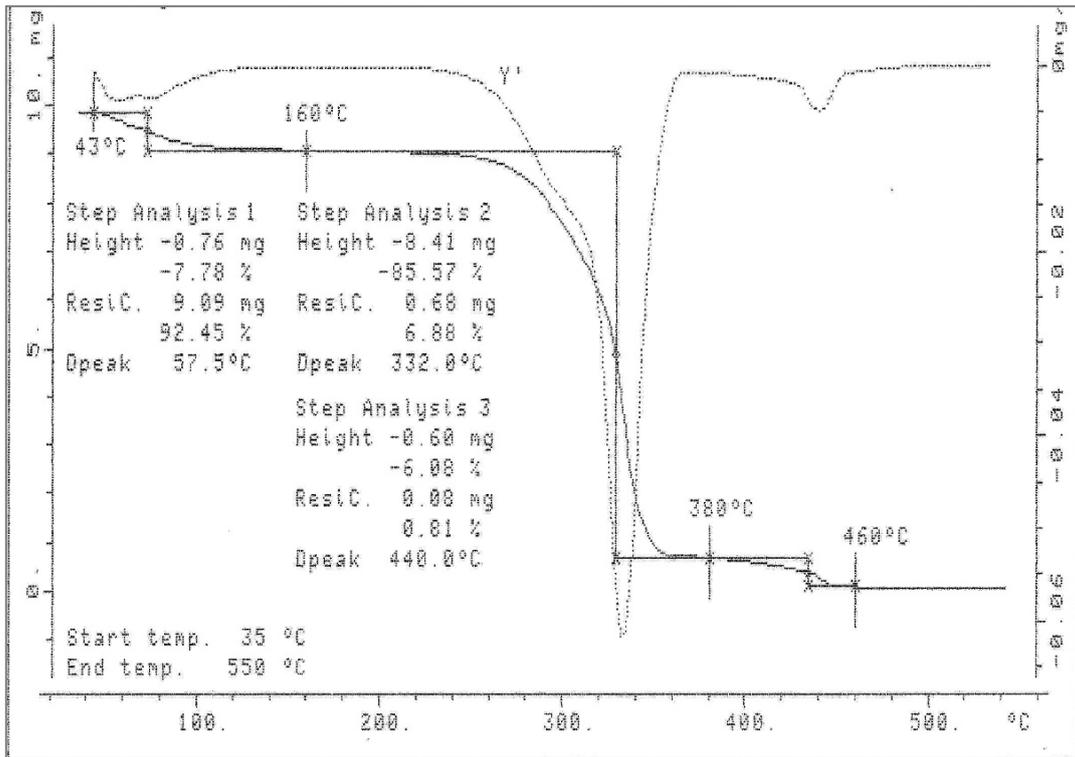
Sida hermaphrodita – TG / DTG analysis (heating rate 5 °C·min⁻¹)



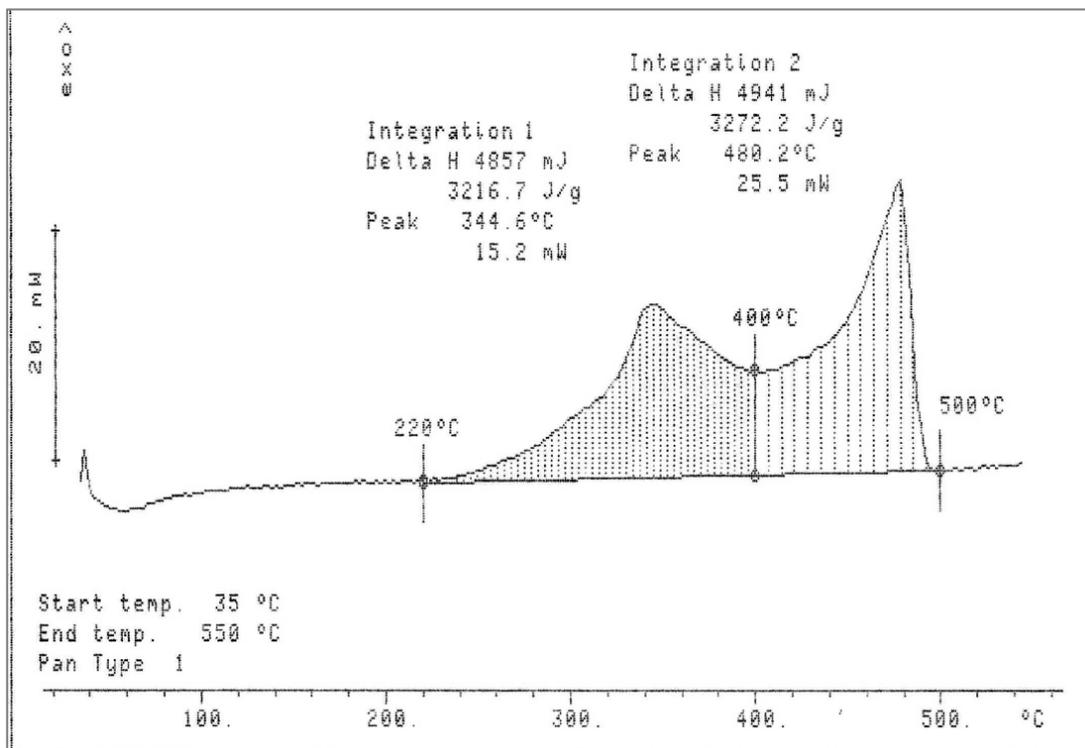
Sida hermaphrodita – DSC analysis (heating rate 5 °C·min⁻¹)



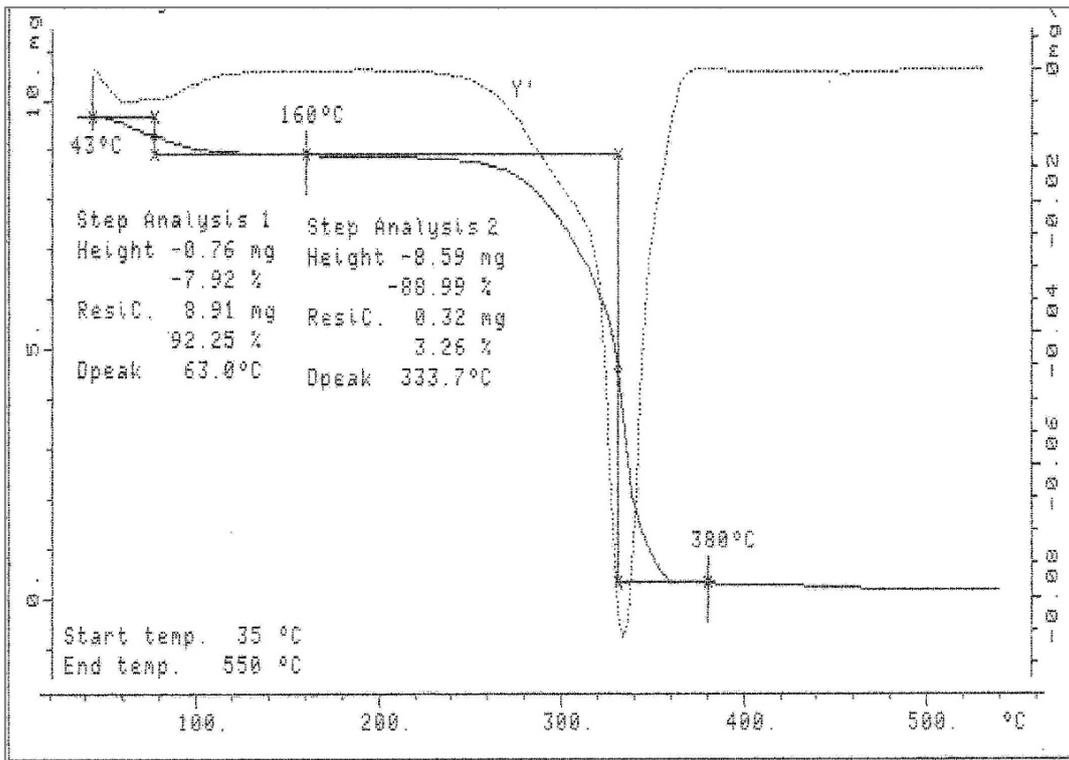
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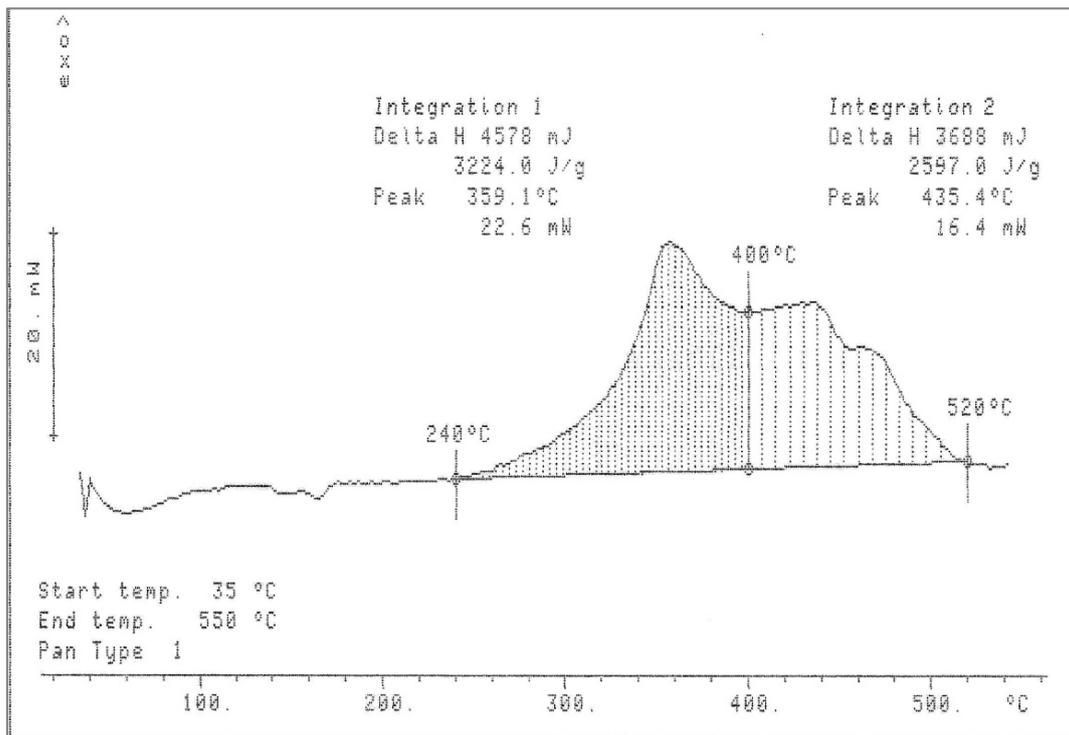
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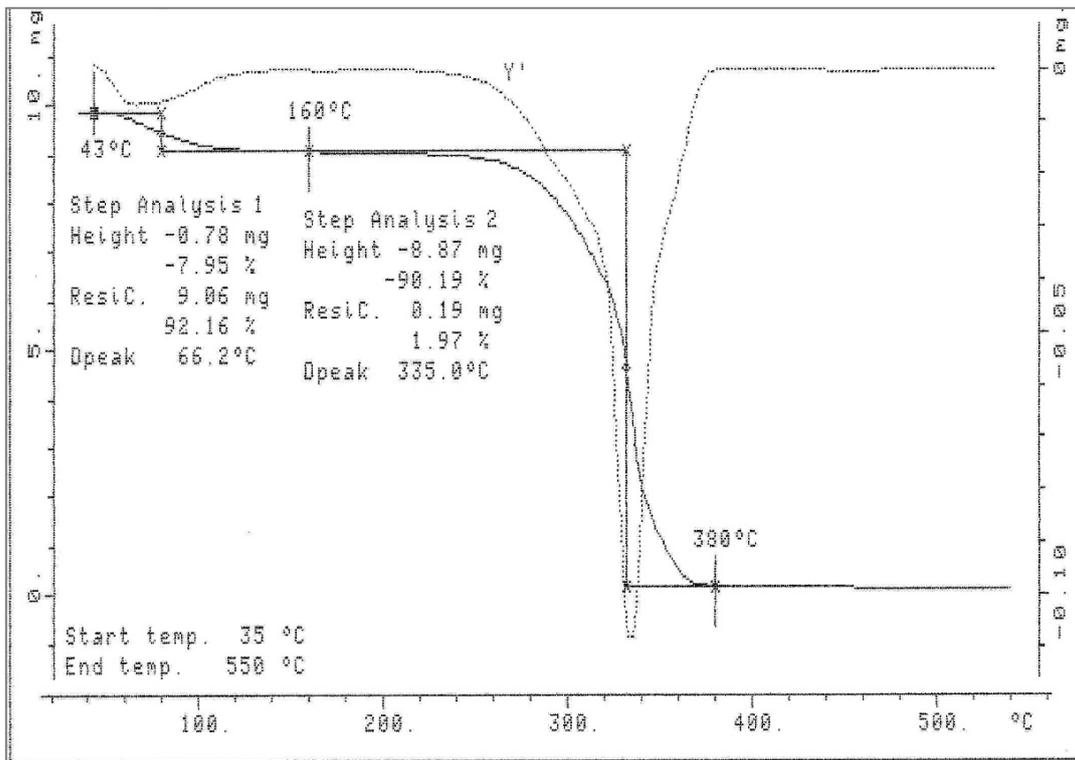
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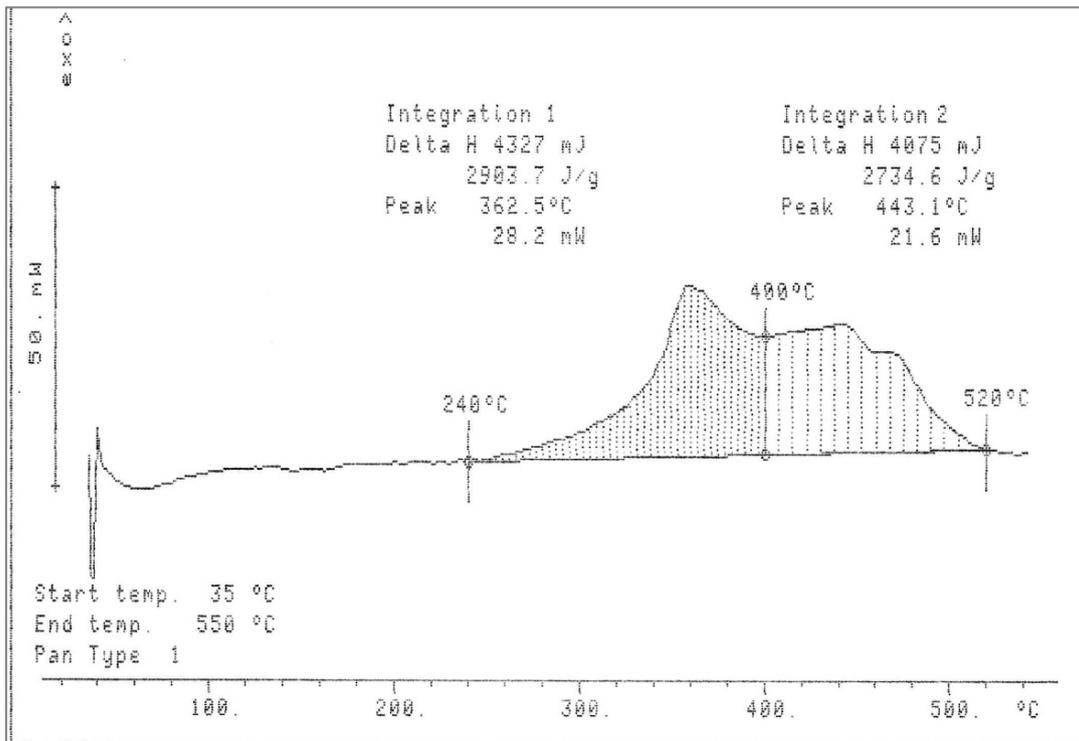
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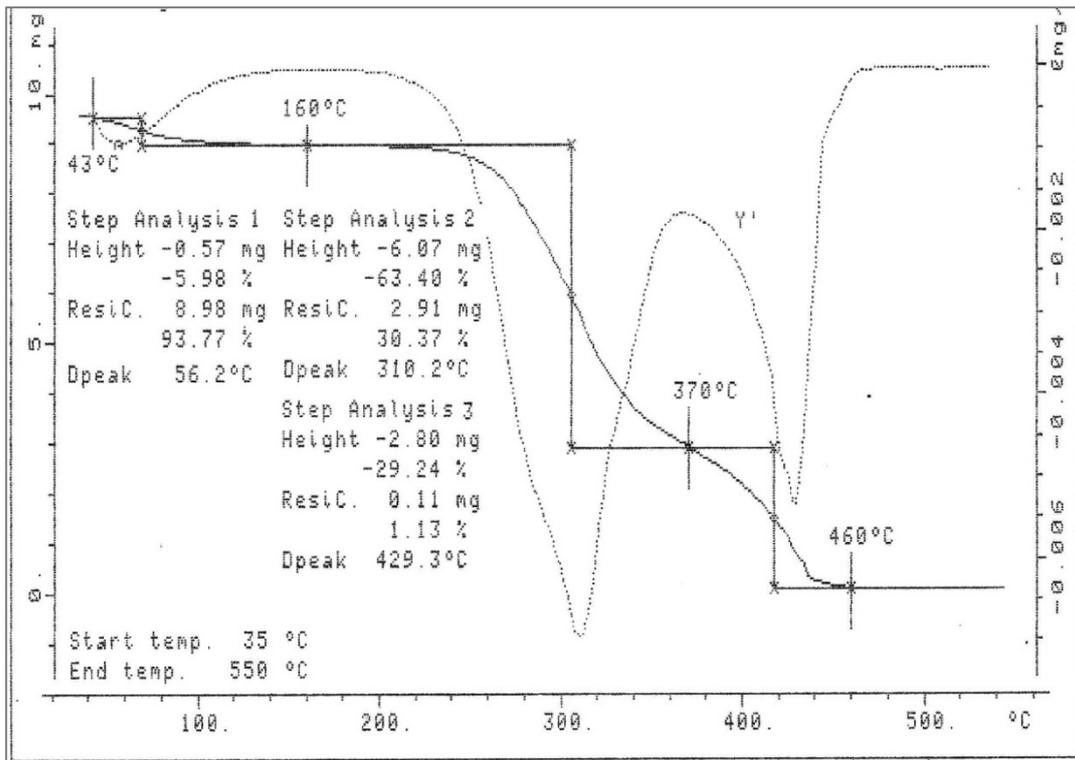
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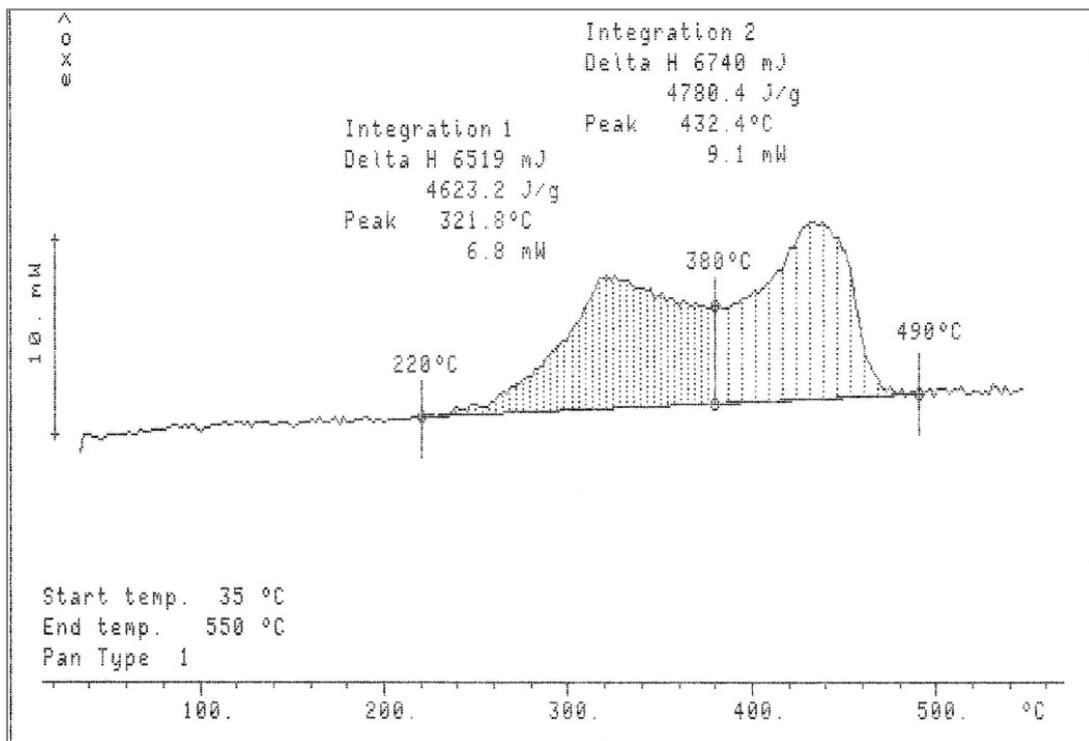
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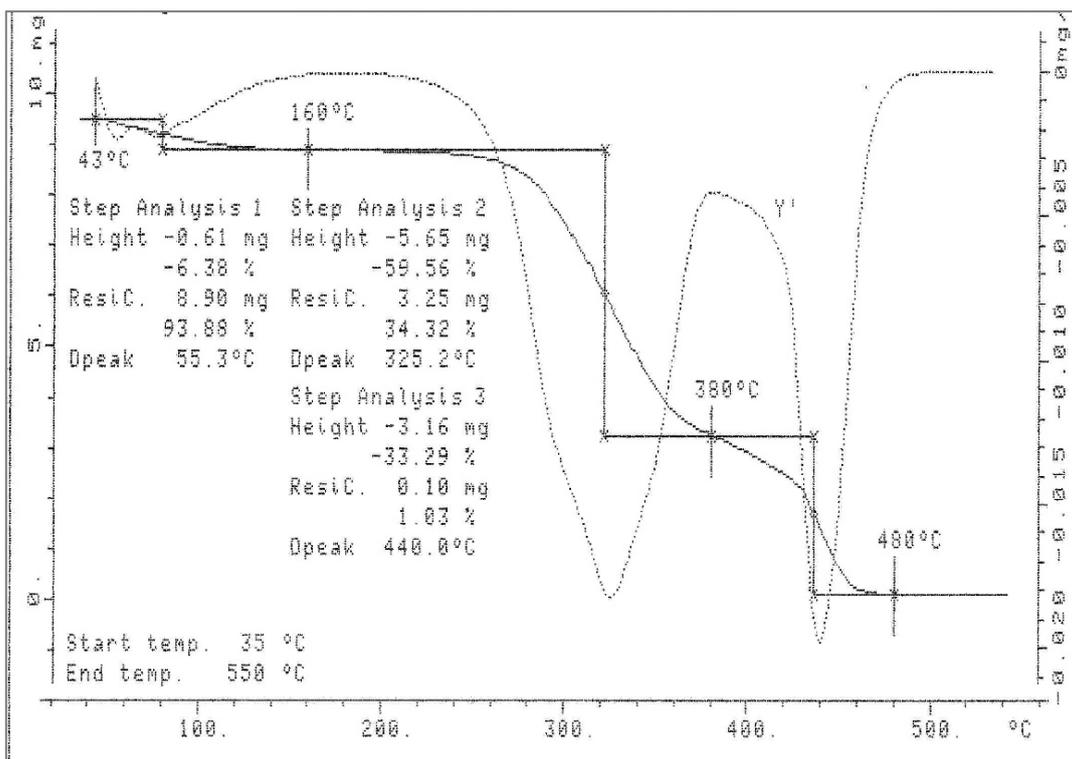
Miscanthus x giganteus – TG / DTG analysis (heating rate 5 °C·min⁻¹)



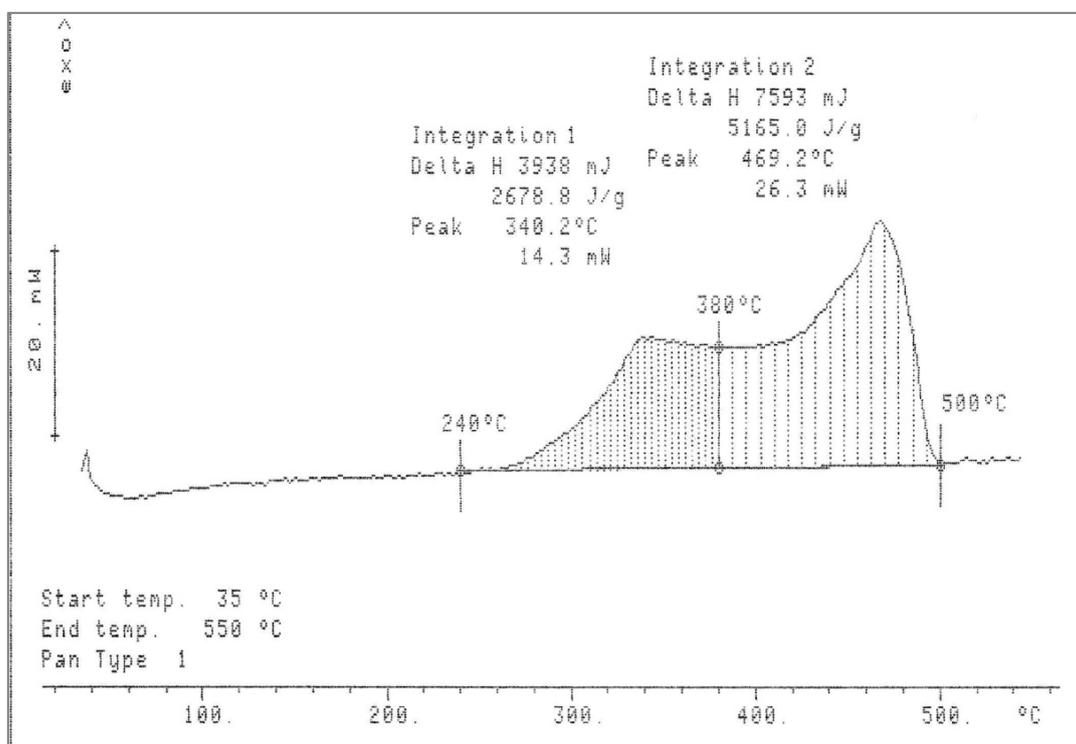
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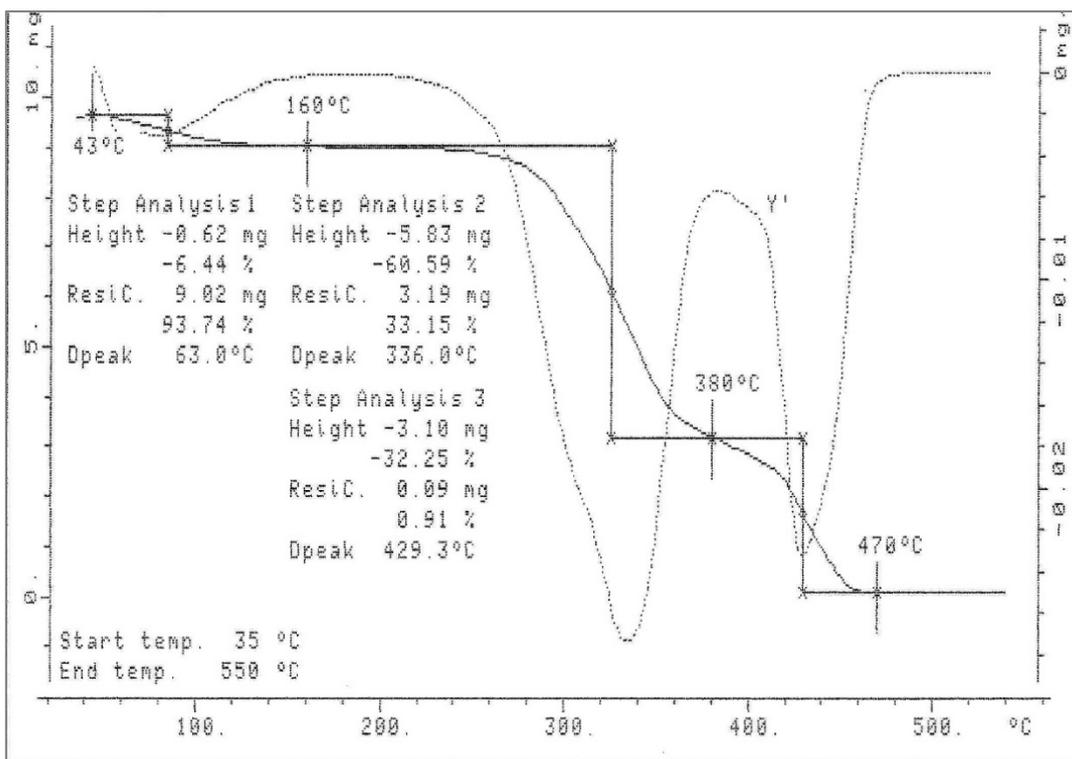
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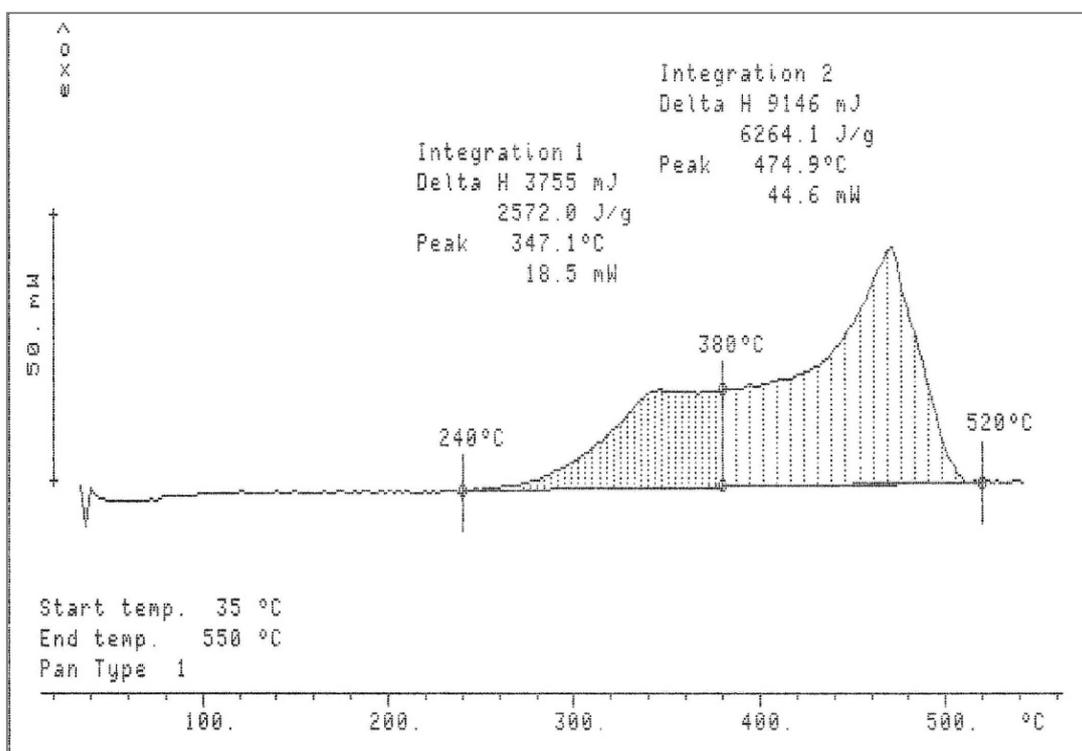
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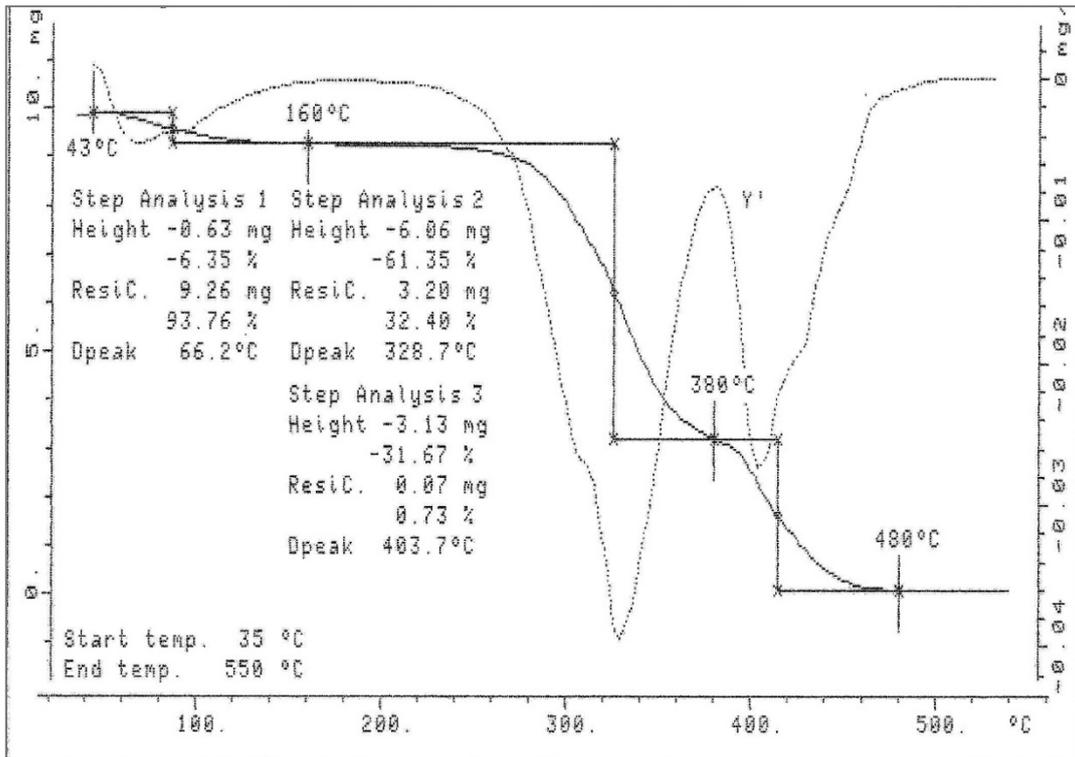
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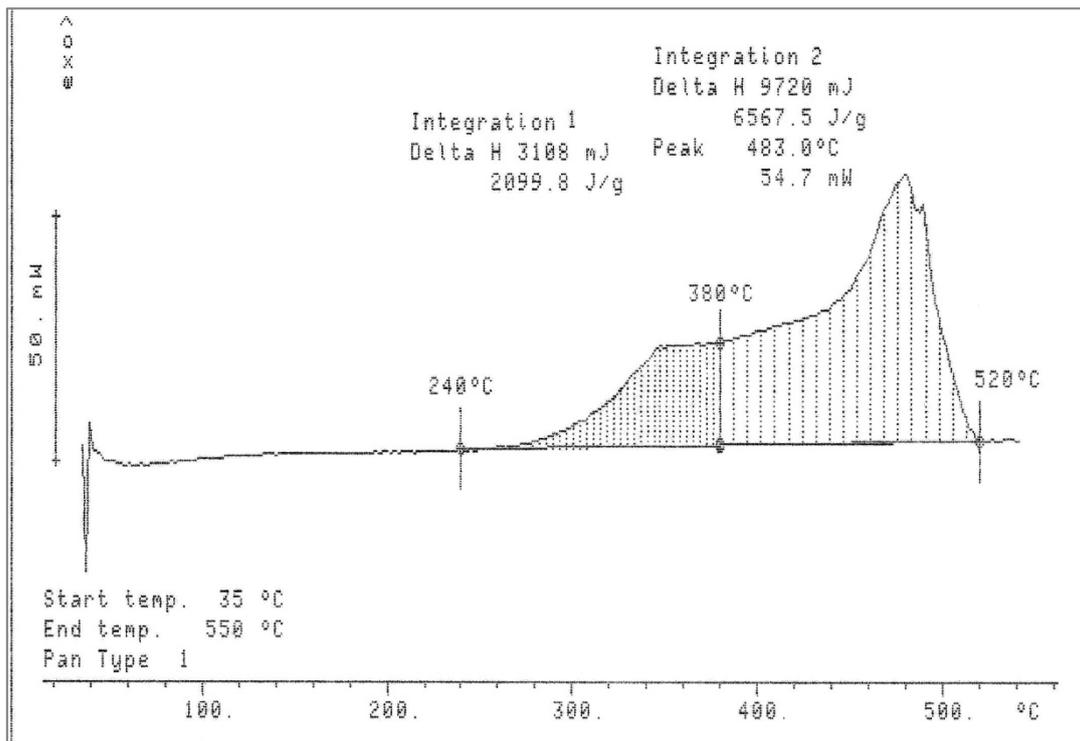
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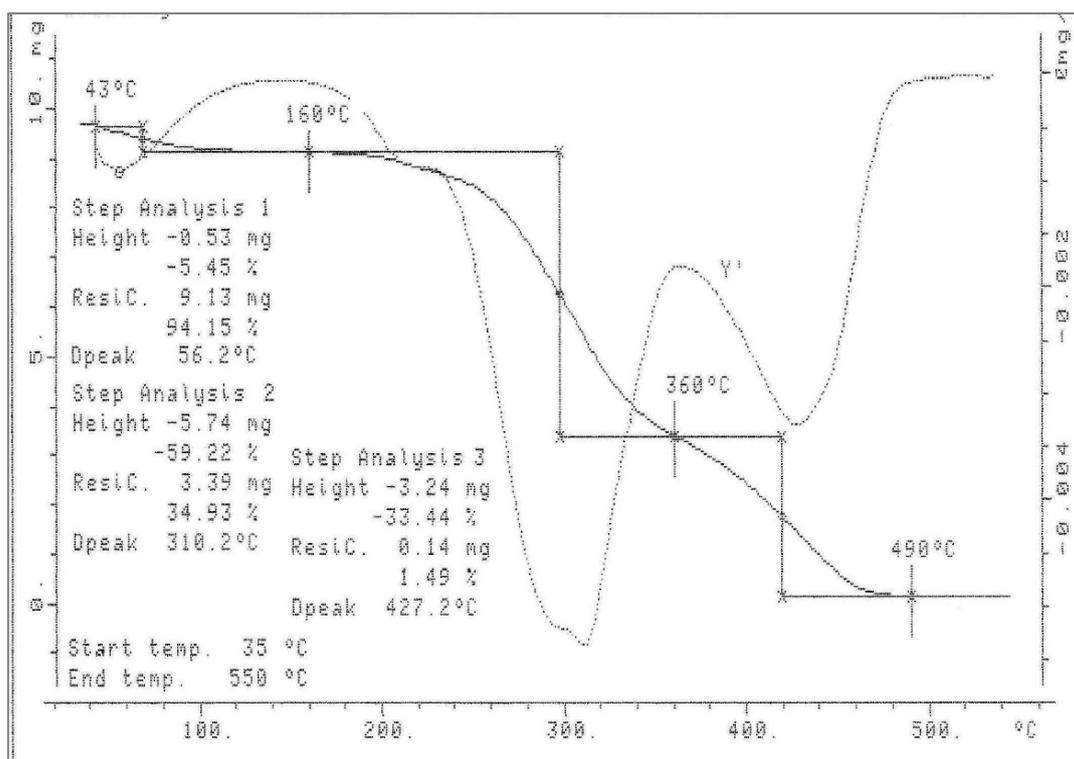
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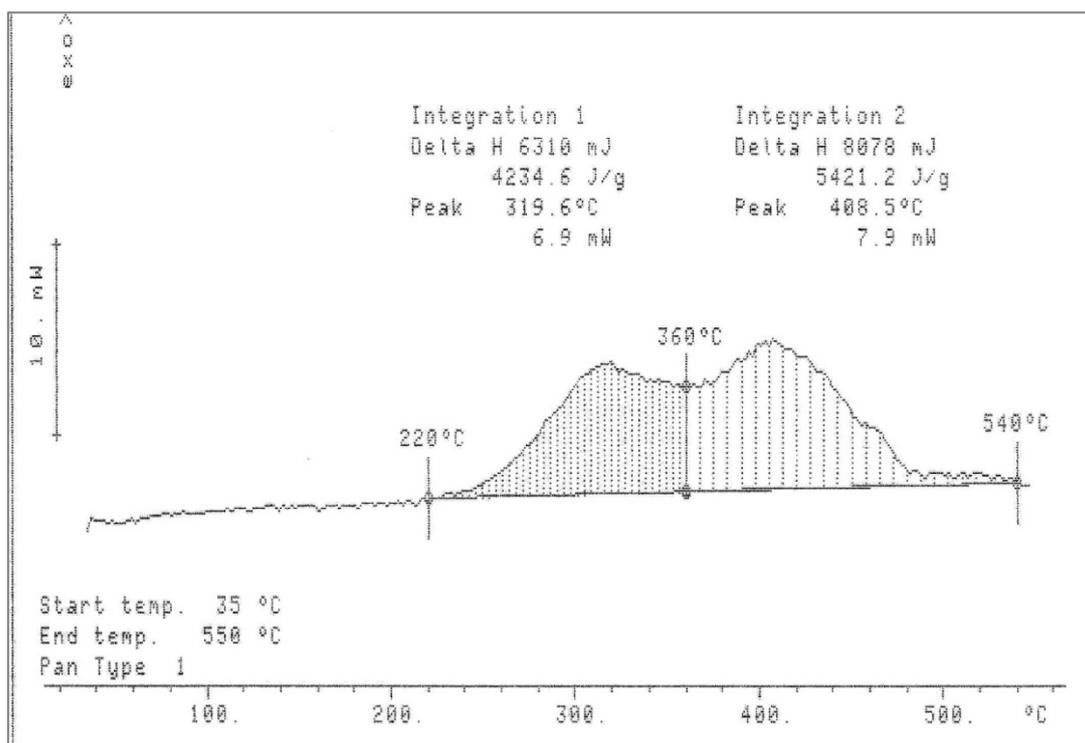
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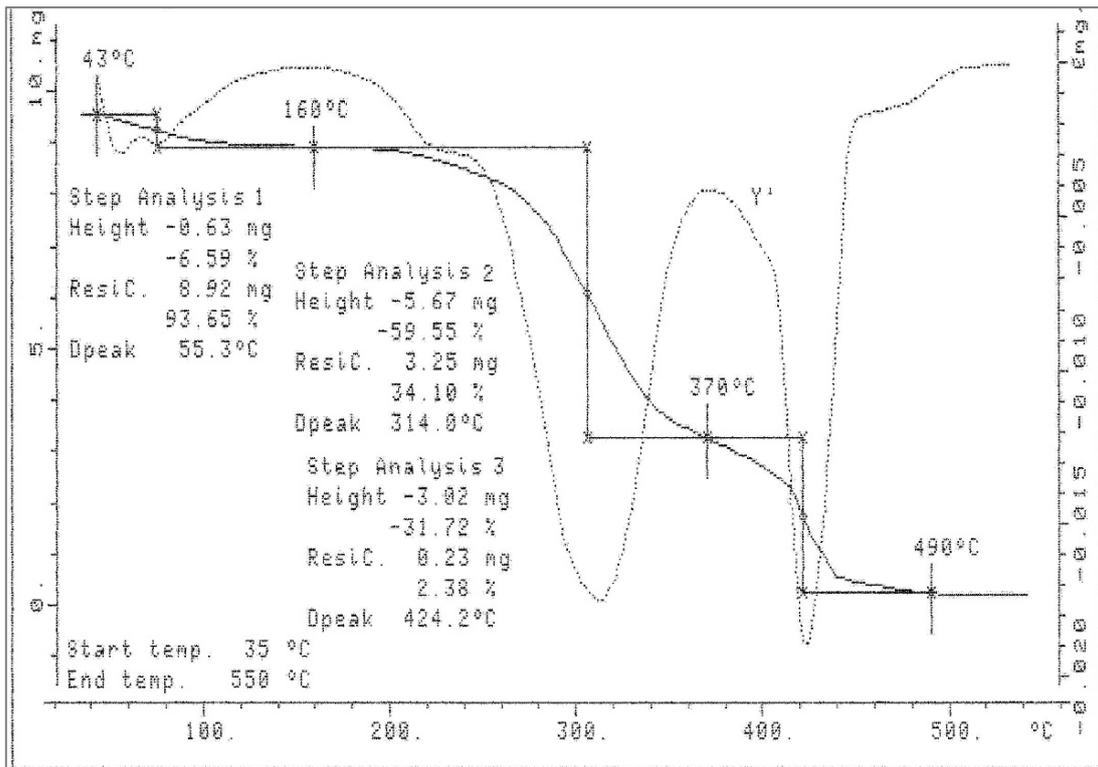
Arundo donax – TG / DTG analysis (heating rate 5 °C·min⁻¹)



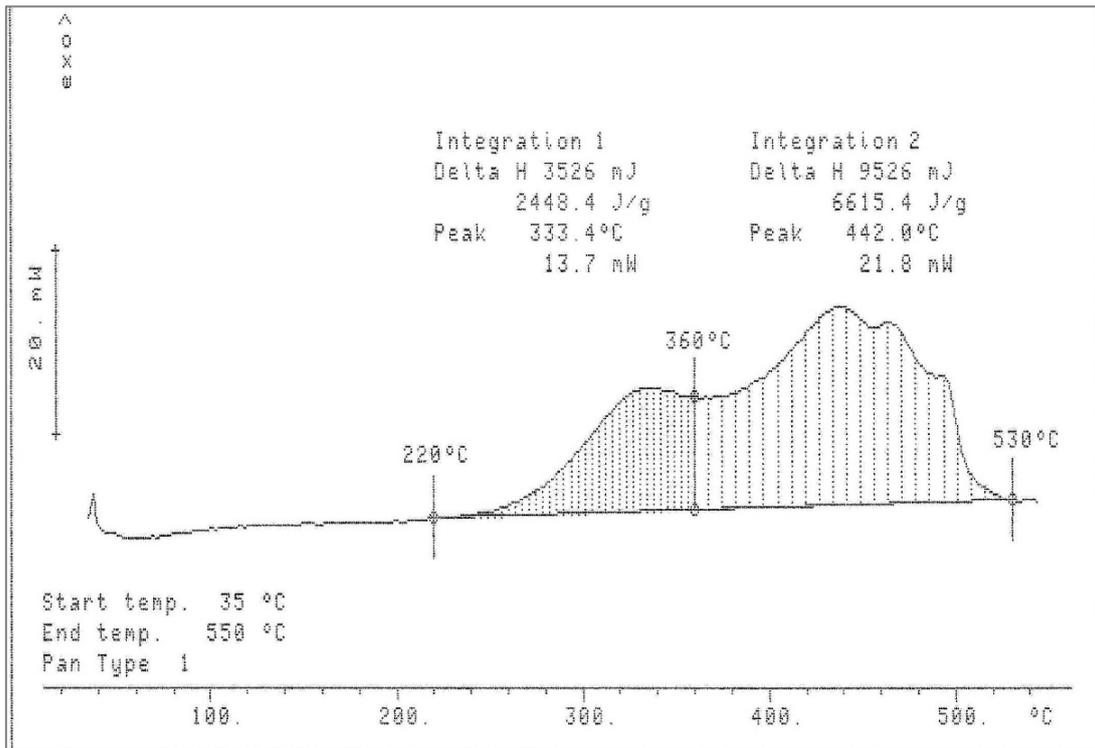
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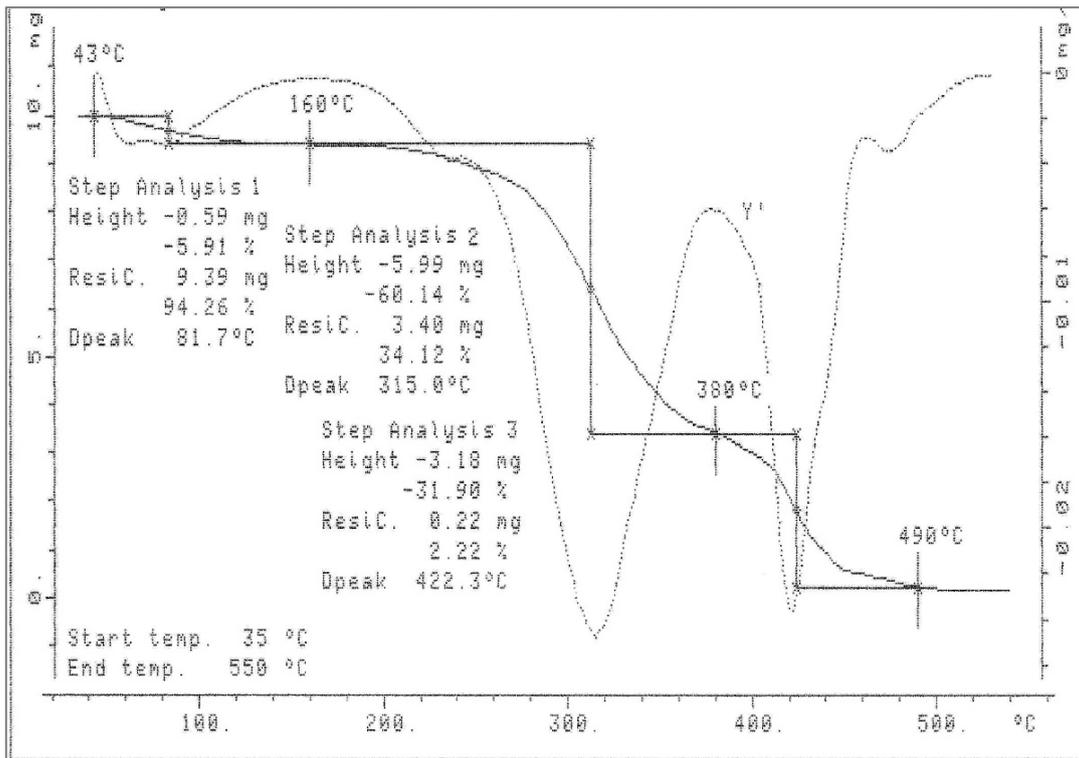
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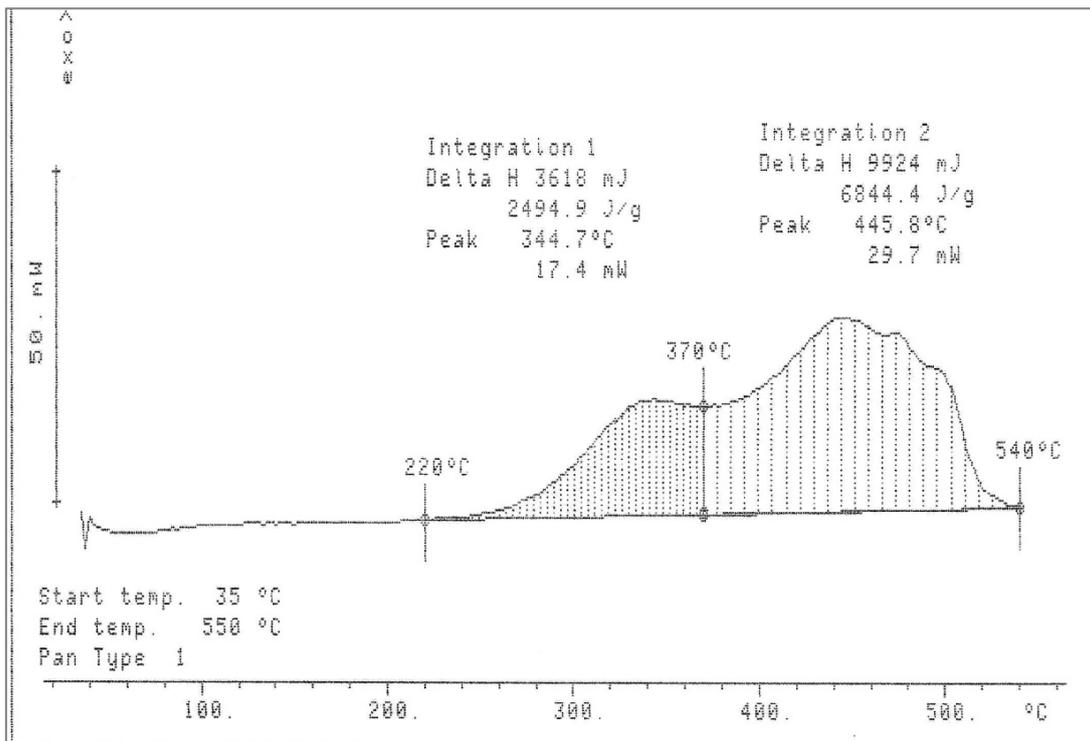
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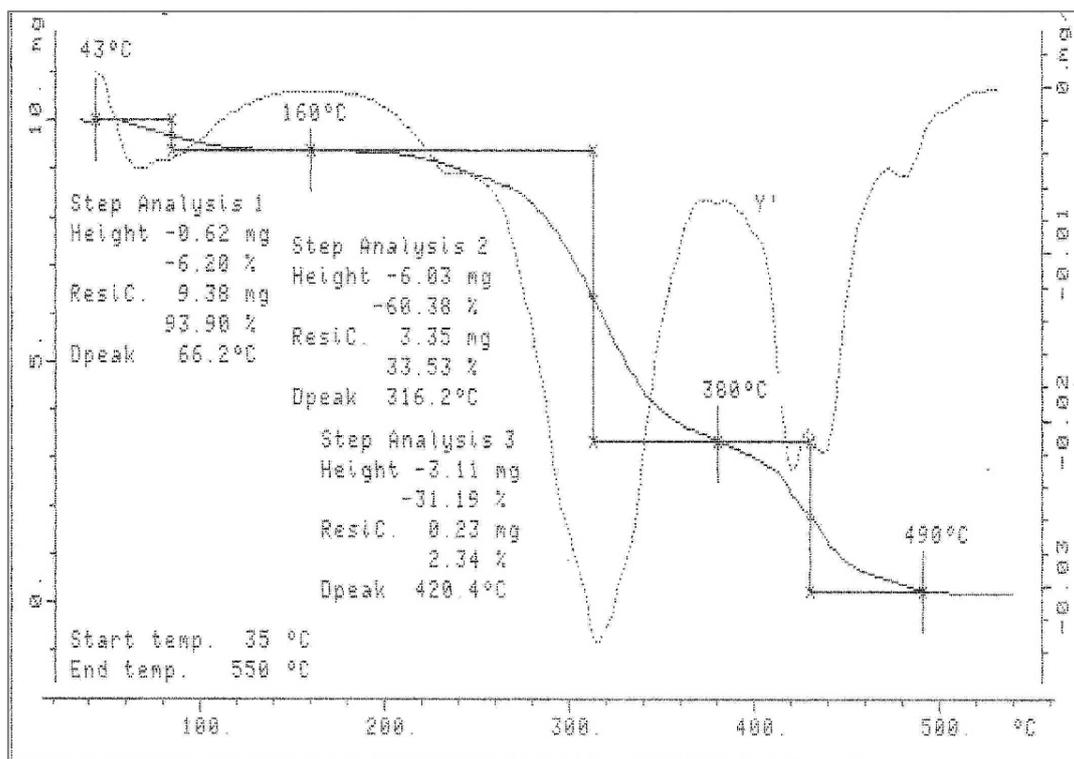
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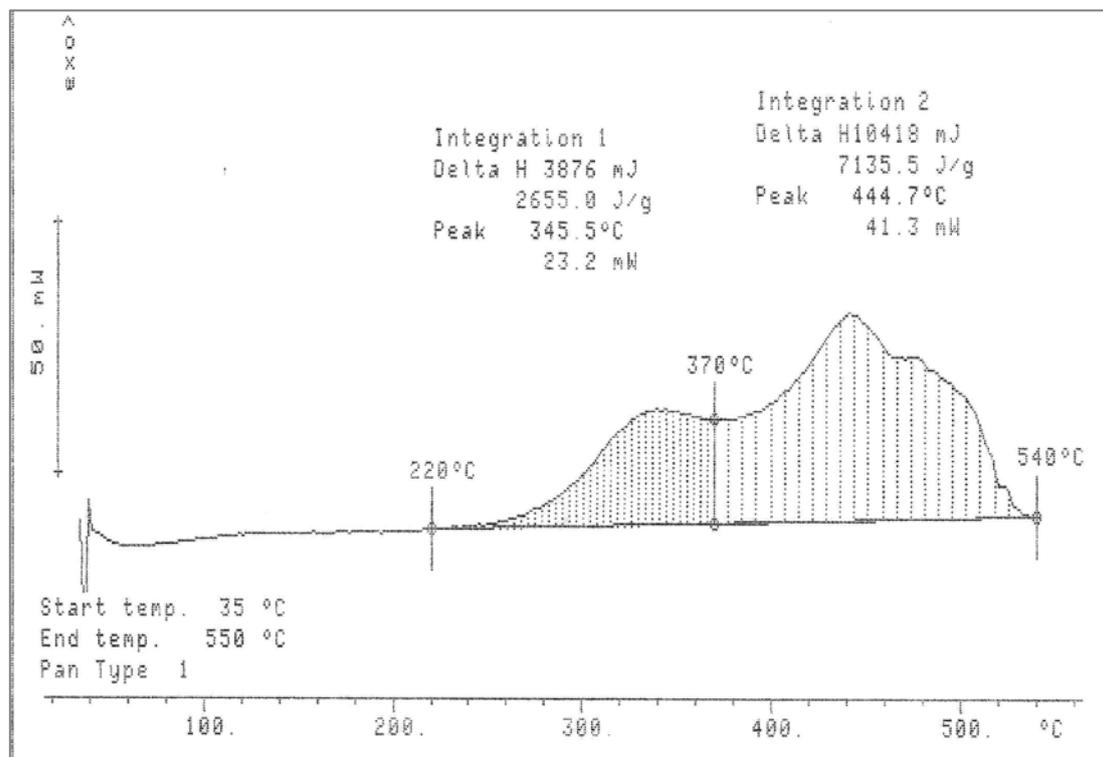
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**FIRE AND ENERGETIC PROPERTIES
OF SELECTED FAST-GROWING TREE SPECIES
AND ENERGY CROP SPECIES**

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