Thermochemical Conversion of Biomass – Kinetics, Gasifier Modeling and Design

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Energy Engineering and Management

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“How sad to think that nature speaks and mankind does not listen.”

-Victor Hugo, 1840

To my beloved parents

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Abstract

In times of global warming phenomenon, that current population must face, there are sought an alternative to fossil fuels methods of energy generation. Since contemporary Europe has set the goal of reducing usage of fossil fuels in energy generation, European Union members should adjust to the set requirements. Within all many possible, alternative routes of energy production, application of biomass as an energy source seems to be a great solution for countries not being gifted by nature with excessive solar radiation, water areas with strong currents or geothermal zones.

For the purpose of this thesis, there were studied the kinetics of the thermochemical transformation of wooden chips (alder) sample provided by Institute of Coal Chemical Processing in Poland. To obtain the results, methods of Thermogravimetry, Differential Thermogravimetry were used along with Differential Scanning Calorimetry (TG, DTG, and DSC respectively). Firstly, it was studied the reactivity during combustion of the char obtained through pyrolysis up to different temperatures 200°C, 300°C, 400°C. After this, there were carried out experiments of sample's pyrolysis, partial oxidation and complete combustion with different heating rates. As an inert gas nitrogen was used. Partial oxidation was performed with the following partial pressures of oxygen in the gasifying agent PO_2: 0.21, 0.18,0.15, 0.10, 0.05, 0.025 atm. To get desired partial pressures of oxygen, flowing gas was a mixture with an appropriate ratio of air and nitrogen. These sets of experiments were carried out to perform kinetic modeling to obtain rate constant and activation energy values for the given sample. The influence of heating rates and applied partial pressures on its values was studied. In the model, reactions were assumed to be first order reactions.

After performing kinetic modeling of the given material, simulation of its gasification process was performed with application of Chemcad software. To perform the simulation, a Gibbs reactor was used with parameters for the process and the material's properties along with its proximate and ultimate analysis, as provided by Institute of Coal Chemical Processing in Zabrze (Poland). Prior to the simulation, there was performed thermal analysis to assess the possible products arising from the different material's transformation modes. The results obtained from the simulation were compared to ones given by Institute of Coal Chemical Processing.

Keywords: Biomass gasification, Kinetic modeling, TG, DTG, DSC, Chemcad

Resumo

Numa época em que se assiste a um fenómeno de aquecimento global, que a população atual tem de enfrentar, há uma procura constante de alternativas aos combustíveis fósseis para a produção de energia. Uma vez que a Europa estabeleceu metas para a redução da utilização de combustíveis fósseis para a geração de energia, os membros da União Europeia têm de se adaptar para cumprir essas metas. De entre as muitas vias alternativas possíveis, a utilização de biomassa como fonte de energia apresenta-se como uma excelente solução pra países que não foram dotados pela Natureza com grande irradiação solar, zonas marítimas com correntes fortes ou fontes geotérmicas.

Para o propósito desta tese foi estudada a cinética das transformações termoquímicas de madeira (amieiro) fornecida pelo Institute of Coal Chemical Processing na Polónia. Para obter estes resultados, foram utilizados métodos termogravimétricos, termogravimetria diferencial em conjunto com calorimetria diferencial de varrimento (TG, DTG e DSC .respectivamente). Primeiramente foi estudada a reactividade em condições de combustão do carvão obtido or pirólise a diferentes temperaturas: 200 ºC, 300 ºC e 400 ºC. Depois foi estudada a transformação deste material em condições de pirólise, oxidação parcial e combustão total em ar com diferentes taxas de aquecimento. O gás inerte utilizado durante a pirólise foi o azoto. A oxidação parcial foi realizada com as seguintes pressões parciais de oxigénio como agente gasificante: pO_2: 0,21, 0,18, 0,15, 0,10, 0,05, 0,025 atm. Para obter as pressões parciais de oxigénio, o gás alimentado com a mistura apropriada de ar e de azoto. Este conjunto de experiências foi efetuado para obter um modelo cinético e as respetivas constantes cinéticas e energias de ativação para esta amostra. Foi estudada a influência nestes parâmetros da velocidade de aquecimento e da pressão parcial de oxigénio. Neste modelo assumiu-se que as reações eram de primeira ordem.

Depois de se ter feito a modelação cinética deste material foi feita uma simulação para a sua gasificação usando uma aplicação de Chemcad. Para efetuar esta simulação foi utilizado um reator de Gibbs utilizando parâmetros do processo e as propriedades do material de acordo com a sua análise fornecida pelo Institute of Coal Chemical Processing em Zabrze (Polónia). Antes da simulação foi efetuada uma análise DTG para prever os possíveis produtos que advêm dos vários modos de transformação do material. Os resultados obtidos pela simulação foram comparados com os fornecidos pelo Institute of Coal Chemical Processing.

Palavras-Chave: Gasificação de biomassa, Modelação cinética, TG, DTG, DSC, Chemcad

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1. Introduction

Today's world must face a number of issues related to energy production by means which are harmful to the environment and to humanity. Application of fossil fuels in energy generation processes is still ongoing due to high availability of the sources and relatively low cost. Because of economic aspects and reliability fossil fuels still surpass renewable sources. However, nowadays the trend is changing. To the joy of majority of people, renewables are becoming more popular and governments are keener on the application of clean energy technologies within their countries to prevent an environmental catastrophe in upcoming years. Thanks to European Union's commitments made in 2007 through 'Climate and Energy Package' program member countries committed to reduce greenhouse gases emissions by 20% below 1990 levels and to increase the renewable energy target up to 20% by 2020. Together with many laws introduced by EU, in 2014 programs were implemented for the sustainable development of Europe, like Horizon 2020 which is EU's biggest Research and Innovation Program aiming at encouraging private investments in different areas to drive economic growth and increase Europe's competitiveness. These drivers have caused the need of seeking for alternative ways of energy production, which are less harmful not only in terms of pollution but also in terms of obtaining the sources like mining or transportation threats.

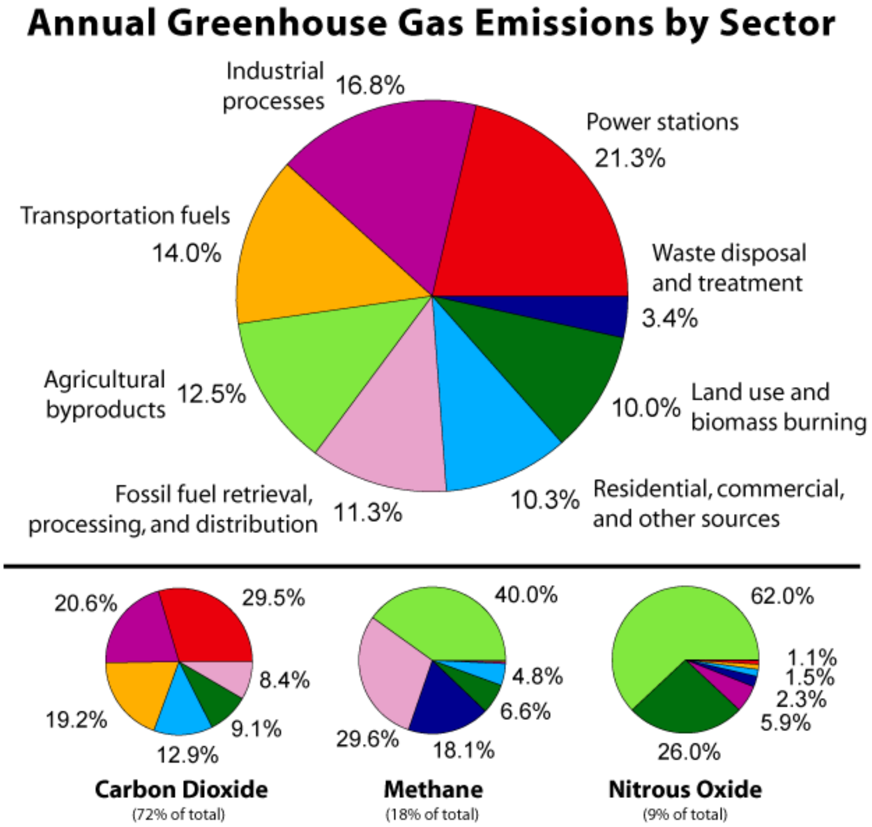


Fig. 1: Relative fraction of anthropogenic greenhouse gases coming from each of eight categories of sources in 2000 [1]

Figure 1 serves to illustrate the scale of greenhouse gases emissions caused by different sectors. According to the author, the panel above bold line shows the summation of all anthropogenic greenhouse gases, weighted by their global warming potential. This consists of 72% carbon dioxide, 18% methane, 8% nitrous oxide and 1% other gases. The panels below bold line show the comparable information for each of these three primary greenhouse gases, with the same coloring of sectors as used in the chart above them.

One of the methods of clean energy generation is the gasification process. It is a process of partial oxidation implying many advantages over regular combustion. One of them is the possibility of different feedstock being used. On a large scale, there are already many implemented gasification process, mainly using coal as their feedstock, operating in such countries like the United States, Australia, Netherlands, Spain, Japan, China, India.

As a feedstock for gasification power plants, biomass is widely used. It is a source which does not contribute to CO_2 emissions accounted for greenhouse gases release and allows to obtain even more clean energy than from coal gasification plants, when just greenhouse gases emission is accounted for. Application of biomass as a gasification feedstock is often a solution for biomass residues and wastes management. The need for new energy sources has also driven usage of biomass to seek for alternative fuels due to depleting fossil energy sources. The objective of this work is to study alder chips gasification process through modeling of the kinetics of their thermochemical conversion and simulation of a gasification process with Chemcad software. The aim is to increase interest in biomass gasification in regions which have no application of that process so far. Besides that, the aim is also to show its advantages over other energy generation processes what would help to meet the challenges imposed by the targets established by the European Union and member states.

1. Literature review

2.1 European energy system-biomass market.

Before the oil crisis in the 1970s, in the Europe governments were focused on electrification and building integrated monopolies to generate, transmit and distribute electricity. [2] Countries paid attention to nuclear power development and fossil fuels supply. [2] In the 1970s these trends started to change to the awareness of Europe's dependency on fossil fuel supply. Mentioned changes are nowadays supported by commitments made by European in 2009. Since that time, the European Union has focused on the application of renewable energy sources and on energy savings and increasing energy efficiency. The aim is not only to promote energy security, but also technology development and innovation. [3,4] Projections for oil and natural gas imports are at the level of 93% and 73% of their total consumption in 2020. [2] So, growth of renewables use is one of the solutions to reduce dependence on import. Also, it became an answer for the increasing prices of oil, gas and uranium, what contributes to the increased prices of energy production from these sources. In the table below the potential of biomass in some countries of Central Europe is presented. The countries that are mentioned as examples are Austria, Czech Republic, Germany, Hungary, Italy, Poland, Slovakia and Slovenia respectively.

Tab: 1 Technical potential of biomass in some countries of Central Europe in 2010 [5]

Central Europe Countries	AT	CZ	DE	HU	IT	PL	SK	SI
Technical potential of biomass PJ/year	368	299	1200-1700	100-190	1000-1200	927	40-90	20-53

AT-Austria, CZ-Czech Republic, DE-Germany, HU-Hungary, IT-Italy, PL-Poland, SK-Slovak Republic, SI-Slovenia

When it comes to Austria, biomass is a major renewable source corresponding to 58,9% of all the renewable energy carries. [5] In 2008 there were 1100 centralized heating power plants operating with forest biomass and straw, with a total capacity of 1300 MW. [5] As far as the Czech Republic is concerned its agricultural land accounts for 54,2% of the total area and the forests to 38,5%. 8,4% of agricultural land and 16,0% of total area in the Czech Republic have some limitations regarding environmental issues banning intensive farming and forestry. Due to that, there is a chance for energetic crops plantation and wood utilization, as it is usually less environmentally harmful. According to Jan Habart, the author of an article titled “Biomass utilization in the Czech Republic and recent legislative condition” published in 2005 there are already 40 district heating systems running on biomass. [6] On the other hand, in Germany the co-firing coal in regular coal power plants with the addition of 5-20% biomass is considered to decrease CO_2 impact on the environment. As it is stated in the article of Andreas Luschen and Reinhard Madlener electrical power potential for biomass co-firing together with coal is around 28TWh per year if 10% of coal is replaced by biomass. [7]

To compare given in the table 1 parameters of technical potential of biomass in Central Europe’s countries, there was created a table with total consumption of electricity and heat in the same countries, based on data provided by International Energy Agency for 2010.

Tab: 2 Total consumption of electricity and heat in some countries of Central Europe in 2010 [8]

Country	Electricity [GWh]	Heat [TJ]
AT	60317	77127
CZ	57204	94171
DE	532424	471767
HU	34207	45625
IT	299313	139503
PL	119063	274106
SK	24135	35649
SI	11945	8030

AT-Austria, CZ-Czech Republic, DE-Germany, HU-Hungary, IT-Italy, PL-Poland, SK-Slovak Republic, SI-Slovenia

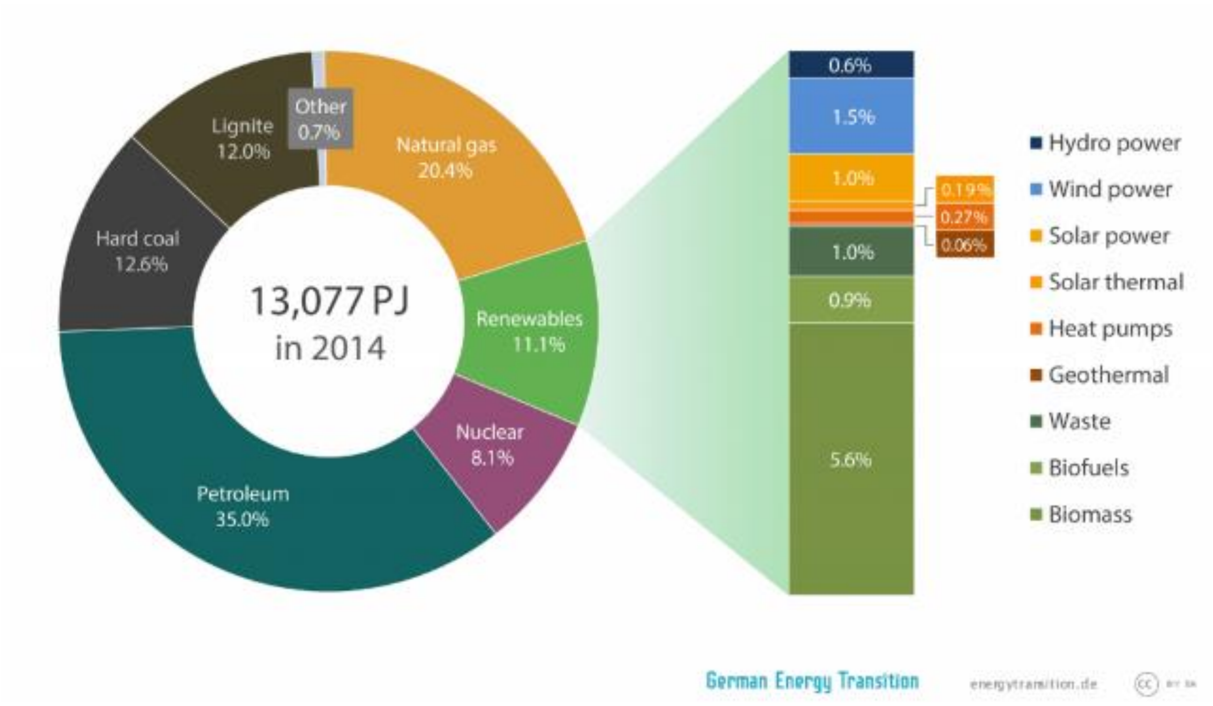


Fig.2 Primary energy consumption mix in Germany in 2014 [9]

From the Figure 2 we can notice, that although oil remains the largest energy source in Germany, within the renewables share, biomass plays the major role. It was stated by Craig Morris in the article published in 2015 on energy transition, that in 2014 the renewables share accounted for roughly 11% of German's primary energy consumption.

2.2 Polish energy system – biomass market

After the collapse of communism in Poland, the national energy sector was focused on the restructuring of the mining industry rather than like most of other countries in Europe on renewable energy technologies development. The government then has not considered renewable energy sources at that time due to the high amount of coal sources on Poland's territory [10].

In Poland, because of high amounts of coal deposits, it is major energy source used in energy production processes. According to Tajduś A., Czaja P., Kasztelewicz P., the highest rate of hard coal mining in Poland was in 1980s and was at the level of 195 million of tons. At the beginning of 1990s started the process of shutting down mines in Poland, so hard coal production being lower became noticeable. In 2000 in Poland, hard coal production accounted for 100 million tons and in 2009 it was 77,4 million tons. [11] Although, polish energy system is based on 95% on national energy sources, according to national energy policy established in 2009 growing demand for electricity due to developing economy is going to be met by increasing amounts of renewables. [11] Besides importing higher amounts of fuels, other ways of meeting the needs of energy production in the country should be figured out. One of the ways proposed by the polish energy policy is the solution of biomass application. It seems to be the most reasonable renewable energy source applied in energy production system in Poland due to relatively low availability of other renewable sources. Unfortunately, Poland has not sufficient number of sunny days, when energy could be produced by appropriate intensity of solar radiation. That causes low (when compared to other, often more developed countries in the European Union) application of photovoltaic systems. [10] When it comes to wind farms installed in Poland, its total capacity accounts for 173,5 MW placed in the north, south, west and east part of the country. According to Ryszard Gajewski from Polish Biomass Chamber, share of electricity production from biomass until 2020 is going to drop from 53,1% of all renewable sources to 31,5%. However, when it comes to heat production biomass accounts for 78% of all renewable sources. [12] So far in Poland only one biomass power plant with capacity at the level of 205MWe has been installed. It is an operating plant, established in June 2013 with the regular combustion of biomass. It is the largest plant in Europe powered by 100% with biomass. [13]

Because of the unfriendly image of Poland on the international stage in terms of high coal combustion level in national energy production, there are going to be begun works on a project called POLYGEN. RAFAKO S.A. group together with InnoEnergy within the project are going to create so-called islands of polygeneration. [13] The aim of the project is to provide district heating in small and medium towns via waste and local biomass gasification and SNG production.

2.3 Role of biomass in meeting growing energy demand and characterization of biomass

As it is well known, because of growing population, energy demand is going to increase in upcoming years.

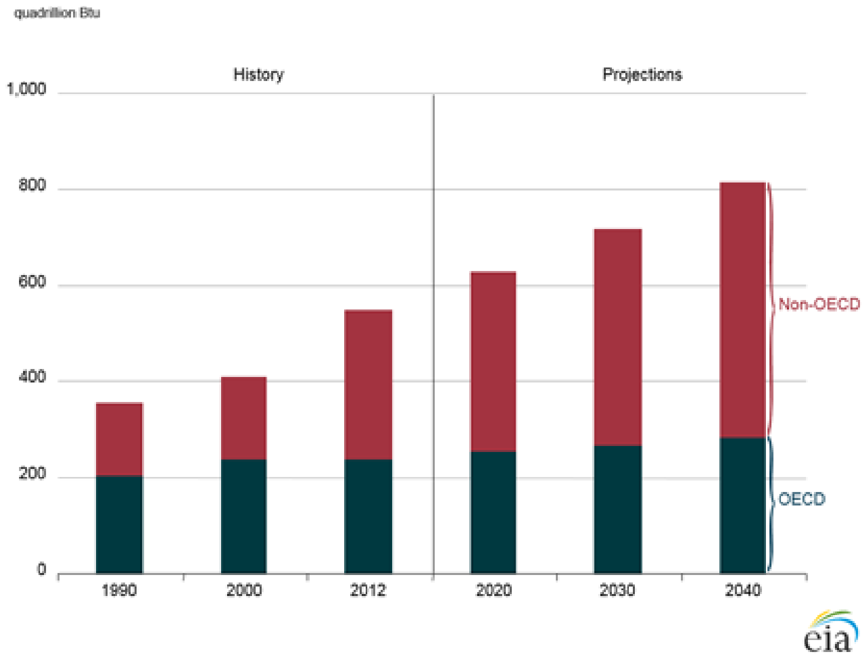


Fig.3 World’s energy consumption, 1990-2040 [14]

As we can observe from the graph in Figure 3, world’s energy consumption is dictated mostly because of growing economy in Non-OECD countries like China or India.

It is not disputed that in meeting increasing demand for energy, renewable energy sources will play a significant role.

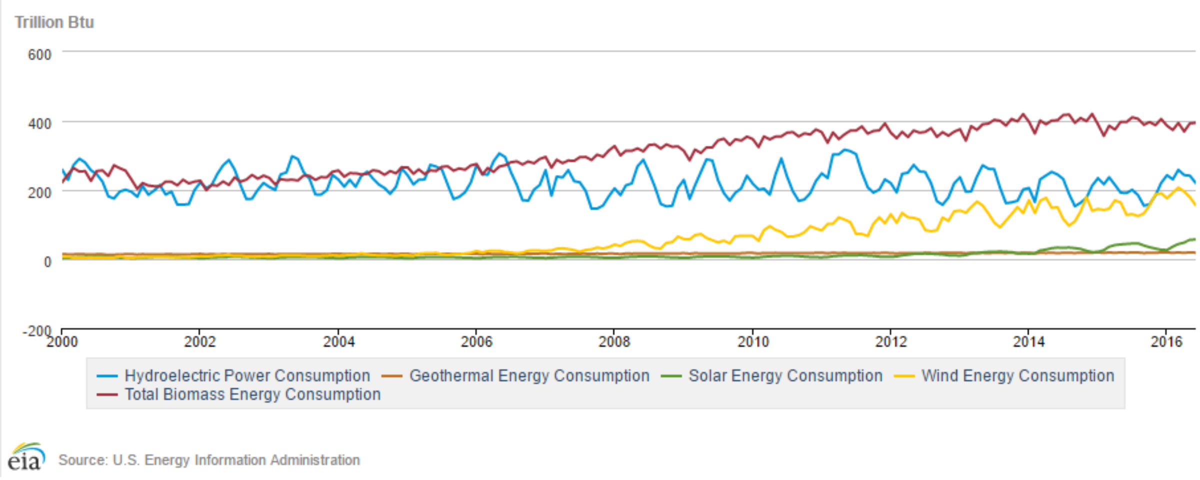


Fig.4 Renewable Energy Production and Consumption by Source [14]

In Figure 4 above we can notice growing production and consumption of total biomass consumption over years. Due to promising aspects of biomass, there is increasing interest in its application worldwide.

It has been stated by National Energy Education Development that currently there are used four types of biomass: wood and agriculture products, solid waste, landfill gas and biogas, alcohol fuels. [15]

Basically, biomass is a type of biodegradable source coming from agriculture, forestry, fishing, aquaculture, industrial and municipal waste. Biomass can be a feedstock for electricity, heat, chemicals, fuels obtaining. [16] When it comes to application in energy production processes, it seems to be reasonable source since it does not contribute to CO_2 emissions when considering greenhouse gases release. Biomass is considered to be carbon neutral and this is because it absorbs CO_2 during photosynthesis, which is then released in the burning process. The scope of biomass application in energy production processes is wide. Biomass can be divided into two major areas, according to its source: plant and animal biomass. For the purposes of this work, there will be paid attention only to plant biomass since the studies within this dissertation were carried out with a sample of alder chips.

Biomass is a mixture of organic compounds and inorganic matter [17]. Inorganic matter is ash (c.a. 1 wt% in wood) containing potassium, sodium, calcium, phosphorus, silicon, magnesium components. Organic matter mainly consists of three major constituents, i.e. cellulose, hemicellulose and lignin. [17]

Cellulose is the basic component being a “long-chain linear polymer with a crystalline structure, a high degree of polymerization (~10,000) and large molecular weight (~500,000), represented by the generic formula $(C6H10O5)_n$” [17]. It is built out of glucose monomers.

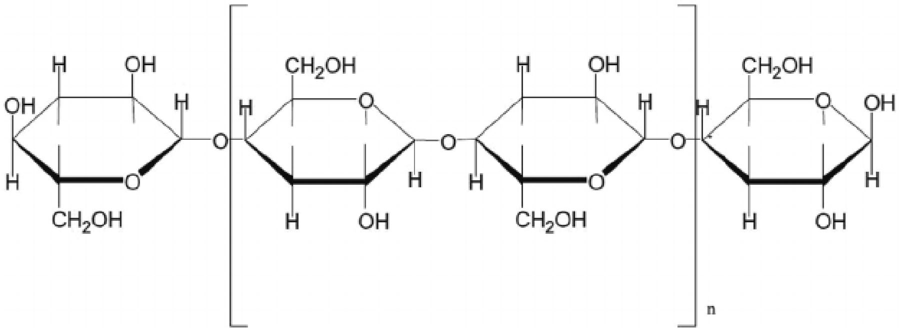


Fig.5 Structure of cellulose [18]

Although cellulose seems to be simple, its morphological structure can cause some issues due to association with other polysaccharides and lignin in plant cell walls. High strength and stiffness characterize it. [19] It is said that because of crystalline and strong structure, caused by hydrogen bonds and van der Waals forces, it is resistant to hydrolysis. [17]

Opposite to cellulose, weak, amorphous structure characterizes hemicellulose. It consists of branched chains of carbohydrates with a lower degree of polymerization (~100-~200). The general formula is $(C5H8O4)_n$. According to the literature, it is said there is ca. 20-30 wt. % of the dry weight of wood. [17]

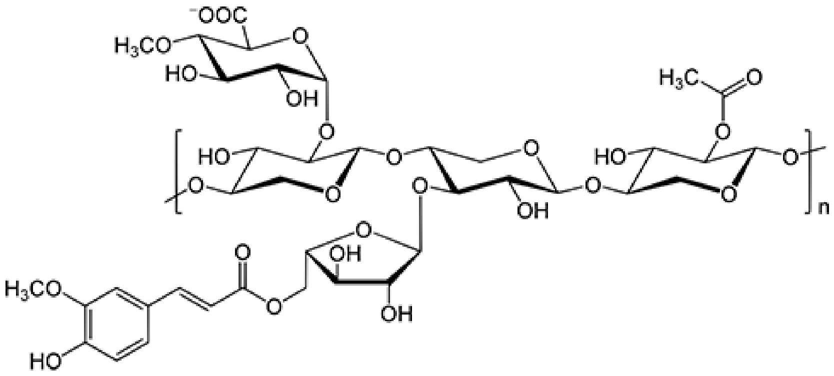


Fig. 6 Example of hemicellulose structure consisting of xylan monomers [20]

Because of the random and weak structure, it decomposes at lower temperatures than cellulose. Due to that, it also produces more volatile matter giving less char, which is an excellent energy carrier with higher energy density. [17] It is soluble in weak alkaline solutions and is way less resistant to hydrolysis, being hydrolyzed in diluted acids and bases. [17] Most weight loss occurs at ca. 180°C [17]

The third organic matter component, lignin, is the most branched and unstructured constituent. [17] It is a part of cell walls of plants, which holds their structure. It provides mechanical strength to the cell wall because is bonded with hemicellulose with covalent bonds. Benzene rings are most dominant units in lignin polymers structure and that makes it highly aromatic and hydrophobic. [17] According to the authors of [17], content of lignin in typical hardwood is ca. 18-25% and in ca. 25-35% for dry basis.

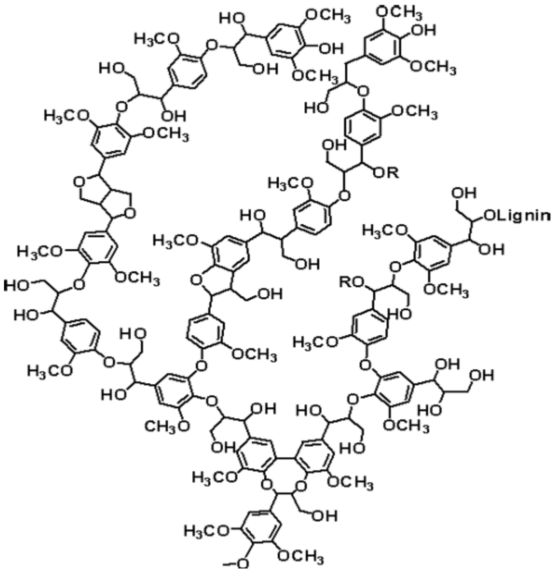


Fig.7 Example of lignin structure [20]

It has been studied, that biomass thermochemical conversion results in low fixed carbon and high volatile matter, what implies low calorific value. However, there is one significant advantage of biomass over fossil fuels, which is usually lower contents of nitrogen and sulfur what gives cleaner combustion and lower need for flue gases treatment high efficiency.

2.4 Characterization of alder wood as a biomass gasification feedstock

Wood is the most studied and commonly used energetic type of biomass. However, that feedstock coming directly from forests is not economically feasible, since it may be destined to more profitable industries, like the furniture industry. [21] Nevertheless, some other wooden sources find application in energy processes. The solution to this issue is the use of residues coming from forestry, which still allows us to obtain energy and at the same time, it is a way to manage these residues in a useful way. Additionally, some species of energetic crops, which in any other case give marginal profit, are specially grown for energy industry purposes providing their beneficial application. [21] Alder wood is the deciduous type of hardwood of birch family, which is considered by many to be a good energy source. People often use it as firewood in their houses. It finds application also as a smoking wood giving a sweet flavor for meats. Alder becomes a very significant energy source when pyrolyzed and transformed into charcoal.

2.5 Routes of biomass thermochemical conversion

Application of biomass in order to release the energy stored in its form has been taking place for centuries. It had been used widely by people a long time before coal and other fossil fuels were discovered. Nowadays it is applied not only in heat and power generation, but also in chemicals production. Biomass, as mentioned earlier, is a so called “green” source. Therefore, lately it has gained much interest. Many types of research are in process to get more knowledge on thermochemical conversion of biomass, since it is the renewable source, broadly available and when it comes to plant biomass, today it does not even have to compete with food crops when used in energy generation processes. In order to obtain the energy from biomass, several processes may be applied. To make it more readable, all processes will be pointed out in order of decreasing oxidant content.

2.5.1 Combustion

The most well-known and widely used is regular incineration, providing around 90% of bioenergy produced worldwide. [22] Incineration provides the fastest and the least expensive energy release. It is an exothermic reaction of feedstock with oxygen, with an excess of air. In the case of biomass, it requires delivery of heat, to provide faster ignition of wood since at room temperature wood does not undergo autoignition (autoignition of wood – around 350°C surface temperature, when direct flaming ignition). [23] Although, combustion is a relatively simple process, from a technological point of view it is rather more complex. This is because of the high reaction rates and high amounts of heat released, as well as to the many reactants that are involved, and to the reaction schemes that take place. According to the authors of [21], subsequent principles of the combustion process are as follow:

- Drying, where water contained in biomass evaporates
- Pyrolysis and reduction, where the fuel undergoes thermal decomposition into volatile matter and solid char
- Combustion of gases released during pyrolysis process, with presence of yellow flame
- Combustion of solid char on the grate, with usually glowing mode and presence of blue, small flame

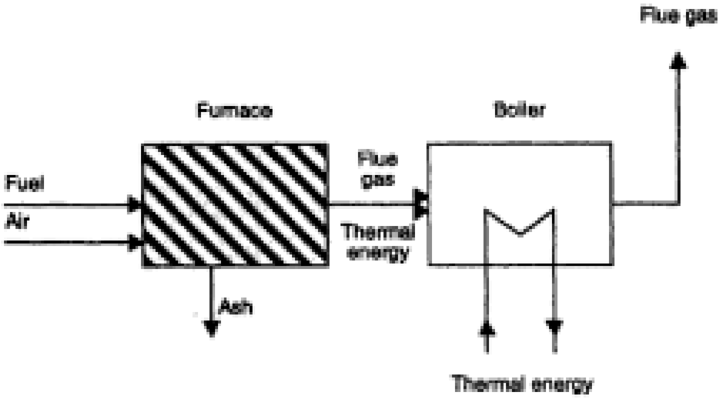


Fig. 8 Simplified scheme of biomass combustion process [21]

Despite the fact, that combustion of biomass is a relatively simple and low-cost process, there are some significant disadvantages associated with it. First, there are high amounts of moisture present, which absorbs heat, thus lowering the combustion temperature, what causes a need to increase excess of air to provide complete combustion. Low contact between the solid particles and the gases contribute to that as well. [24] Second of all, however, wooden biomass contains a lower amount of sulfur and nitrogen than for instance coal, still during combustion emission of greenhouse gases is higher than any other thermochemical conversion process. Due to significant emissions during process high efficient flue gas cleaning system is needed to meet the environmental concerned directives set by various authorities. The design of biomass combustion facilities depends on fuel's characteristic, local environmental legislations, equipment's cost, performance and energy, and capacity required. [23] Usually, low-quality fuels are used for large scale combustion and high-quality fuels feed small scale systems. [23] Low-quality feedstock stands for inhomogeneous characteristic material such as ash-melting behavior, moisture content particle size etc. [23]

2.5.3 Gasification

Gasification is a complex process in terms of chemistry. Mainly, it is a reaction of partial oxidation leading to obtaining the gaseous main product, so-called syngas, which is a mixture of CO and H_2, having multiple applications. It may be used in a gas turbine or in an internal combustion engine to produce electricity and heat, or it may find application in chemicals production through Fischer-Tropsch reaction.

Tab: 3 Reactions occurring during gasification [17]

Reactions name	Reaction formula	ΔH^0 [kJ/mol]
Heterogeneous reactions		
Water gas-primary	$C+H_2O=CO+H_2$	131,3
Water gas-primary	$C+H_2O=CO_2+2H_2$	90,2
Boudouard	$C+CO_2=2CO$	172,4
Oxidation	$C+O_2\text{->}CO_2$	-392,5
Partial oxidation	$C+1/2O_2\text{->}CO$	-110,5
Methanation	$C+2H_2\text{->}CH_4$	-74,6
Homogeneous reactions		
Water-gas shift	$CO+H_2O=CO_2+H_2$	-41
Steam reforming	$CH_4+H_2O=CO+3H_2$	205,9
Steam reforming	$CH_4+2H_2O=CO_2+4H_2$	164,7
Oxidation reactions	$CO+1/2O_2\text{->}CO_2$	-283
	$H_2+1/2O_2\text{->}H_2O$	-242
CO2 reforming	$CH_4+CO_2=2CO+2H_2$	247

As gasifying agent air, pure oxygen, steam and carbon dioxide may be used. The least expensive is obviously air, as it is widely available and it does not require separation like in oxygen case. The quality of producer gas (heating value and composition) depends on amount and type of used oxidant. [24] When air as a gasifying agent is used, the gas that is obtained is diluted with atmospheric gas what decreases energy density of it. Therefore, that syngas is immediately combusted in boilers to produce electricity and heat. [24] When it comes to chemicals production, it is advisable to use oxygen as a gasifying agent, due to higher producer's gas energy content caused by lack of nitrogen in stream flow. Steam is used mostly in case of hydrogen production, since when steam/biomass ratio increases H_2 content increases and CO and CH_4 amounts decreases. It implies also higher energy content because hydrogen is most calorific gas from all present in the process gaseous products (HHV=141,8 MJ/kg).

Tab: 4 Heating values of combustible gases [25]

Gas	HHV	LHV
	MJ/Nm^3	
H_2	12,7	10,8
CO	12,65	12,65
CH_4	39,79	35,86
C_2H_6	70,39	64,45
C_3H_8	101,73	93,68
C_4H_{10}	132,37	122,27

The composition of producer gas may vary depending on process conditions and type of feedstock. It is said, that typically syngas consists of 30-60% of carbon monoxide, 25-30% of hydrogen, 0-5% methane and 5-15 % of carbon dioxide, additionally containing some amounts of water vapor and small quantities of hydrogen sulfide, carbonyl sulfide, and ammonia. [26] The contaminants like ammonia and hydrogen sulfide must be removed before going to downstream processes.

The equation below represents overall reaction occurring during gasification in air gasifier.

CH_xO_y (biomass) + O_2 (21% of air) + H_2O (steam) = CH_4 + CO + CO_2 + H_2 + H_2O (unreacted steam) + C (char) + tar (1)

Currently, mostly used gasification technologies in the industry are: fixed bed gasification, fluidized bed and entrained flow gasification. [27] All of them are still under research either to get to know its phenomenon better or to optimize the process. There are many advantages of the gasification process. First and foremost, gasification is a cleaner alternative for regular combustion, since it produces mainly CO and H_2, so combustible gases unlike combustion, which produces significantly greenhouse gas CO_2. Although, when syngas is combusted it also produces carbon dioxide in the flue gases stream, because it is not obtained through complete combustion what implies excess of air applied, it is not that much diluted by excessive presence of nitrogen. That means, the concentration of carbon dioxide in flue gases is higher, what makes it easier to absorb in flue gases cleaning unit. In the case of coal application, gasification is a great way of its utilization, because coal contains relatively high amounts of sulfur and nitrogen that during combustion are emitted in the form of NOx and SOx. During gasification, they are emitted in the form of H_2S and NH_3, which are more easily removed by processes, for instance, through absorption. Also, concentration of these contaminants is higher and because of that, cleaning processes are carried out with higher efficiencies.

The second significant advantage is feedstock diversity that may be applied in the process. Gasification is used for coal, biomass, waste utilization and converts it into useful products. Regarding plastic wastes or even biomass residues this process converts less valuable products into more valuable ones.

When it comes to disadvantages, the main one is the high capital cost of gasification facilities that discourages when considering different types of biomass or any other feedstock conversion into the energy plants.

Gasification, when compared to incineration process, is not that much well examined and developed like the much simpler process of combustion. That may imply many difficulties when designing, implementing, or developing gasification plant.

In Figure 9 a gasification process scheme from feedstock to its end products is presented.

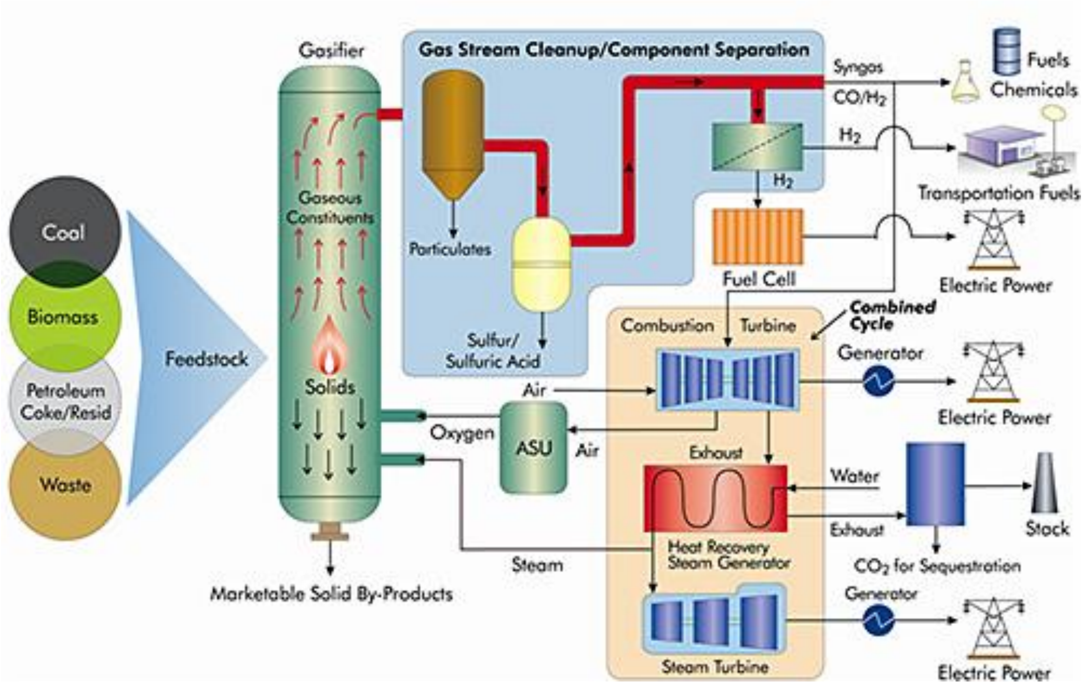


Fig. 9 Gasification plant scheme [26]

2.5.3 Pyrolysis

Next thermochemical conversion of biomass route is pyrolysis. It is a complex process of large hydrocarbon decomposition carried-out in the absence of oxidant while being heated up. Bonds' vibration between molecules may simply describe this phenomenon. Molecules vibrate at any given temperature. As the temperature rises, the frequency of molecule's vibration also rises. Because hydrocarbons are subjected to high temperatures during pyrolysis process at the certain point of being stretched and shaken they start to break down into lower molecules. [28] It is considered as green technology. For instance, it is widely used for extracting materials from used tires or as cleaning process when removing organic contaminants from soil or sludges, or producing biofuels. [29] Biomass is an energy source that stores solar energy in its composition. It consists of cellulose, hemicellulose and lignin materials. Due to that, when subjected to pyrolysis it breaks down these constituents into smaller molecules causing the production of the gaseous phase, that part of it condenses to the liquid state giving bio-oil. Remaining products are so-called biochar, which is usually consisting of the remaining lignin and non-condensable gases. [29]

There may be pointed out three variations of pyrolysis:

- Torrefaction
- Slow pyrolysis
- Fast pyrolysis

Torrefaction refers to the mild thermal processing of biomass to make it more energy dense for energy production applications. It improves a lot of the feedstock's properties such as grindability, particle shape, size, its distribution. By decreasing moisture content simultaneously increases carbon content what implies higher calorific value. [30] An interesting fact is, that when the material is torrefied it loses ~OH functional groups what causes higher hydrophobic nature of biomass. Then it becomes more stable, also in terms of chemical stability. [30] Temperature of the process ranges between 200°C-300°C. [30] It is said, that typically after this process 70% of the mass is obtained as a solid fuel with 90% of its initial energy content. [30]

Slow pyrolysis is applied when biochar production is an objective. It involves low heating rates like around 10°C/min [31]. It is characterized by higher solid and vapor residence time and operates at much lower temperatures than fast pyrolysis (ca. 400°C). [32] Biochar obtained in the process has increased energy density, what makes it better fuels for industrial applications. Moreover, it has been studied that carbonized biomass improves the fertility of agricultural soils, at the same time reducing greenhouse gases emissions by carbon sequestration (because it comes from biomass absorbing carbon dioxide in the photosynthesis process). [33]

Fast pyrolysis operates at the heating rates of ca. 1000°C/min. [34] Usually, it is associated with temperatures in excess of 500°C. The objective of fast pyrolysis application is mainly to obtain bio-oil. Usually, the yields of products during fast pyrolysis are as follow: 60-70% of bio-oil, 15-25% of biochar and 10-15% of syngas. [34] Produced bio-oil has increased density what makes it more cost effective in terms of transportation and storage than primary biomass feedstock. Table 4 presents typical products distribution depending on pyrolysis modes.

Tab: 5 Weight yields of products obtained by different wood pyrolysis modes [35]

Mode	**Conditions**	**Liquid**	**Solid**	**Gas**
Fast	~500°C, short hot vapour, residence time ~ 1 s	ca. 75%	ca. 12%	ca. 13%
Intermediate	~500°C, hot vapour residence, time ~10-30 s	ca. 50%	ca. 25%	ca. 25%
Slow (Carbonisation)	~400°C, long vapour, residence time hours->days	ca. 30%	ca. 35%	ca. 35%
Gasification	~750-900°C	ca. 5%	ca. 10%	ca. 85%
Slow (Torrefaction)	~290°C, solids, residence time ~10-60 min.	ca. 0%	ca. 80%	ca. 20%

2.6 Gasification technologies

Gasification is a complex process involving many various reactions. These are both exothermic and endothermic reactions. A reactor in which where gasification occurs is called a gasifier. From the time since the process was discovered till now, many different designs of gasifiers have arisen. The challenge is to optimize the process mostly by minimization of energy consumed in endothermic reactions, feedstock consumption and obviously economical construction [36]. Gasifier designers also face the problem with tar generation during the process, which in the case of power generation in combustion engines should be removed with high efficiency. Therefore, a lot of works done on gasifiers production were focused on such design which would provide the smallest amount of tars arose in the process. Within gas generator four zones may be distinguished: drying zone, pyrolysis zone, reduction zone and oxidation zone. In the drying zone, external water evaporates. In the oxidation zone, apart from the external heat source, the reaction often provides heat for endothermic gasification reactions. Types of gasifiers can be specified depending on bed applied in reactor and flow of gasifying agent. In the upcoming sub-chapters different types of gasifiers will be specified with increasing velocity of flowing gasifying gas.

2.6.1 Fixed bed gasifier

This type of gasifiers is characterized with relatively low gas velocities in order to maintain the bed fixed, high carbon conversion, long fuel or bed residence time and low ash carry over. They usually operate at pressures in the range of 25-30 atmospheres. [26] There are two operating modes: dry-ash or slagging. [26] In dry-ash mode, ash occurring below oxidation zone is cooled down by steam and oxidant such as air or oxygen, to produce solid ash. Because the distribution of temperature is uneven, in the case of fixed bed gasifiers, that causes the formation of so-called hot spots. [37] This, in turn, causes ash fusion, low specific capacity, long time when heating up and some limitations when scaling up is considered. [37] Thus, when high power output is required, fixed bed gasification technology may not be economically feasible, since limitations in scaling up cause need for installation of fixed bed gasifiers cascades. That, unfortunately, causes higher investment costs. [37] Operating temperature is decreased to below ash-slagging one through char-steam reaction. [26] Below are going to be provided the following characteristics of moving-bed gasifiers [26]:

- ✓ Simplicity of gasifier construction and operation
- ✓ High equipment efficiency
- ✓ Relatively low oxidant requirement
- ✓ Product gas at relatively low temperature, thus there is no need for expensive heat-recovery equipment
- ✓ Feedstock flexibility
- ✓ High methane content in product gas

✓ Generation of tars, thus there is need for cleaning system if product gas is going to be used for applications other than direct heating

The names fixed-bed and moving-bed are used synonymously, however there is no such thing like fixed bed exactly. What is meant behind this statement is, that bed is always moving. Sometimes with such low velocities, that it is not noticeable. There are three categories into which fixed bed gasifiers may fall: updraft, downdraft and cross draft gasifiers. [38]

Updraft gasifiers are commonly used for biomass or solid waste gasification when the objective is to produce heat. Because of the principle of their operation, they tend to produce quite significant amounts of tars. That causes the need for highly efficient flue gases cleaning systems if the gas generator is subjected to produce electricity through combustion engines. This results in higher capital, operating and maintenance costs. In updraft gasifiers, solid fuel is fed at the top and goes downward. Gasifying agent flows from the bottom, through the grate and produced syngas flows counter currently to the feedstock. Afterward it exits at the top of the gas generator. [38] The order of zones within the reactor are as follows: drying zone, pyrolysis zone, reduction zone, and oxidation zone. In oxidation zone CO_2 and H_2O are liberated, having a temperature around 1000°C. [39] Further they pass through fuel above and they get reduced to H_2 and CO with temperature decreasing to around 750°C. Next, as moving upward these gases pyrolyze dry feedstock and above pyrolysis zone, dry wet incoming feedstock, leaving gas generator with the temperature around 500°C. [39]

One of such innovative solutions was created in Institute for Chemical Processing of Coal in Zabrze, in Poland. That gas generator was created under the project aiming at 1MWt co-generation installation design to produce heat and power. The gasifier GazEla is fixed, updraft type of gasifier with power at the level of 60 kWt. [40] Its unique construction allows producing gas with lower tar improving its applicability in electricity production. That allows combining advantages of updraft reactor with downdraft which gives better results of tar content in produced gas.

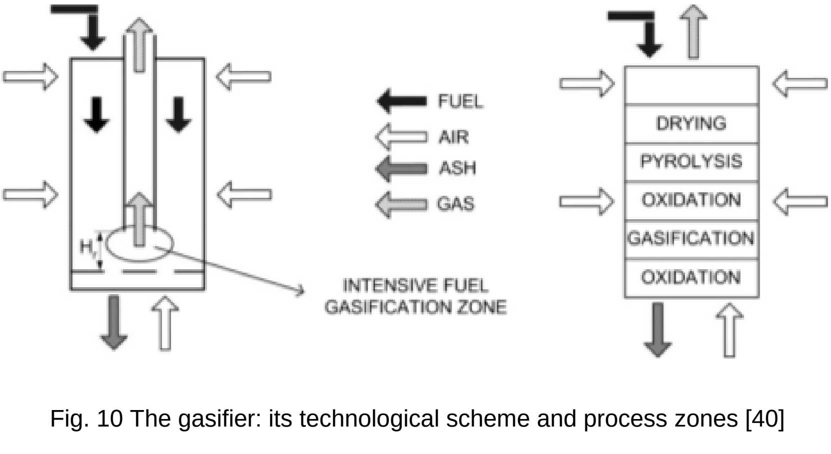


Fig. 10 The gasifier: its technological scheme and process zones [40]

Characteristics are [38]:

- ✓ High feed rates up to around 150 tons/day
- ✓ Feedstock is pre-dried before it reaches pyrolysis and reduction zones
- ✓ Good for high moisture biomass (up to 50%) and wastes
- ✓ High efficiency
- ✓ High amounts of tars in syngas

Downdraft gasifiers find application in motive power generation. It converts high volatile feedstock into low tar syngas [38] Gasifying agent flows co-currently with produced gas and solid fuel being fed at the top of the reactor. Therefore, syngas is drawn at the bottom. [39] Air is injected at the height of oxidation zone, so more or less in the middle of the reactor. The order of zones is as follow: drying zone, pyrolysis zone, oxidation of volatiles zone, reduction zone.

In the pyrolysis zone volatiles are produced, that are partially oxidized in the combustion zone, providing heat for reduction zone. [38] The gas at that height has around 800-1200°C, what causes tar's cracking. Gases coming from oxidation zone (CO_2 and H_2O) are reduced to CO and H_2 by hot char. Then syngas exits at the bottom of the gasifier with the temperature around 600-800°C. [38]

Characteristics are [38]:

- ✓ Feed rates up to around 65 tons/day
- ✓ Requires low moisture (<20%) and low ash content
- ✓ Low tar content in syngas because of high operating temperatures

Crossdraft gasifiers have many characteristics in common with updraft gasifiers. The main difference is that the air is injected from the side of reactor and gas is drawn off at the other side of the reactor. Fuel enters from the top and thermochemical reaction occurs progressively while fuel goes downward. It has the fastest start-up time, 5-10 min, of all these three types of reactors. [39] It operates with high temperatures, up to 2000°C. That influences produced gas composition as follow: a higher amount of CO, lower of H_2 and CH_4. [39]

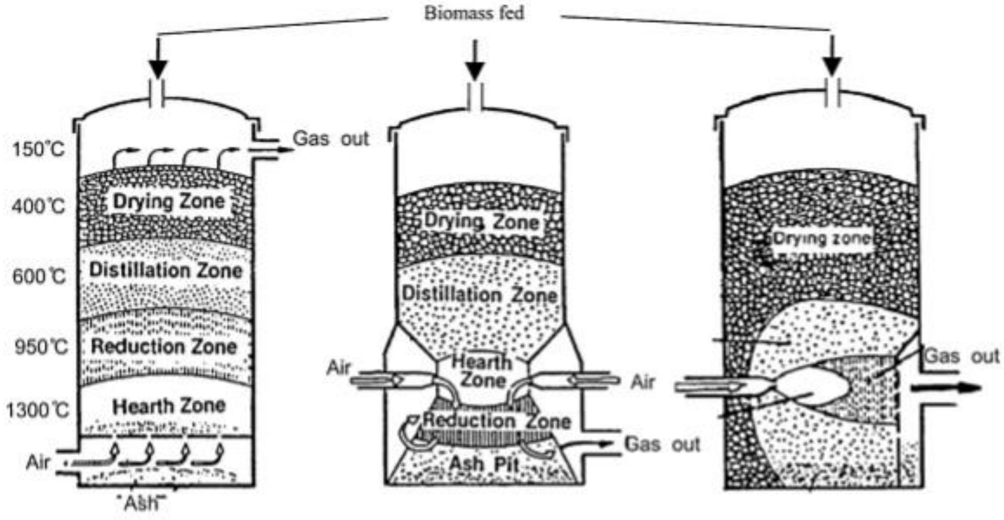


Fig. 11 Types of fixed bed gasifiers: left-updraft, central-downdraft, right-cross draft [39]

2.6.2 Fluidized bed gasifier

When the gasifying gas is fed from the bottom of the gasifier, with increasing gasifying agent velocities pressure drop within the bed increases too. At the certain point, it stops to increase, despite the growth of gas velocity, and it is maintained at the same level within the certain range of gas velocities. [41] That means the bed starts to behave like a fluid and it is suspended within the reactor. [41] Heat is provided from the external source and as soon as sufficient temperature is reached, the fuel is introduced at the bottom or at the top, depending on the design. It mixes with reactor's bed. It results in fuel being pyrolyzed very fast, what implies quite significant amounts of gases being produced. Then, as it passes further gaseous phase and tars go under reduction stage. To prevent char's blow-out, there are often installed cyclones to provide kind of circulation system. Ashes are carried over at the top of the gas generator with syngas stream. So, before it reaches engine, it has to be cleaned from any solid particles. [39] Usual operating temperature is in the range of 1100°F-1600°F. Oxidation of fuel provides heat to maintain bed's temperature at the proper level and also to provide heat for newly injected biomass. [39] The bed's temperature needs to be at such level, so that we can obtain complete devolatilization of biomass but below ash fusion temperature to avoid clinker formation and bed's de-fluidization. [39,42] This type of gasifier has many advantages over fixed bed reactor. For instance, it provides more uniform temperature's distribution throughout the gas generator, what results from high heat transfer. [39] It provides also good mixing. It is characterized by high conversion efficiency and low tars content in syngas stream. [39] They have a high tolerance for various fuel's quality and particle's size distribution. [37] Unfortunately, they produce gas with high dust content and ashes with low melting points, what causes slagging. [37] Mostly, it finds application in coal gasification with relatively reactive coals and low-rank coals. [26,42]

Some fluidized bed gasifier's characteristics [39,42]:

- ✓ Rates of feed up to 1000 tons per day
- ✓ Load and fuel flexibility
- ✓ High heat transfer
- ✓ Moderate gasifying agent's demand
- ✓ Uniform temperature's distribution throughout bed
- ✓ Moderately high temperatures
- ✓ Higher cold gas efficiency than in case of entrained bed gasifiers, but also lower carbon conversion
- ✓ Need for char recirculation
- ✓ Good for not too much reactive feedstock
- ✓ Relatively high carbon conversion
- ✓ Low content of tars in syngas stream

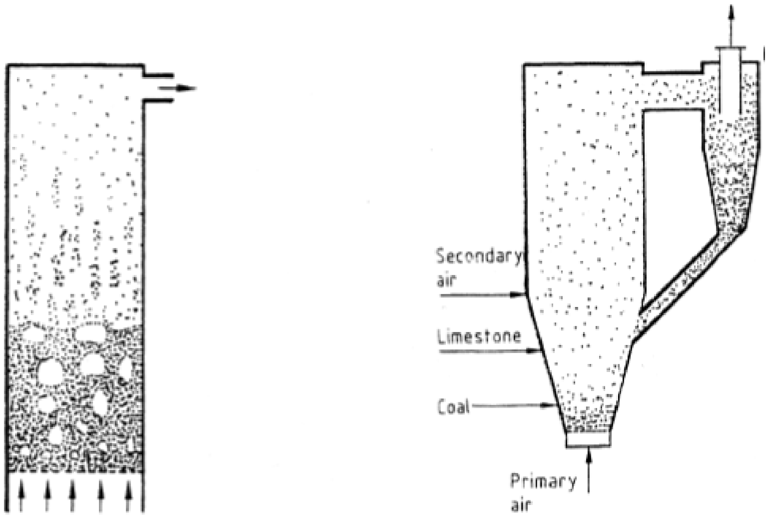


Fig. 12 Two types of fluidized bed reactors: left-bubbling bed, right: circulating bed [37]

2.6.3 Entrained bed gasifier

As the gas velocity increases after fluidization mode, pressure drop starts to decrease, because some solid particles present in dense phase of the fluidized bed are entrained. [10] Drastic drop is observed when dense phase disappears and particles transport mode transforms into pneumatic transport when particles are carried away from the reactor. [41] Feedstock, oxidant, and steam are fed co-currently. [42] These types of gasifiers operate at high temperatures in order to convert fuels with as much efficiency as possible (around 98-99,5%). This is due to the residence time of feedstock at the level of few seconds. [42,43] Also to obtain high efficiency some pre-treatment processes should be applied to the feedstock. That means solid fuels should be grounded to the small sizes. [44] Then it is pneumatically transported to pressurized gas generator or fed as slurry fuel. [44] There is high feedstock conversion because of high operating temperature and pressure, and turbulent flow. [42] That makes entrained bed gasifiers application suitable for high power outputs. It should be taken into consideration, that high temperatures and pressures shorten the lifespan of the reactor. [42] Also, because of the high temperatures significant amount of ash is converted into vitreous (inert) slag. [41] Due to bad slagging characteristics, the fuel should be blended with other components or to add fluxes in order to improve it. [42] This kind of gasifier allows obtaining very clean, tar-free syngas because tars and any other liquids occurring in gasifier during pyrolysis process are converted to hydrogen, carbon monoxide and some amounts of light, gaseous hydrocarbons. [42] Feedstock may be introduced as a dry fuel or slurry. [42] Although, feed in form of slurry is easier in operation, because it introduces water into the system it lowers final thermal efficiency of the gas generator. [42] In the case of entrained flow gasifiers pure oxygen is mostly applied as a gasifying agent to avoid dilution of product gas with nitrogen. [44] There are two operating modes of this type gasifiers: slagging and non-slagging. [44,45] In slagging mode operation is carried out at a higher temperature than ash melting point. That causes slag flow down along the gasifier’s walls. It solidifies partially and thanks to that there is to the certain point corrosion of walls prevention. In non-slagging mode, temperature is below ash melting point. That keeps the reactor's walls free of slag. It is suitable for low ash containing fuels. [44] When it comes to entrained bed gasification technology of biomass it is still under development, while for coal and pet coke it has already been well-researched [44]

Some entrained bed gasification technology characteristics [42]:

- ✓ Good, more uniform temperature distribution throughout reactor;
- ✓ Large gasifying agent demand
- ✓ Short feedstock's residence time
- ✓ High carbon conversion
- ✓ Low cold gas efficiency
- ✓ High level of sensible heat in produced gas
- ✓ Need for heat recovery in order to increase efficiency of the process
- ✓ The least polluting type of gasification technology: tar-free syngas, consisting mostly of H_2, CO and CO_2; ash in the form of inert vitreous slag, easier to remove

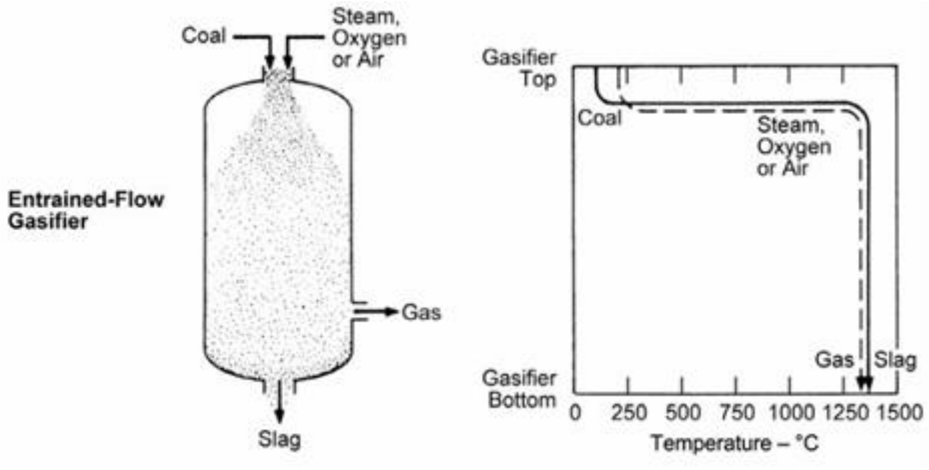
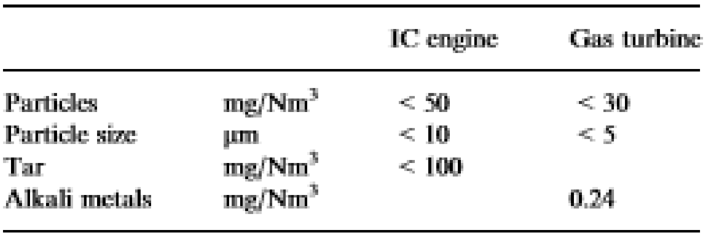


Fig. 13 Entrained flow bed gasifier and components' temperatures profile within reactor [42]

2.7 Flue gas cleaning operation unit

Depending on the produced gas appliance target, there is a need for the different level of cleaning process application. When syngas is subjected to direct combustion in order to produce heat then cleaning of the generated flue gas along with gas tars is not necessarily given the priority. [46] On the contrary to the heat production, as far as electricity generation is concerned, produced gas has to be highly efficiently cleaned in order to provide internal combustion engine's proper operation. Usually, the efficiency required is set around 90% in case of engine application. [47] Moving bed reactors are usually subjected to internal combustion engine's application for power generation. It has been examined that significant amounts of tar are produced when co-current fixed bed gasifiers are used. Small gasifiers, using air as gasifying agent and dry wood chips as a feedstock reactors generate particles along with produced gas in the range of 50-500 mg/Nm^3 and tars in the range of 50-1000 mg/Nm^3. [46] Thus, their application implies additional cost allocated to produced gas cleaning unit.

There are different solutions for purifying the generated gas giving various efficiencies. Their application depends mostly on generated power capacity and cleaning efficiency requirements. There can be distinguished two divisions of tars removal systems based on operating conditions: wet and dry produced gas cleaning systems. [47] Methods of flue gas cleaning after gasification may fall into two categories: primary and secondary; this means that they are carried-out inside the reactor and as downstream processes respectively. [46]



		IC engine	Gas turbine
Particles	mg/Nm^3	< 50	< 30
Particle size	µm	< 10	< 5
Tar	mg/Nm^3	< 100	
Alkali metals	mg/Nm^3		0.24

Fig. 14 Requirements for gas quality [46]

Secondary methods are reported to be efficient in terms of tars removal, but usually they imply high capital costs and in some cases, may occur not to be economically feasible [46]. They fall into the following categories [46]:

- Tar removal by thermal or catalytic cracking
- Mechanical solutions like fabric filters, rotating particle separators (RPS), scrubbers, electrostatic filters etc.

Secondary methods may be divided into two subcategories:

- Wet technologies
- Dry technologies

Wet methods include cooling/scrubbing venturi towers were heavy tars condense. [48] There efficiencies range from 51% up to 91%. [48] Before the produced gas reaches the venturi scrubber it is diluted by recycled gas at a ratio ca. 20:1, so that at the inlet of the scrubber tar content decreases significantly. [48] Another wet method of produced gas cleaning is the application of the granular filter that may be used for cold and hot gas purification. Usually, silica or alumina sand are used with static or mobile configurations. [48] In hot filtration application, in which particles are removed above 500°C, while tars remain in the gaseous phase. In cold filtration application particulates and condensed tars are removed by adhesing to the sandy bed. Another method is the application of wet electrostatic precipitators, since the dry mode of electrostatic precipitation should not be used in case of tars removal, because they may gather on electrodes ipso facto inhibiting the particles elimination from flue gases. [48] Efficiency of wet ESPs application are reported by [48] as ranging from 0% to 60%.

Dry technologies, in turn, include usage of fabric filters, usually covered with ceramic fibers. It is well known for removing dust from produced gas stream during incineration and their application in the case of gasification has been not well established yet. The efficiency of particle removal varies between 99,95-99,99% [49], however, for tars, it ranks at ca. 70% in gasification [45] After fabric filters activated carbon adsorption may be applied. Granules of charcoal or activated carbon are used in the form of fixed bed through which producer gas passes [48]. Their load varies between 20 wt.%-80 wt.% [46] another possibility may be so called sand filters. Before entering sand filter, produced gas has to be quenched with water. [46] After filtering gas exits sand bed with temperature in the range of 5-25°C.

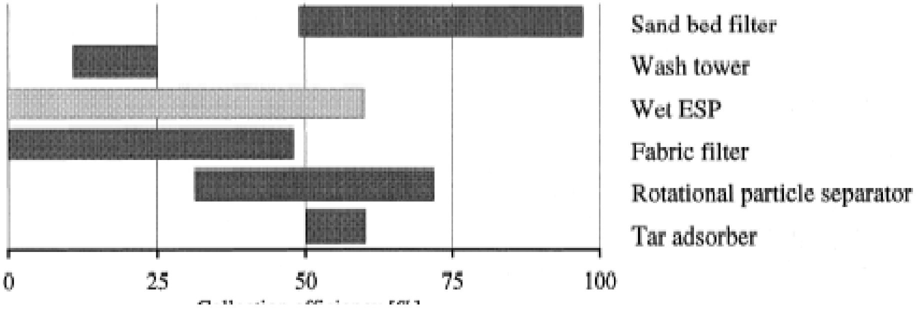


Fig. 15 Different reduction levels of particles and tars in various flue gas cleaning systems [46]

2.8 Routes of syngas application

In the past, main driver for gasification application was the production of heat and electricity when exploitation of fossil fuels was limited. That lack on the market due to a crisis or second world war was a driven force for seeking other than coal incineration solutions. Gasification systems could also be scaled down to generate motion power in vehicles.

Bundesarchiv, Bild 183-V00670A
Foto: o.Ang. | 1946

Fig. 16 Car powered with gas generator [50]

To produce electricity gasification plants are equipped with internal combustion engines or gas turbines powered by producer gas. Before combusting gas in one of these devices it must be cleaned up to provide its proper operation. For big scale electricity through gasification process is produced in IGCC systems (Integrated Gasification Combined Cycles). It is simply a combination of gasification and regular power generation units. It has been using gas turbines where syngas is combusted producing heat. Excess of heat produced while gasification occurred or combusting heat in a gas turbine is recovered. It is then subjected to steam production that at the end drives a steam turbine to extend electricity generation. [38]

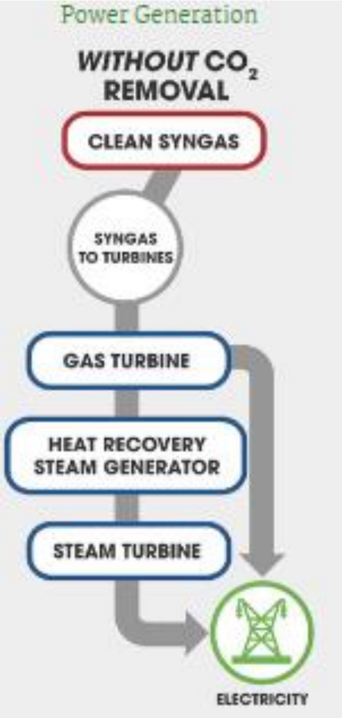


Fig. 17 Scheme of power generation without CO_2 removal in IGCC system [38]

Because power generation processes imply some energy losses, to reduce them CHP units have been implemented. That means the heat produced at some stages during the process was recovered and produced steam was used as a heat carrier.

Although gasification may be mainly considered as heat and electricity generation process, however, it finds many other applications as well. A well-known syngas application is so-called Fischer-Tropsch reaction. This method of syncrude production was discovered and developed by two German researchers Franz Fischer and Hans Tropsch in 1920's. The main principle includes conversion of carbon monoxide and hydrogen into hydrocarbons with the presence of catalysts. It has been examined as a process of synthetic fuels production. The process goes in general according to the following equation:

$$(2n+1)\, H_2 + n\, CO \rightarrow C_n H_{(2n+2)} + n\, H_2O \text{ , where n is an integer} \qquad (2)$$

Products distribution occurs according to Schultz-Flory distribution formula. [42] Although the desired products are higher molecular hydrocarbons, methane appears as a by-product. Some amounts of oxygenates may form too. [42] What products are obtained depends on operation conditions, such as temperature and catalyst. When it comes to the catalysts, transition metals are used such as iron, cobalt, nickel, and ruthenium. [42] Fischer-Tropsch provides a substitute to regular crude. It brings some advantages over it. The main one is becoming less dependent on oil resource, which is a huge pain relief in some cases. The second thing is during synthesis of syncrude via Fischer-Tropsch process, it contains mainly higher paraffin without resins and asphaltenes like in the case of fossil crude. It makes it less harmful to the environment and provides better properties. Below, in the graph, are presented possible routes of syngas application.

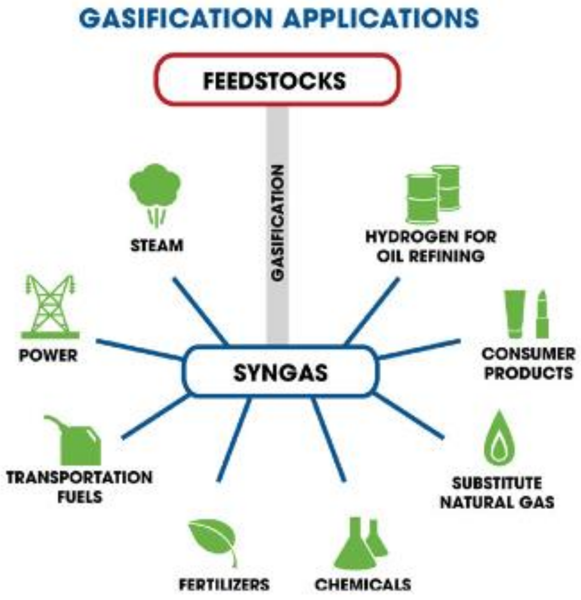


Fig. 18 Possible routes of syngas application [38]

2. Motivation and scope of the thesis

This thesis is written to obtain the master degree of Clean Fossil and Alternative Fuels Energy Program provided by InnoEnergy. The main objective of any action taken by InnoEnergy is to contribute to the fight against global warming problem. Aiming at sustainable energy systems development and the overall world, InnoEnergy company provides to the young people opportunity of gaining proper knowledge to change current trends in the energy world, spread the custom among people to live sustainable live, and become aware of possible world's energy forecasts if nothing changes. It gives the opportunity to become familiar with the best quality, innovative solutions. It brings the path of gaining the knowledge through experience and co-creations with other students. While searching for thesis opportunity it was taken under consideration to work on a project which is in line with personal and InnoEnergy program targets.

Biomass is appearing as an interesting energy source due to its abundant availability, the depletion of fossil fuels sources and the fact that it is carbon neutral, overall not contributing to the increase in carbon dioxide concentration in the atmosphere. It may be utilized locally, what brings opportunities to areas not being supplied with regular fuels. In fact, it is not the only reason it becomes so popular among energy producers. Biomass contributes to the reduction of greenhouse gases emissions. Although, while being burned it produces some streams of CO_2, it is neutral feedstock, since it absorbs CO_2 to grow. Due to CO_2 taxes and some CO_2 emissions regulations that had been implemented, biomass has become a resource, that may help overcome that problem. Some countries decide to apply biomass as a feedstock in energy production to become more independent from oil and other fuels import or it occurs to be more economically feasible to export some natural sources instead of burning it. It is also good and useful solutions for some agricultural and forestry waste utilization.

The motivation to study the kinetics of wooden chips sample gasification, provided by Institute of Coal Chemical Processing in Zabrze, is to examine its rate of reaction, both in terms of thermal decomposition under pyrolysis conditions and under oxidation conditions. Knowing how fast the feedstock decomposes (with what rate) it allows predicting what the expected yields of gasification products are. It is hard to figure out exact results of kinetic parameters.

3. Research methodology

3.1 Review

To study the thermochemical conversion of sample, thermogravimetric analysis, and differential scanning calorimetry (TGA-DSC) method was used. TGA method gives information about the mass evolution (gain or loss) in time or temperature, and its rate under controlled conditions and atmosphere. [51] This analysis is used to study the thermal and oxidative stability of samples. Through it can be obtained the information of compositional properties. It gives valuable knowledge of polymeric materials behavior under different thermal conditions. The technique is useful when it is subjected to obtain:

- Measurement of materials composition when multi-component or blend
- Thermal and oxidative stability
- Product's lifetime estimation
- Kinetics of decomposition of polymeric material
- Influence of different types of atmospheres applied

Differential scanning calorimetry, in turn, measures heat effects involved with material's transition in time or temperature. It is measured based on heat evolved or absorbed during experiments with respect to the temperature difference between studied material and the reference material. [52] There are two modes DSC technique may be carried out: heat flux and power-compensated DSC. In the first mode (the one applied in research for this thesis) there are two pans: one with examined material and the second one with reference material (an empty pan). Pans are placed on thermoelectric disks in a furnace. The furnace heats the sample with linear heating rate. Heat is transferred to the pans through the thermoelectric disk. [52] Because sample has its own heat capacity, there will be noticed temperature difference between the sample and empty pan. Heat flow is measured by means of the thermal equivalent of Ohm's law:

$$Q=(Ts-Tr)/R \tag{3}$$

Ts stands for sample's temperature, Tr is reference material temperature and R is the resistance of thermoelectric disk

3.2 Sample

The sample that has been examined was alder wood chips provided by Institute of Coal Chemical Processing. Thanks to kindness and courtesy of the Institute, ultimate and proximate analysis of fuel was done and provided for the research's sake. Below some results of ultimate and proximate analysis are given in the form of table

Tab: 6 Ultimate and proximate analysis of the sample.

parameter	sign	unit	the value of the parameter	uncertainty (+/=)
proximate (analytical state and total moisture content)				
total moisture	W_{tr}	%	11,7	1,2
moisture	W_a	%	8,9	0,1
volatile	A_a	%	76,66	0,43
fixed carbon	C_a	%	11,14	-
ash	A_a	%	0,5	0,2
ultimate analysis (analytical state)				
total carbon	Ct_a	%	47,6	0,7
total hydrogen	Ht_a	%	5,29	0,32
nitrogen	N_a	%	0,15	0,16
total sulfur	St_a	%	0,04	0,03
oxygen	O_a	%	46,837	-
chlorine	Cl_a	%	0,08	0,02
fluorine	F_a	%	0,003	-
heating values (analytical state)				
HHV	Qs_a	J/g	18536	148
LHV	Qi_a	J/g	17164	152

When proximate analysis is taken into consideration, it can be noticed, that the material mostly consists of volatile matter giving only 11,14 wt.% of fixed carbon, while ash was accounted for 0.5 wt.%

When it comes to ultimate analysis, it can be concluded, that two major species of given material are carbon and oxygen, on mass basis in total giving roughly 95%. The other species are hydrogen; roughly 5 wt.% in weight, nitrogen and sulfur, plus chlorine and fluorine.

Heating values were also examined. According to experimental data on table 5, studied sample has Higher Heating Value at the level of 18536 J/g and Lower Heating Value being accounted for 17164 J/g.

3.3 Sample preparation

Before the study was carried out, the sample had been grounded in one's of Institute of Coal Chemical Processing laboratories. It had to be done to make a sample, which originally was in the form of wooden chips, to be homogenized and fit the crucible that was used in the TG/DSC experiments.

3.4 Equipment

The experiment has been performed in TA Instruments SDT 2960 Simultaneous DSC-TGA device. It includes a furnace, that can be heated up to 1500°C, two thermoelectric disks measuring heat flow, balance to measure sample's weight evolution with time or temperature. The DSC-TGA instrument is linked with wires of nitrogen and air gases flow to provide proper atmosphere. Digital flow meters control the gases flow. Cooling is managed with instrument air directed inside the furnace. The analyzer is connected to a computer where TA Instruments software is installed. Thanks to that software, experiment's condition could be set and results displayed in the form of graphs. Both, heat flows and weight evolution of the sample are measured in a controlled atmosphere simultaneously thanks to that equipment. Below the picture of TA Instruments SDT 2960 Simultaneous DSC-TGA is presented.

Fig. 19 TA Instruments SDT 2960 Simultaneous DSC-TGA

3.5 Procedure

At the very beginning of each set of experiments, a blank probe was carried out. That means, both crucibles were empty and placed in the TGA holder. In this condition, the experiment run in the specific atmosphere (either under air or nitrogen condition). Every experiment's data was then corrected with blank probe results.

In each set of experiments first the apparatus was tared with both empty pans to get the mass difference to zero value. After it was tared roughly 10 mg of sample were weighted and placed in an alumina crucible.

There were different sets of experiments carried out. There will be presented below:

- Pyrolysis and then combustion of obtained char (carried out up to 200°C, 300°C, 400°C)
- Pyrolysis with heating rates of 10°C/min, 20°C/min or 50°C/min
- Partial oxidation with heating rates of 10°C/min, 20°C/min or 50°C/min
- Combustion with heating rates of 10°C/min, 20°C/min or 50°C/min

The flow of gases was set to be in total around 50 ml/min. In the case of pyrolysis, it was a flow of nitrogen, in the case of combustion it was a flow of air and in the case of partial oxidation a mixture of both gases in total giving flow at the level of 50 ml/min.

The experiments were performed with both temperature conditions: non-isothermal and isothermal, since when temperature which was desired was reached it was carried on for some time at constant temperature.

3.5.1 Pyrolysis of the fuel and char combustion

There were three experiments with pyrolysis and further combustion of char performed. It was pyrolysis up to 200°C and then combustion up to 800°C. The same with pyrolysis up to 300°C. Programming of TA Instrument was as follow:

- Equilibrated at 40°C
- Isothermal for 10 min.
- Ramp 10°C/min up to 200°C (300°C, 400°C)
- Isothermal for 60 min.
- Air cooling down to 40°C
- Equilibrated at 40°C
- Isothermal for 10 min.
- Ramp 10°C/min up to 800°C
- Isothermal for 30 minutes
- Air cooling down to 40°C

3.5.2 Pyrolysis up to 800°C

Pyrolysis in this mode was performed with three different heating rates: 10°C/min, 20°C/min or 50°C/min. The inert gas used in the experiment was nitrogen. After experiment residue of char was noted. Programming for this experiment was as follow:

- Equilibrated at 40°C
- Isothermal for 10 min.
- Ramp at the desired heating rate up to 800°C
- Isothermal 10 min.
- Air cooling down to 40°C

3.5.3 Partial oxidation up to 800°C

Partial oxidation was specified by the amount of oxygen in gas stream mixture in percentage. There were performed experiments with 18%; 15%; 10%; 5%; 2,5% of oxygen in a gas stream of air and nitrogen. They were carried out with different heating rates as well (10°C/min, 20°C/min, 50°C/min). Programming for this experiments was as follow:

- Equilibrated at 40°C
- Isothermal for 10 min.
- Ramp at the desired heating rate up to 800°C
- Isothermal 10 min.

- Air cooling down to 40°C

3.5.4 Combustion

Combustion in this mode was also performed with three different heating rates: 10°C/min, 20°C/min and 50°C/min. The oxidative gas used in the experiment was oxygen. Programming for this experiment was as follow:

- Equilibrated at 40°C
- Isothermal for 10 min.
- Ramp at the desired heating rate up to 800°C
- Isothermal 10 min.
- Air cooling down to 40°C

3.6 Calculations

In this chapter techniques of relevance for this thesis, calculations will be presented. Calculations regarding kinetics and thermal analysis were carried out in Excel software. After this part of thesis, simulation of biomass gasification with application of Gibbs reactor has been carried out in Chemcad software.

3.6.1 Sample's conversion

It has been pointed out in [54] that wood/biomass char's reactivity is measured as a function of conversion rate per remaining mass. When applied degree of conversion, formula giving char's reactivity is as follow:

$$R = \frac{1}{1-X} \times \frac{\partial X}{\partial t} \tag{4}$$

where X is defined as:

$$X = \frac{m0 - m_t}{m0 - m\infty} \tag{5}$$

Symbol of m0 stands for initial mass of sample, m∞ stands for its final mass and m_t represents mass of sample at the given time.

3.6.2 Curve fitting

To study kinetic parameters of given feedstock method of curve fitting has been used. There were 3 pseudo components distinguished: water, hemicellulose (cellulose) and lignin. Before the patterns of this part of calculations will be presented, Arrhenius equation for the rate of component's transition changes with temperature should be shown. The Arrhenius equation is presented below:

$$k(T) = A \times e^{\frac{-Ea}{RT}} \tag{6}$$

A stands for frequency factor [1/min], Ea is so called activation energy [cal/mol], R is gas constant [cal/mol*K] and T stands for temperature [K].

The biomass was considered to be constituted by three different pseudo-components, which can tentatively be associated with water, cellulose and hemicellulose, and lignin. The kinetic parameters corresponding to the thermochemical conversion of these three components were estimated separately, as follow:

1. As first, masses of three pseudo components were estimated according to TGA graphs of mass at given time vs. time or temperature
2. The rates of components' decomposition were estimated using Arrhenius equation written using a reference temperature, as in equation 7:

$$\frac{dmi}{dt} = ri = kref(T) \times e^{\frac{-Ea}{R} \times \left(\frac{1}{Tt} - \frac{1}{Tref}\right)} \times mi_t \tag{7}$$

   Which was obtained by dividing origin Arrhenius equation by Arrhenius equation for component's decomposition at reference temperature (assumed reference temperature was T_{ref}=298K).

   This was done to make the fitting procedure easier by reducing the correlation between the pre-exponential factor and the activation energy.

$$kref(T) = A \times e^{\frac{-Ea}{R*Tref}} \tag{8}$$

3. The change in mass was computed by integrating equation 7 using the Euler's method.

$$mi_{\Delta t} = mi_t + \frac{dmi}{dt} \times \Delta t \tag{9}$$

   Symbol of m_{it} is a mass of sample at given time and Δt time step equals to 0,001.

4. The fourth step referred to calculating total modeled weight, which was performed as follow:

$$m_{(water)}+m_{(hemicellulose+cellulose)}+m_{(lignin)}=m_{(total.modeled.weight)} \qquad (10)$$

5. The objective function for the fitting was calculated using the error arising from the difference between experimental material's weight and total modeled weight. The error was used as an objective function for Solver application to obtain the best fitting curve via changing values of k, m_i and Ea parameters for all pseudo components. The optimization was carried-out using a non-linear least square fitting method. [55]

$$Error = \sum_{j=1}^{N}(m(experimental) - m(total\ modeled\ weight))^2 \qquad (11)$$

where j=1,2,3….N is a total number of steps within the experiment.

6. Finaly, curve's fitting quality was estimated. To do so, the following formula was applied [54]:

$$Fit\ (\%) = 1 - \frac{\sigma}{\left[\left(\frac{dmi}{dt}\right)exp\right]max} \times 100\% \qquad (12)$$

Symbol of σ is standard deviation of error values

3.6.3 Modeling of kinetics for pyrolysis model

A kinetic model for pyrolysis mode is developed in this thesis using the curve fitting methodology described in sub-chapter 3.6.2. Kinetic parameters within this zone were modeled using formula (7).

3.6.4 Modeling of kinetics for combustion model

In the case of combustion mode, the influence of oxygen partial pressure had to be taken under consideration. Due to that equation (6) is changed by adding the partial pressure of oxygen part, as follow:

$$\frac{dmi}{dt} = ri = kref(T)_c \times mi_t \times Po_2 \qquad (13)$$

Partial pressure is set at the level of PO_2=0,2 atm.

3.6.5 Modelling of kinetics for partial oxidation mode

As far as partial oxidation is concerned, the influence of oxygen partial pressure should be taken under consideration. In general, kinetic parameters of material's partial oxidation were modeled with equation (13). To minimize error, in some cases of low oxygen partial pressure, the kinetics were modeled with following formula:

$$\frac{dmi}{dt} = ri = kref(T)_c \times mi_t \times Po_2 + kref(T)_p \times mi_t \tag{14}$$

Symbol of kref(T)p stands for rate constant obtained in pyrolysis mode.

Partial oxidation is in these cases treated as a combination of pyrolysis and combustion modes, where partial pressure of oxygen used in the model was equal to the one set in the experiment. As mentioned before used partial pressures of oxygen were 18%, 15%, 10%, 5%, 2,5%.

3.7 Thermal Analysis of experiments

Thermal analysis was carried out to estimate what kind of reactions may occur within experiments and consequently what may be the products. The pattern of estimation is as follow:

1. Identifying exo- and endothermal peaks (at what time or temperature they occur)
2. The amount of heat evolved at given time was calculated by dividing heat flow (mW) by derivative weight (mg/min)
3. The heat at peak point was taken as one to compare with heats of assumed reactions

Sucrose was chosen as representative of cellulosic components, because when compared reactions occurring with sucrose to the reactions running with xylose and glucose, it seemed heats of sucrose reactions are the most compatible with heats evolved during experiments. Next step was to estimate how far the oxidation/decomposition goes, by comparison to the closest heats of certain reactions to the heat noted in the experiment.

3.8 Gasifier modeling

Gasification modeling may be performed using different types of models. The main ones are kinetic rate models and thermodynamic equilibrium models [55, 56]. Modeling may be also carried out by using CFD model, Aspen software or Artificial Neural Networks. [55,56]

Modeling is performed based on a design provided by Institute for Chemical Processing of Coal (Poland). The gasifier is an updraft moving bed reactor that has 400 mm of internal diameter and 900 mm of height. [38] The thermal power that may be obtained is around 60 kW_t. In the design, there are three air inlets: at the top, to prevent upcoming gases from becoming stagnant, in oxidation zone in the middle and at the bottom to provide additional combustion of remaining char. The reactor is subjected to produce syngas for IC engines applications. Electricity generation through gasification requires highly efficient flue gas cleaning system to maintain proper operation of engines. The innovative solution that has been implemented by the authors of its design is the application of vertical tube to collect hot gases from reduction zone. This arrangement allows the producion of cleaner syngas, since tars produced in pyrolysis zone perform thermal cracking when they flow through hot, reduction zone.

Tab: 7 Comparison of gas composition from different biomass gasifiers and GazEla gas generator. [57]

Component	Reactor		
	Counter-current	Co-current	GazEla
CO, %	15-20	10-22	19,8
H_2, %	10-14	15-21	5,9
CO_2, %	8-10	11-13	7,5
CH_4, %	2-3	1-5	1,7
H_2O, %	10-20	10-20	20,8
N_2, %	the rest	the rest	the rest
Dust in gas phase, mg/m^3	100-3000	20-8000	600
Tars in gas, mg/m^3	10^4-15*10^4	10-6000	12*10^3

As it can be noticed GazEla gas generator can produce fewer tars than regular updraft fixed bed gasifier. On the other hand, downdraft gasifiers are still in favor when subjected to electricity generation, through their ability to produce the lowest content of tars in the syngas.

When performing gasifier mathematical modeling, reactions were assumed to run according certain patterns based on thermal analysis resulting in products predictions and ultimate analysis of material.

It also has to be assumed as the authors of [59] did, that the char is presented as graphitic carbon, the process of gasification is isobaric.

Based on sample's ultimate analysis the formula of modeled biomass at as received state basis could be obtained. Despite fact, there was a content of sulfur, nitrogen and other species, they were omitted to simplify representative formula. So, the basic biomass pattern was as follow: CxHyOz, where x, y and z stands for molar ratio of these three species within sample. Assuming to have 100 g of sample we would obtain roughly 47 g of carbon, 47 g of oxygen and 6 g of hydrogen. These masses divided by molar masses of respective species give their moles being represented by x, y and z respectively in the formula.

Having moles of each biomass species, the molar mass of sample in kg/kmol could be calculated as follow:

$$M_{biomass} = x * M_C + y * M_H + z * M_O \tag{15}$$

Next step of the model was performing the simulation of the process. This was carried out by means of Chemcad CC-STEADY STATE software. To present the principle of operation of Chemcad in this thesis, the definition of it given by Chemstations Inc. will be provided. "It is chemical process simulation software that includes libraries of chemical components, thermodynamic methods, and unit operations to allow steady-state simulation of continuous chemical process from lab scale to full scale." [60] Basically, it allows us to simulate chemical processes providing the user with mass and energy balance, at the same time giving information about economic valuation. It provides the users with 5 types of reactors: stoichiometric, kinetic, Gibbs, equilibrium and batch reactor. Each one has different principles of calculations to be performed, that correspond to the simulation procedure. Stoichiometric reactor (REAC) performs simulation based on one reaction with specified stoichiometric coefficients of the reaction, key component and conversion rate. There are three thermal modes with which simulation may run: adiabatic, where there is no heat flow between reactor and the external environment, isothermal (constant temperature mode) and with specified heat duty.

When it comes to kinetic reactor model (KREA), it allows to design or rate two types of reactors: plug flow reactor (PFR) and continuous stirred tank reactor (CSTR). They can be used in case of liquid and/or vapor phase of the reaction. There is possible mixed phase reaction simulation, however it takes place only in one phase. Simulation may run with up to 300 simultaneous reactions with two modes. One of them is Design mode, where conversion rate of key component must be specified and software performs calculation of reactor's required volume. The second one, the Rating mode work inversely, that means the user must specify the volume and software perform calculation of outlet composition and conditions.

In both cases, CSTR and PFR model, there are made assumptions. The CSTR model makes the following ones:

- Perfect mixing
- Uniform temperature, pressure, and composition throughout the reactor
- Reaction's rate is constant

It may operate in one of three thermal modes:

- Heat duty calculated by software when reactor's temperature specified
- Reactor's temperature calculated by software when adiabatic mode
- Reactor's temperature calculated when heat duty specified

The PFR model, in turn, makes the following assumptions:

- There is no axial mixing or axial heat transfer occurs
- There is equal duration of transit times for all fluid elements through the reactor, from inlet to outlet

It may operate in one of five thermal modes:

- Isothermal
- Adiabatic
- With specified utility conditions
- With specified temperature profile
- With specified heat duty

Plug flow may run in co-current or counter-current flow mode. In case of co-current flow, the user must specify inlet temperature to get outlet utility stream conditions.

In addition, there must be specified two sets of data: general definition of reactor and stoichiometry, and rate data for each of reaction occurring in the process. There might be running up to 20 reactions simultaneously.

When it comes to the Gibbs reactor (GIBS), it is usually used to perform heat and material balance. Results, such as compositions, product rates and thermal conditions, are obtained through minimization of Gibbs free energy, considering an overall mass balance. All components in current simulation sheet are considered in the calculation, unless specified as inert. The simulation might be performed in liquid or vapor phase, or as mixed phase reactor. The process may run at constant temperature or at feed temperature. Temperature limits may be set and heat can be added or removed. If there is any user-specified component in the flowsheet, it must be specified with free energy of formation, molecular weight, and heat capacity. Additionally, if it is solid component, there must be heat of formation specified. This model is based on principal of the total Gibbs energy of the system being at its minimum value, at its chemical equilibrium. The reaction's species are taken in to consideration when performing simulation. Their distribution is established through mathematic technique to obtain system's minimum free energy.

In case of equilibrium reactor model (EREA), simulation with multiple reactions undergoes according to their defined conversion or equilibrium ratios. All the results obtained through equilibrium reactor, so product rates, compositions, thermal conditions are calculated by reactor equilibrium equation together with mass and energy balances. There is the following formula stated by Chemcad 6 Help and Reference [58]:

$$\ln(k_{eq}) = \ln\frac{(P_1)^{x_1}\cdot(P_2)^{x_2}\cdot\ldots\cdot(P_i)^{x}}{(R_1)^{y_1}\cdot(R_2)^{y_2}\cdot\ldots\cdot(R_j)^{y_j}} = A+\frac{B}{T}+C\ln(T)+DT+ET^2 \tag{16}$$

Respective components of the equation stand for partial pressure (if vapor) or mole fraction (if liquid) of particular product (P_i), the same is R_i, but regarding reactants. Whereas power coefficients, x_i and y_i are equal to stoichiometric coefficients of products (being positive) and reactants (negative, what place them in the denominator). A, B, C, D are coefficients for the equilibrium reaction equation and T stands for temperature (in K). There are three thermal modes in which simulation may run: isothermal, adiabatic or with specified heat duty. There might be running up to 20 simultaneous reactions. To run simulation with EREA reactor there must be specified two sets of data: general definition of the reactor and stoichiometry and equilibrium data for reactions taking place in the reactor. The equilibrium reactor operates at two phases, but reaction may only in one of them.

Batch reactor model (BREA) within Chemcad software environment is the most complex one. This unit simultaneously solves the mass balance involving up to two feed streams, the reaction rate and phase equilibrium conditions. Along with mass balance, the heat balance is solved, taking into consideration enthalpies of feeds, outlets, and holdup. Additionally, heat of reaction and heat transferred from/to jackets and coils agitator horsepower and heat losses or gains. Considering the reactor's geometry and phase equilibrium conditions pressure is calculated. To present the principle of its operation, it will be provided with figure being sort of summary of this model.

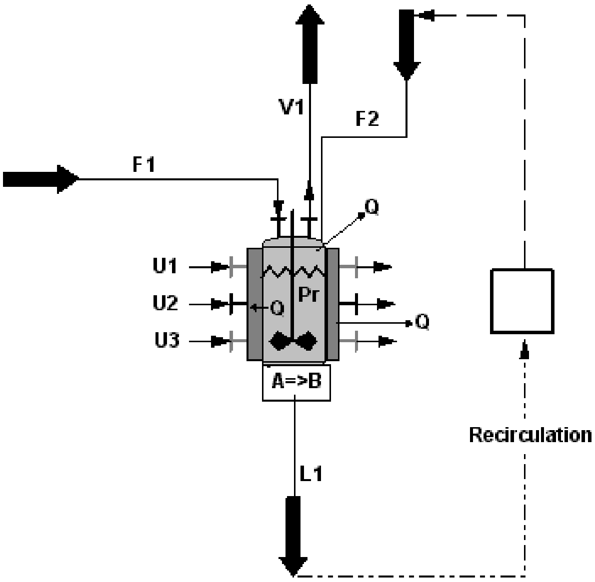


Fig. 20 Batch reactor model illustration in Chemcad 6 Help and Reference [60]

4. Results and discussion

In this chapter, results of experiments and modeling are presented. In the first part, the results of pyrolysis mode experiments with different upper temperatures are discussed along with an analysis of arising char's reactivity. Then, the modeling of the kinetics of different gasifier's zones is discussed to provide the whole description of sample's behavior when pyrolyzed, oxidized and partially oxidized. In the second part the simulation of an actual gasifier in Chemcad software is presented. The simulation was performed on gasifier, whose design had been provided by Institute of Coal Chemical Processing in Zabrze (Poland).

4.1 Biomass char reactivity

As it was mentioned before, there were three experiments of sample's pyrolysis followed by char combustion performed. It was noticed, that with higher temperature applied the higher conversion of sample is occurring. It has a simple explanation of breaking bonds more easily with higher energy inputs since activation energy of these species decomposition is reached faster.

Tab: 8 Results of sample's pyrolysis process

pyrolysis temperature [°C]	initial sample mass [mg]	mass converted [mg]	residue mass [mg]
200	8,91292	0,5278	8,38512
300	8,0253	3,45925	4,56605
400	9,72742	7,23947	2,48795

Ash [mg]	fixed carbon [mg]	Volatile residue [mg]
0,445646	0,986660244	6,952813756
0,401265	0,88840071	3,27638429
0,486371	1,076825394	0,924753606

Tab: 9 Results of generated char combustion process

Parameter	Combustion of char at 800°C after pyrolysis at:		
	200°C	**300°C**	**400°C**
initial sample mass	8,32565	4,43738	2,4501
mass converted [mg]	8,32565	4,43738	2,4501
residue mass [mg]	0	0	0

After performing this process, it could be noticed, that char combusts entirely. That gives the information what temperature may be applied to get complete char's combustion. No ash remaining may represent the fact, that because the material prior to experiments' performance had to be grounded, that could cause sedimentation of ashes (inorganic material heavier than organic material) in the bottom of the box/container. The char's reactivity results are as follow:

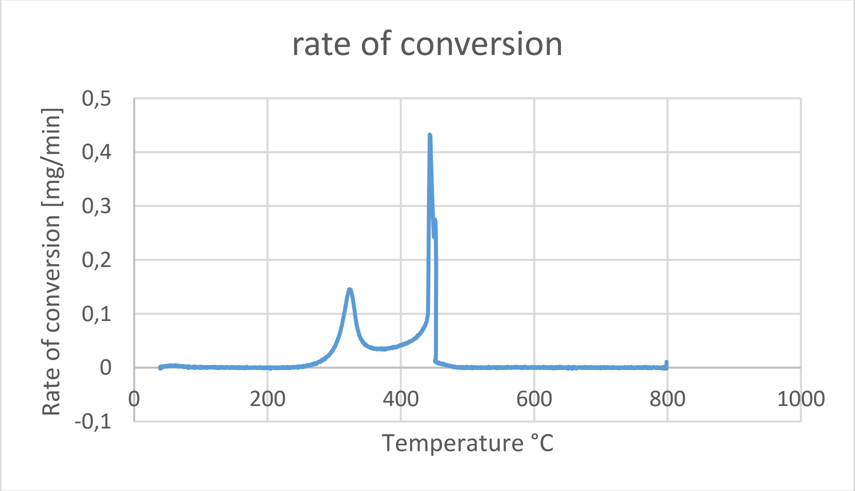


Fig. 21 Char's reactivity versus temperature for char obtained through pyrolysis at 300°C.

Graph placed above is so called burning profile of char. [61] Burning profile allow to obtain useful information about fuel's oxidative characteristic. Technique is used when unusual fuel is subjected to be evaluated, but there is no sufficient quantity of sample for full-scale test. [60] It may be applied, when not evaluated material is compared with well-known burning profiles of the same species of materials, that are predicted to behave similarly when combusted.

With increasing temperature of the process, there are observed changes on the Figure 21. On the graph, there can be noticed two peaks. Fuel, that have moisture, would present three peaks during the experiment, with first peak being at 100°C or below. [59] This one is associated with moisture loss. In case burning profile presented on Figure 21, there is no peak related to moisture loss, since it is char, so all water evaporated during former pyrolysis process.

After water evaporation, slightly negative change might be observed associated with mass gain. That mass gain occurs due to organic matter oxidation. [61]

The peaks have two characteristic temperatures: ignition temperature and peak temperature. Ignition temperature is associated with changes in burning profile after negative deflection from organic matter combustion to positive deflection. [61] Whereas, peak temperature is related to the maximum combustion rate and means the completion of event occurring in the whole process. [61].

First peak occurring presented on the Figure 21 can be associated with charring process, since char obtained through former pyrolysis might have some remaining volatile matter. Its ignition temperature and peak temperature are respectively 243°C and 322°C, with peak mass loss rate being 0,14 mg/min.

Second peak is associated with char's combustion showing ignition temperature being 376°C and peak temperature 443°C. Peak rate accounts for 0,43 mg/min.

4.2 Kinetic parameters

In this sub-chapter, kinetic modeling results are presented.

For graphic representation of curve fitting quality, graph of experimental mass and modelled mass evolution curves with time will be presented.

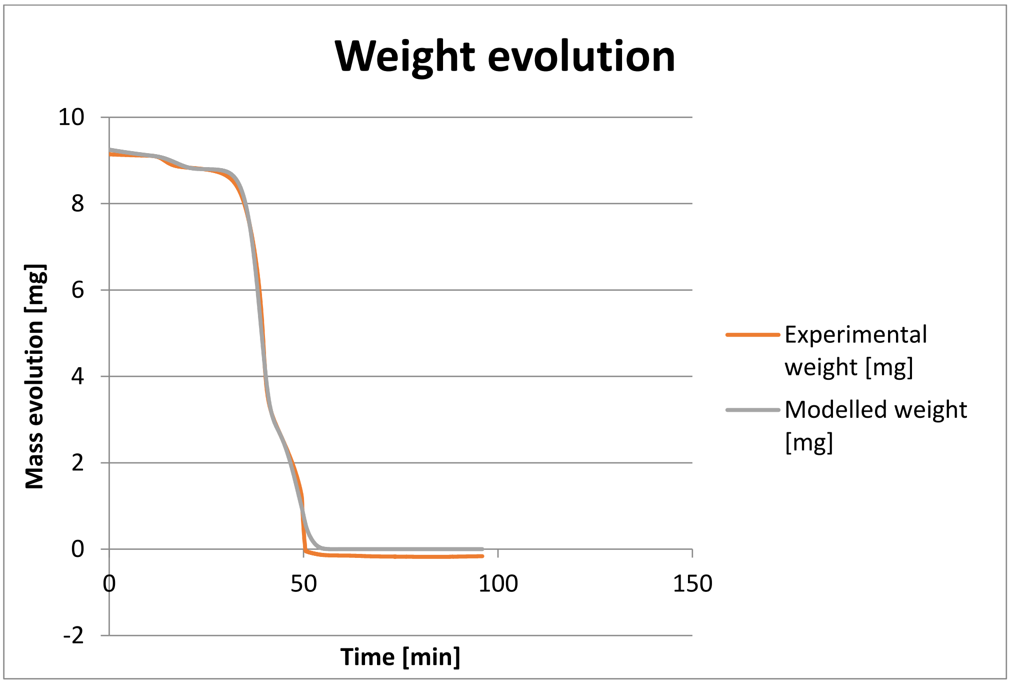


Fig. 22 Weight evolution of experimental mass of sample and modelled mass of sample for 20% of oxygen in the gasifying agent with heating rate 10°C/min

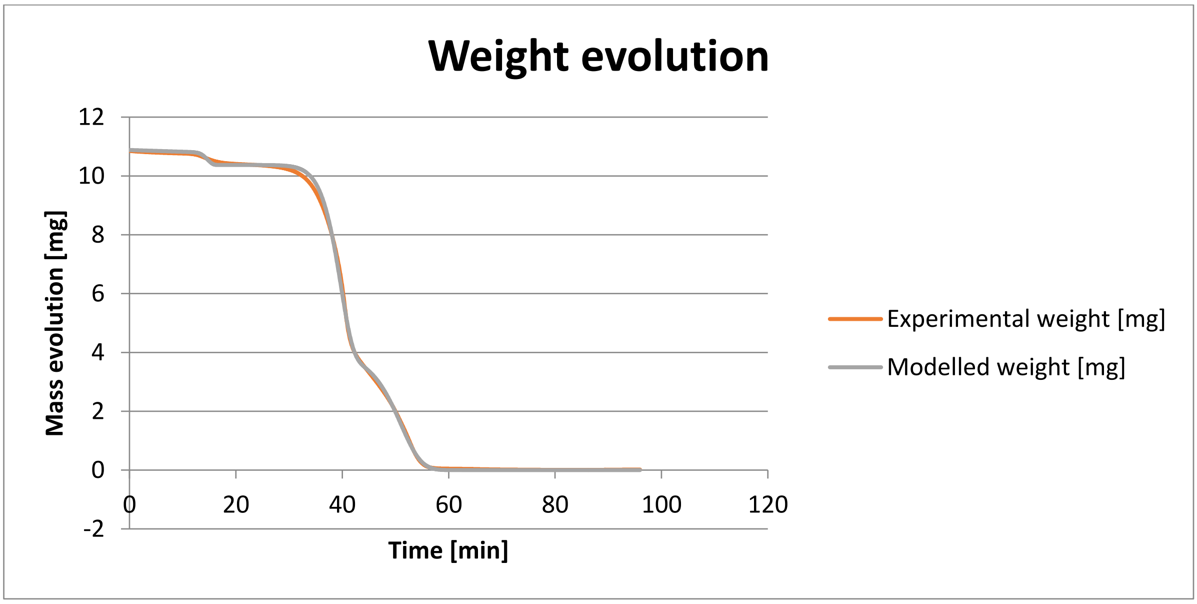


Fig. 23 Weight evolution of experimental mass of sample and modelled mass of sample for 10% of oxygen in the gasifying agent with heating rate 10°C/min

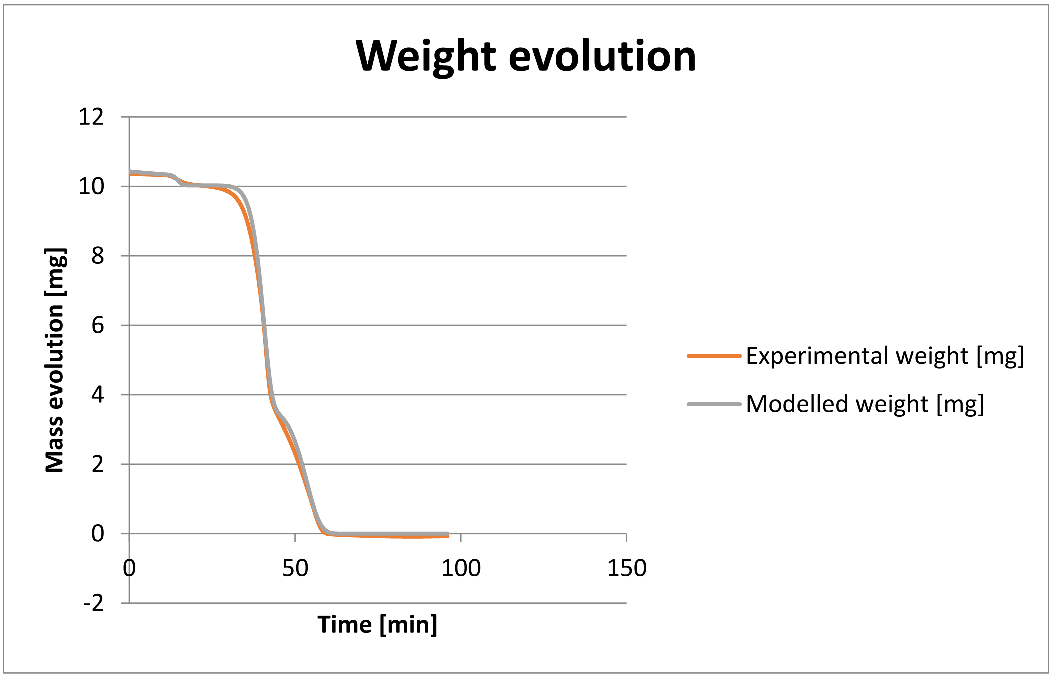


Fig. 24 Weight evolution of experimental mass of sample and modelled mass of sample for 5% of oxygen in the gasifying agent with heating rate 10°C/min

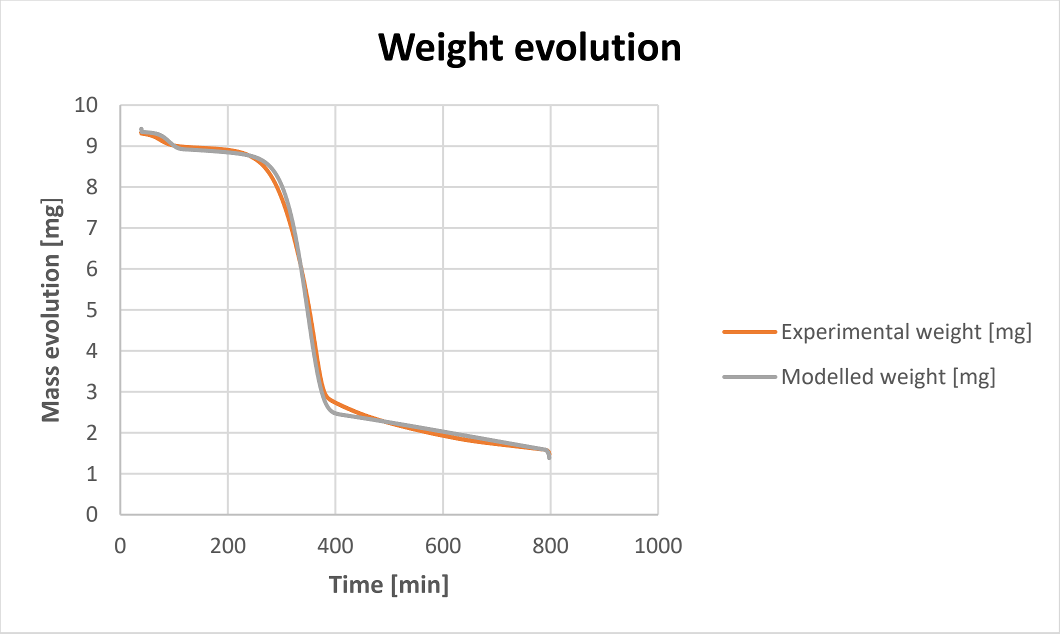


Fig. 25 Weight evolution of experimental mass of sample and modelled mass of sample for pyrolysis with heating rate 10°C/min

The graphs show good curve fitting quality, as in all cases the grey curve (modeled weight) coincides with orange one (experimental). The k and Ea kinetic parameters were fitted to the global equation with application of excel add-in, Solver, in the way it allowed to obtain the lowest possible error.

Thereafter, the results of curve fittings and obtained kinetic parameters are going to be presented in the form of tables.

Tab: 10 Rate constants at reference temperature kref [1/min] an activation energies Ea [cal/mol] for three pseudo components (moisture, hemicellulose and lignin) and different heating rates (°C/min):

water						
PO_2	**k [10°C/min]**	**Ea [10°C/min]**	**k [20°C/min]**	**Ea [20°C/min]**	**k [50°C/min]**	**Ea [50°C/min]**
20	0,016446	10063,2	0,016446	10063,2	1,33E-02	2,13E+04
18	0,016446	10063,2	0,016446	15000	1,49E-02	2,98E+04
15	0,01600	15550	0,016446	15000	2,73E-03	2,63E+04
10	0,016446	25551,07	0,016446	15500	5,41E-04	3,07E+04
5	0,016446	10063,2	0,016446	15900	1,15E-01	8,85E+03
2,5	0,026446	10063,2	0,096446	15550	1,55E-01	7,85E+03
0	0,001811	19100	0,021446	16900,2	3,15E-09	24790,07

hemicellulose						
PO_2	**k [10°C/min]**	**Ea [10°C/min]**	**k [20°C/min]**	**Ea [20°C/min]**	**k [50°C/min]**	**Ea [50°C/min]**
20	1,26E-10	25784,68	1,26E-09	25084,68	5,21E-09	24081,99
18	1,16E-10	25484,68	1,26E-10	28500	5,26E-11	29707,91
15	1,26E-10	25784,68	1,26E-10	28000	6,26E-11	29756,48
10	1,29E-10	28758,13	1,26E-10	28550	6,26E-11	29972,26
5	1,14E-10	25784,68	1,26E-10	29000	6,26E-11	30184,39
2,5	1,01E-10	25784,68	1,26E-10	29500	6,26E-11	30287,05
0	1,16E-10	28100	6,5E-10	23300,68	9,12E-11	25548,21

lignin						
PO_2	**k [10°C/min]**	**Ea [10°C/min]**	**k [20°C/min]**	**Ea [20°C/min]**	**k [50°C/min]**	**Ea [50°C/min]**
20	1,38E-11	24760,57	2,91E-10	23600	7,34E-10	22956,11
18	1,55E-11	23760,57	2,55E-10	24000	6,35E-10	23050,62
15	1,85E-11	23760,57	1,85E-11	25950	5,65E-10	23186,2
10	2,29E-11	25975,97	1,85E-11	26000	5,65E-10	22846,88
5	1,14E-11	23760,57	1,85E-11	26000	6,65E-10	22086,33
2,5	7,83E-12	23558,57	4,09E-11	25000	5,65E-10	21156,81
0	0,001	2200	0,000404	3890,23	0,012477	99,53944

From the tables placed above it may be observed, that for water and hemicellulose values of kinetic parameters increase with increasing heating rate. This may happen due to fitting sensitivity caused by relatively small amount of water as one of three pseudo-components. When it comes to lignin we can notice, that values of activation energy drops when heating rate changes from 20°C/min to 50°C/min. That may mean when performing decomposition of lignin, mostly exothermic reactions occur, such as dewatering.

It can be also noticed, that values of kinetic parameters change drastically for pyrolysis, which nature of reaction is different than under oxidizing conditions. The rate of reaction is higher for pyrolysis.

Kinetics for hemicellulose and lignin results are similar for each experiment with different oxygen partial pressure applied. However, from the results it may be deduced, that when sample is pyrolyzed lignin undergoes decomposition first, since its values of activation energy are much lower than for hemicellulose.

To prove graphical curve fitting quality representation, it was also calculated and presented in the form of graph placed below.

Tab: 11 Fitting quality and errors calculated for all heating rates and oxygen partial pressures

PO_2 [%]	10°C/min		20°C/min		50°C/min	
	Fit [%]	Error [(mg of residual)^2]	Fit [%]	Error [(mg of residual)^2]	Fit [%]	Error [(mg of residual)^2]
20	96,9	73,3276	98,64552	67,80067	99,4552	3,640641
18	98,68	58,76449	98,78344	55,38715	98,79063	23,33477
15	97,55	180,6397	98,30368	80,97339	99,26319	7,092643
10	99,01	19,25296	98,97088	24513,32	99,02959	13,18043
5	98,37	82,08632	98,32057	104,9969	98,25152	51,23487
2,5	95,63	50,07917	97,98353	85,47604	98,48757	32,49121
0	98,71	41,36753	98,39037	54,25696	98,03584	55,09937

Fitting quality averages are 97,8 %; 98,5 % and 98,8 % for 10°C/min, 20°C/min and 50°C/min.

It can be noticed, that the higher heating rate, the higher fitting quality. Overall, it can be deduced, that curve fitting quality is at proper level.

There were drawn graphs of rate constant versus applied partial pressures of oxygen during the experiments relation to show its independance. The results for three-pseudo components are presented below. The scales of rate constant axis were changed to logarithmic scale to provide more meaningful data. Reaction rate constant depends on reaction pattern according to which material runs. Due to that, they are expected to be independent on partial pressure of oxygen applied.

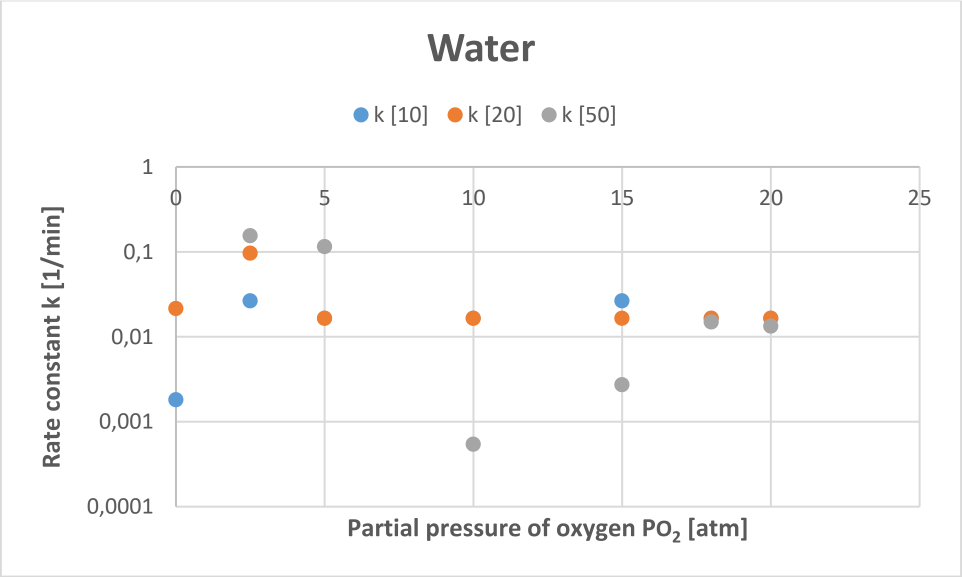


Fig. 26 Relation between modeled rate constant and applied partial pressure of oxygen for water

It is relevant to explain occurring changes of reaction constant in terms of water vaporization. This may be reasoned with small amount of water present in the material when compared to other material's pseudo-components. This causes the fittings being sensitive to changes.

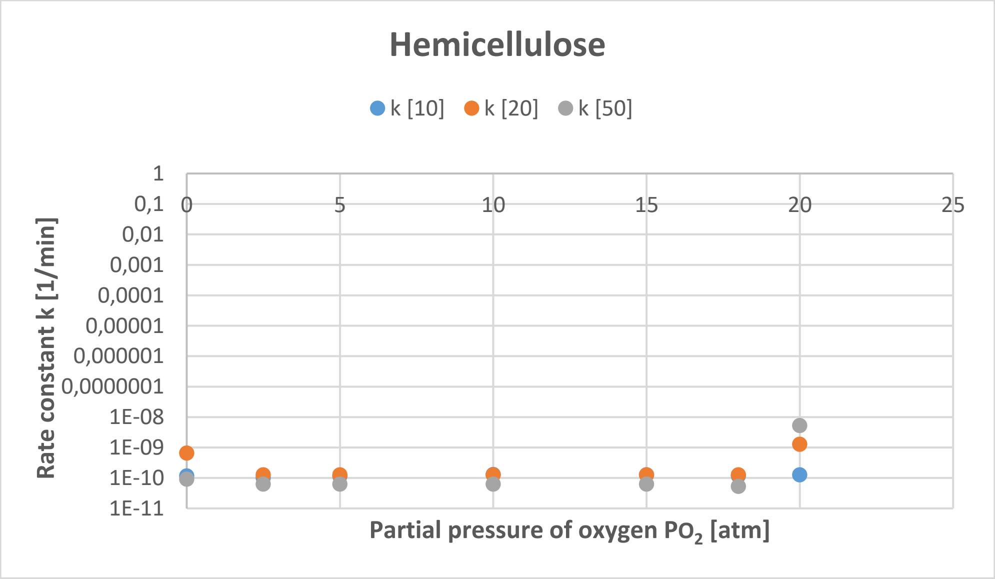


Fig. 27 Relation between modeled rate constant and applied partial pressure of oxygen for hemicellulose (cellulose)

When it comes to hemicellulosic component, it is to be noted, that reaction rate constants are stable and independent on partial pressure of oxygen applied.

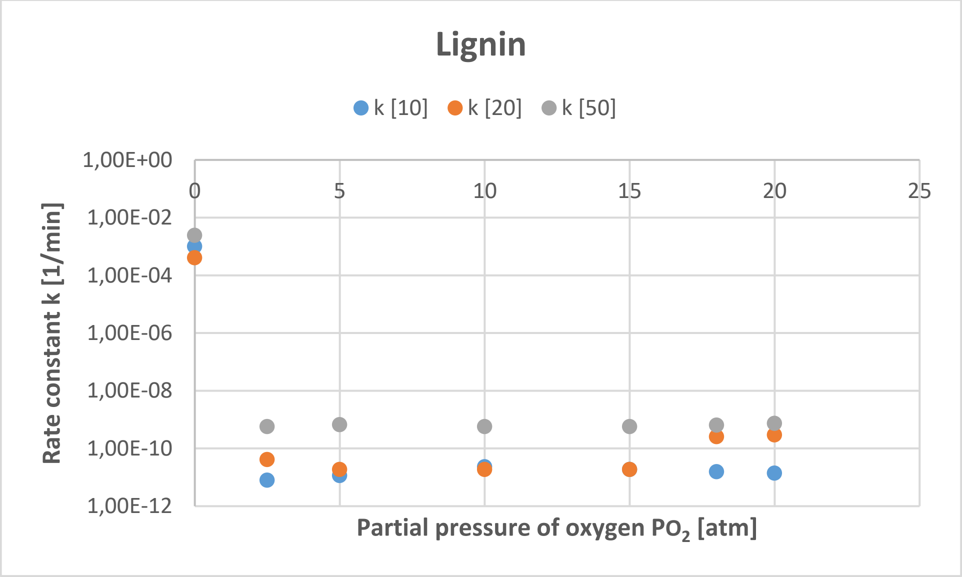


Fig. 28 Relation between modeled rate constant and applied partial pressure of oxygen for lignin

In case of lignin, the picture of kinetic dependence on oxygen’s partial pressure seems to be the truest. The reaction rate constants stay the same within all oxygen’s contents in the gas flowing apart from pyrolysis mode. It is expected to be changed, because of pyrolysis’ reaction different from oxidation pattern.

4.3 Mass evolution of sample and thermal analysis

Graphs of mass evolution versus time or temperature allow to see material’s behavior when different operating conditions are applied. Thanks to that, sample may be examined in isothermal or non-isothermal conditions. In the research, based on sample’s mass loss there were distinguished three pseudo components: moisture, hemicellulose, lignin. Three components refer to curve inflections, where the change in curve’s slope is observed. Knowing wooden biomass basic components and on the basis of their transformation temperature it can be calculated how much of each constituent is in given biomass. First, component undergoing transformation is moisture, that evaporates up to 160°C [16]. As second component, that undergoes decomposition is hemicellulose and cellulose. It decomposes within range of temperature 220°C-400°C [16]. Third and last constituent decomposes within temperature range 400°C-900°C [16].

Chart placed below presents change in mass evolutions with different oxygen partial pressures applied. It can be noted, that higher share of oxygen in gasifying agent causes higher decomposition line slope. That means transformation of biomass components goes faster with higher oxygen content in the gas phase. That refers to oxygen adsorption on biomass surface, that speeds up its decomposition.

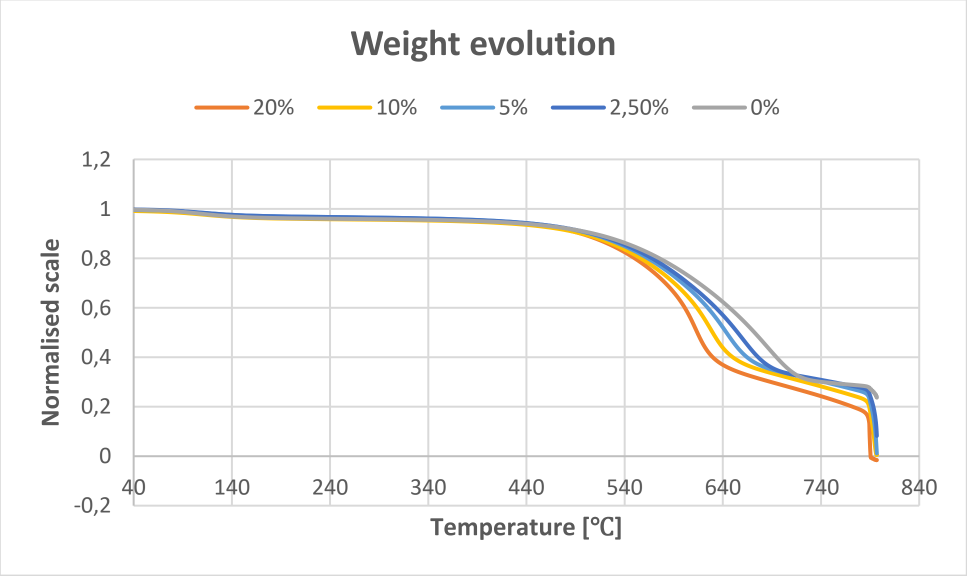


Fig. 29 Sample's mass evolution with temperature for heating rate 20°C/min for different oxygen partial pressures

Interesting might be showing applied material's mass change versus time or temperature for different heating rates applied. Due to that, below is presented graph of such relation for different heating rates used within experiments carried out for the purpose of this thesis.

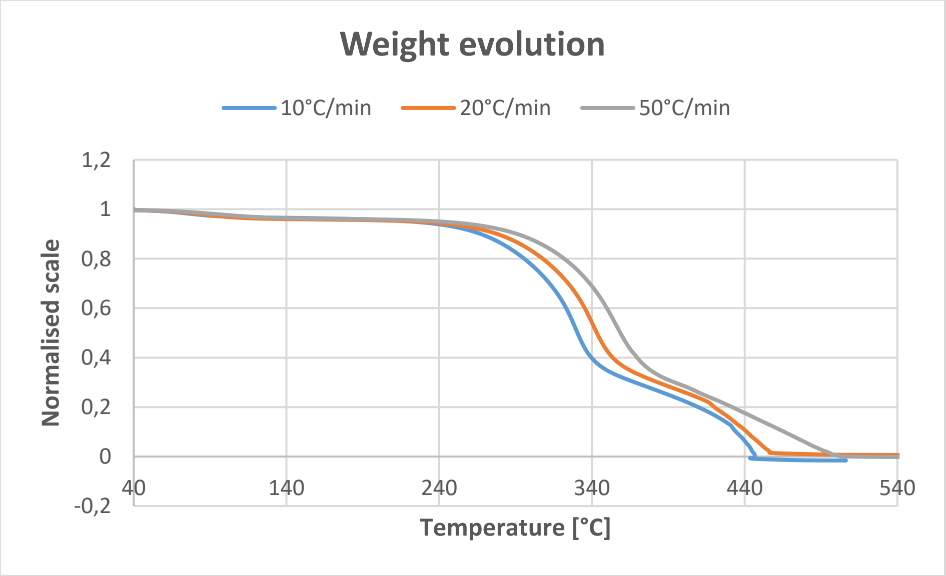


Fig. 30 Sample's mass evolution with temperature, when combusted, for different heating rate

As it can be noticed with higher heating rate, the slope of lines become lower. That means, the constituent's decomposition is faster with lower temperature's change.

When it comes to thermal analysis, the relation of weight's loss rate versus time when isothermal conditions or temperature when non-isothermal conditions, allows to study temperatures of material's transformation. When peak temperatures compared the findings in literature, it may be assumed what kind of products are released within experiment. Below is going to be presented chart of derivative weight versus temperature for single experiments at heating rate 20°C/min when sample was being combusted, partially oxidized and pyrolyzed. First peaks being present at around 100°C in every case refer to water evaporation. Next peaks refer to other possible products occurring, which so far are assumed to be CO, CO_2, CH_4, H_2.

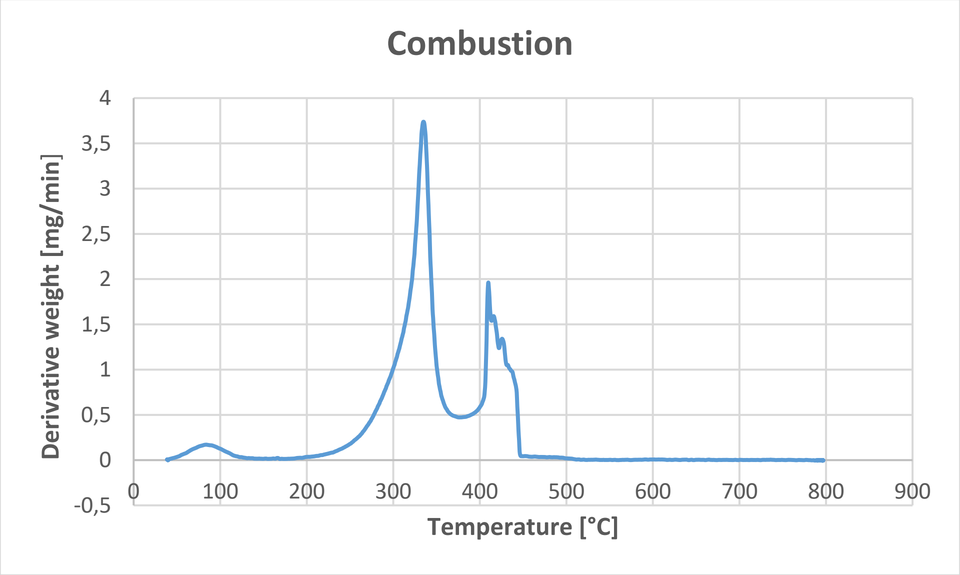


Fig. 31 Weight's loss rate during combustion of sample at heating rate 20°C/min

In case of combustion, the second and third peaks occur at 334°C and 410°C. Because it is combustion mode, it is expected to get the release of CO_2 gas mostly.

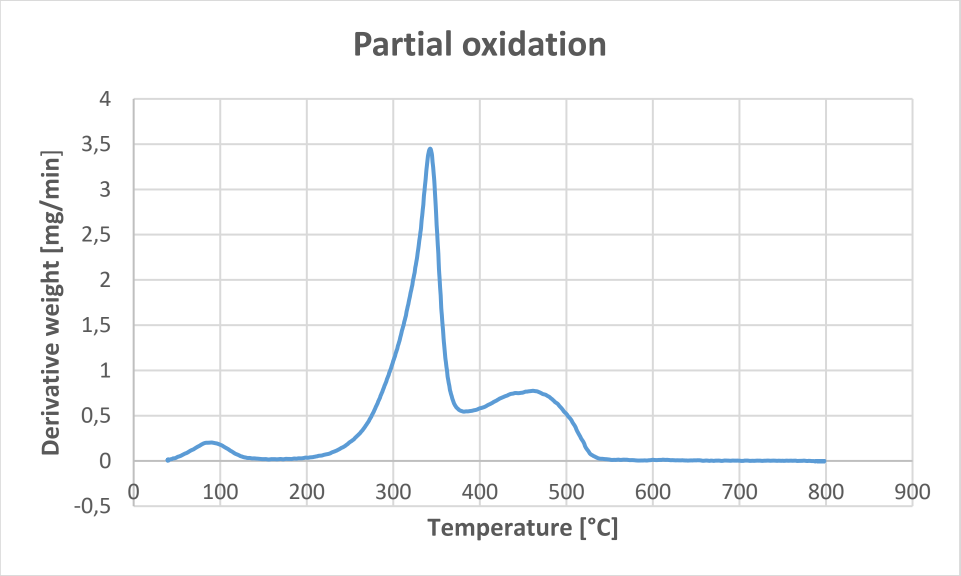


Fig. 32 Weight's loss rate during partial oxidation of sample (10% of oxygen) at heating rate 20°C/min

With lower oxygen content in gasifying agent, the peaks temperatures are higher than in case of combustion. Peaks occur at the temperatures 344°C and 473°C respectively. Due to lower oxygen share, there is occurring combination of combustion and pyrolysis reactions pathways. Thus, it is expected to CO_2, CO, H_2, CH_4 and volatile organic compounds be produced during the process. However, because of external oxygen being present during process it is assumed that the biggest share in produced gas is CO_2.

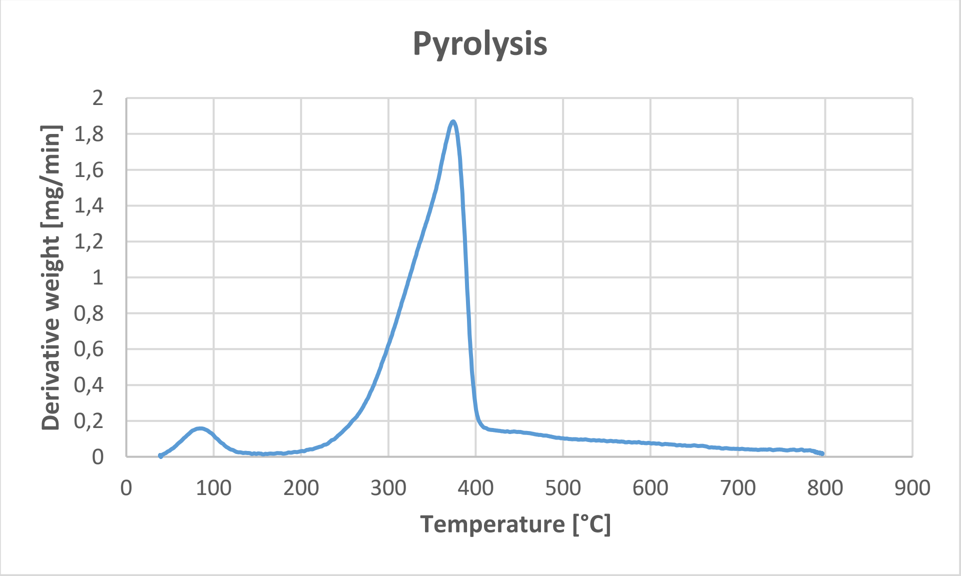


Fig. 33 Weight's loss rate during pyrolysis of sample at heating rate 20°C/min

The Figure 33 placed above illustrates pyrolysis process conditions of given sample. Except water evaporation peak, there is only one peak present at the temperature 378°C. The author of [36] have studied gas release during pyrolysis patterns. According to their results, around 380°C are released either CO_2 from cellulose or CO from cellulose. It may be concluded, that both gases are released with unfortunately unknow ratio. So, the produced gases are expected to be like in case of partial oxidation but with higher amount of CO gas than CO_2.

Another thing that should be studied is evolution of heat flow recorded by analyzer with temperature for different parameters. This allows to analyze sample's behavior during oxidation, partial oxidation and pyrolysis modes. It might be interesting to see, how heat flow during sample's heating changes with different partial pressures of oxygen applied, and with different heating rates. It might be studied with so called DSC curves, i.e. curves showing the evolution of heat flow occurring during experiment with time or temperature. Below is going to be shown graph of heat flow in relation with temperature changes for different oxygen partial pressures.

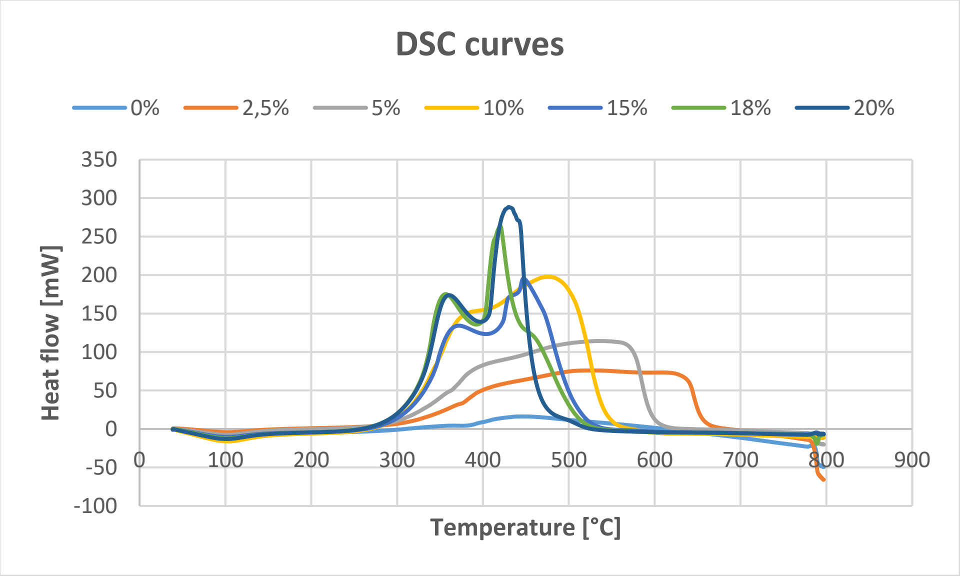


Fig. 34 DSC curves presented for different partial pressures of oxygen for 20°C/min heating rate

Patterns of DSC curves coincide with patterns shown on DTG curves (evolution of derivative weight with temperature). It can be observed, that the higher the content of oxygen in gasifying agent the more visible two peaks become. For pyrolysis, apart from peak related to moisture loss, which is endothermic, there is one peak more related to volatile matter loss. On the other hand, when complete combustion occurs with excess of air there are two peaks present (apart from first one associated with moisture loss) related to volatile matter loss and combustion of char. It is to be noted, that the closer to complete combustion, the higher peaks are. That comes from process being more exothermal with higher oxygen content in the gasifying agent. The more oxygen, the more heat is released. Heat measured in mJ is calculated as area under DSC curve, so due to that the higher the peak is, the bigger area under, hence the more heat is released. It is to be noted, that at the end of the process, series of pyrolysis and 2,5% of oxygen decrease to the negative level. It means, that in case of pyrolytic processes, at the end occur some endothermic changes. The closer to the complete combustion curves tend, the less endothermic peak is, and finally become zero.

The other relation, that is going to be presented in this thesis, is evolution of DSC curves with temperature for different heating rates, namely 10°C/min, 20°C/min, 50°C/min at combustion mode. This illustrates, how heating rate influences heat release during the process studied.

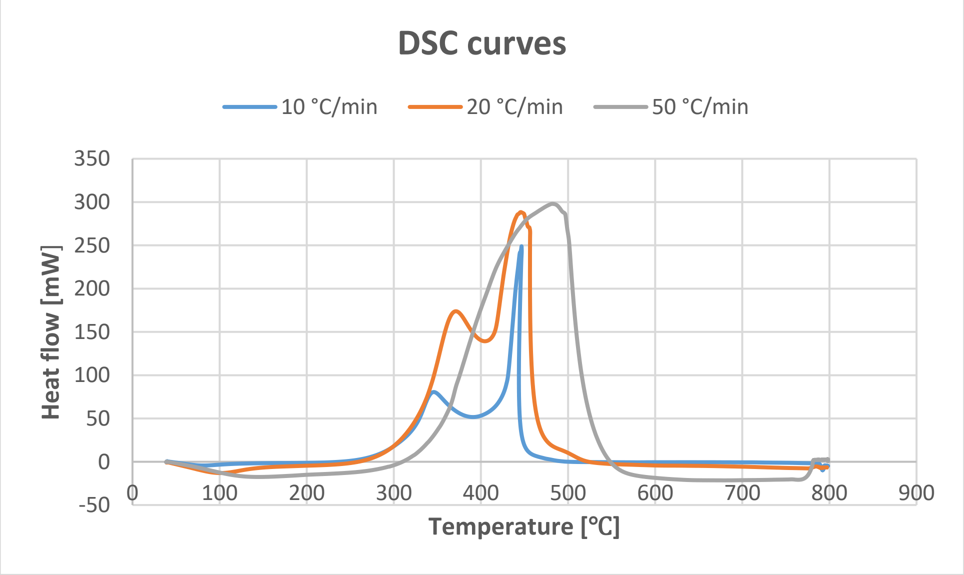


Fig. 35 DSC curves presented for different heating rates at combustion mode

As it can be observed, the higher the heating rate is, the higher peak become. Also, it can be noticed, that in case of heating mode 10°C/min, there are two visible peaks which as mentioned before, refer to volatilization and char combustion respectively. In case of heating rate 20°C/min these two peaks are visible as well, however they become higher and less separated from each other like in case of previously described curve. When it comes to heating rate 50°C/min, process runs according to different pattern, hence there is not the occurrence of two peaks, but one, which shows up just right after peak related to moisture vaporization. That may be happening, because of high heating speed reactions occur almost simultaneously as respective for them temperature reach their level with high speed rate.

To get to know more deeply which reactions occur within the process, the DSC results (specific heat evolved in the process) are going to be compared with heats of the reactions that are likely to occur. This allows us to understand how far process runs and what might be the possible products. Firstly, it is going to be shown a graph of heat flow along with mass changes versus temperature.

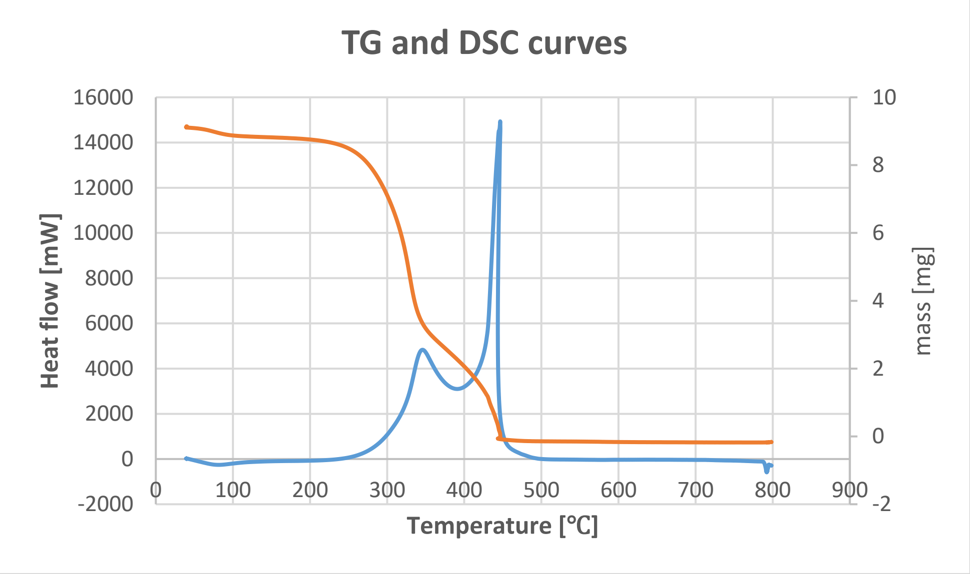


Fig. 36 TG and DSC curves presented for heating rate 10°C/min combustion mode

Addition of mass curve is done to see where certain events of the process occur and then the evolved heat can be measured regarding these events. As it can be noticed from graph, apart from water vaporization peak, there are two peaks occurring. Their beginning coincides with the beginning of the mass changes and as it reaches the peak, the mass change stops. To measure heat evolved within that event, there must be calculated specific heat, which is simply done through dividing heat flow in [mJ/min] by the derivative weight in [mg/min]. The sought heat is one referred to the peak then.

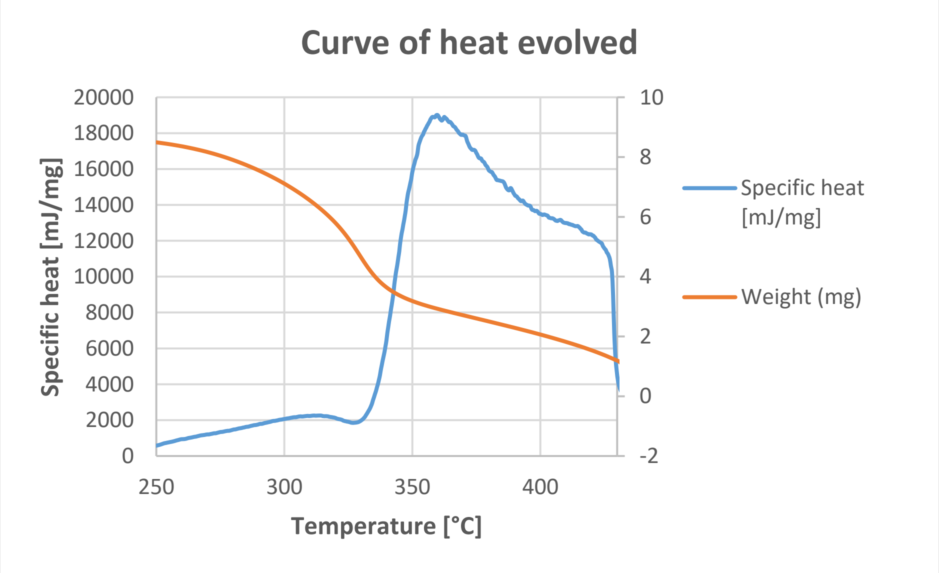


Fig. 37 Specific heat curve presented for heating rate 10°C/min combustion mode

On the Figure 37 specific heat curve along with mass change curve are presented. It is to be noted, that on the Figure 37 only first peak is presented. Because first peak of heat flow (and specific heat) curve refers to cellulosic components, the focus is on it, as lignin's nature (lignin's transformation refers to the heat evolved shown as second peak on heat flow curve) is more complex. It is harder to assume the most accurate routes of its transformation than for cellulose then. Because it is not known, how exactly processes for separate components in the experiments go, to minimalize the error, only cellulosic components are examined within thermal analysis. The temperature range was adjusted to make evaluated peak more visible. To make it more visible, next graph is going to be presented with lowered vertical axis scale. Before the figure will be presented it has to be set, what kind of reactions may occur and which heats are going to be compared with an actual heat evolved. This going to be presented in the form of table.

Tab: 12 Possible routes, that reaction of sucrose may run in the process

No.	Formula	Compound	kJ/kg mass lost	Reaction's formula
1	$C_{12}H_{22}O_{11}$	sucrose	5144,51	$C_{12}H_{22}O_{11}+6O_2=12CO+11H_2O$
2	$C_{12}H_{22}O_{11}$	sucrose	15368,01	$C_{12}H_{22}O_{11}+12O_2=12CO_2+11H_2O$
3	$C_{12}H_{22}O_{11}$	sucrose	7590,20	$C_{12}H_{22}O_{11}+13/2O_2=12CO_2+11H_2$
4	$C_{12}H_{22}O_{11}$	sucrose	2515,64	$C_{12}H_{22}O_{11} +1/2O_2= 12CO+ 11H_2$
5	$C_{12}H_{22}O_{11}$	sucrose	2187,20	$C_{12}H_{22}O_{11}=12C+11H_2O$

Heats of reactions per mass lost were calculated based on heats of formation and heats of combustion of present compounds. Mass lost was taken as experimental one. Assumed products then are carbon monoxide, carbon dioxide, water, hydrogen and carbon. It must be clarified before presenting the result, that evolved heat is contributed by different reactions heats release, with certain ratio. To see, what it looks like when compared to an actual specific heat, the graph will be presented below.

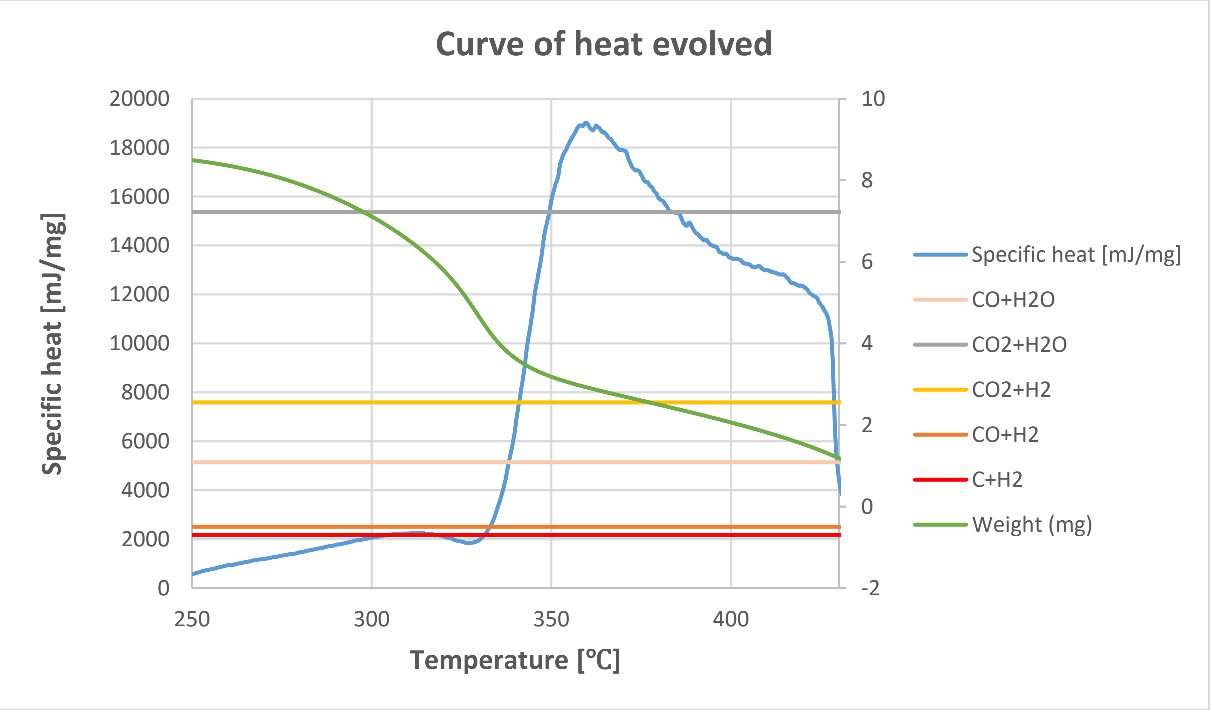


Fig. 38 Specific heat curve presented for heating rate 10°C/min combustion mode with lowered Y axis scale and series of reactions' heats

Thanks to these results it may be assumed what are possible reactions occurring and with what ratios. Although, this assumption will be burdened with error, since occurring products were not confirmed by appropriate experiment, but it gives an initial picture of an actual state and allows for further application in simulation process for the purpose of this thesis.

The closest to the actual specific heat evolved is reaction giving carbon dioxide and water as products. This suggests, that the highest share in the evolved heat has release of CO_2 and H_2O from cellulosic component of given biomass. However, it is likely to happen, that there is release of CO and H_2 occuring during the process. As it can be noticed in the part of gasification simulation, some amounts of methane are assumed too, based on the results of gasification process in Institute of Coal Chemical Processing in Zabrze. [57]

4.4 Simulation of gasification process

For the purpose of this thesis, the simulation has been carried out with Gibbs reactor. The sample material had to be specified by the user, as it was not available in the database. Because Chemcad software is mostly applied in case of simulation with liquid or vapor phase substances, the biomass material had to be specified as solid. To create new component its name was given and correlation as combustion solid set (other possibilities were pseudocomponent, group contribution – Joback, group contribution – UNIFAC and electrolyte). After this, solid element analysis had to be specified. In case of biomass sample used in the research there were given stoichiometrics obtained through weight % basis for each biomass species. Although, ultimate analysis of material has shown presence of sulfur, chlorine, fluorine and nitrogen, their content was relatively small, so material's formula has been stated as containing only carbon, hydrogen and oxygen, being most relevant species. According to that, biomass presents the following formula: $C_{3,92}H_{5,29}O_{2,81}$. Along with solid element analysis, net heating value (obtained through material's ultimate analysis) and solid heat capacity have been set.

Primarily, components of the process had to be selected. As the product streams, knowing composition of sample and taking into consideration the DTG curves presented before, as well as knowing the reactions which occur in the biomass gasification process, the product species had been assumed, as follow: CO, CO_2, CH_4, H_2O, H_2, C, C_6H_6 and $C_{10}H_8$ as tar representation. Feed stream has been separated into two streams: oxygen and nitrogen joint stream calculated from air flow, the same as used in case of running experiment by Institute of Coal Chemical Processing in Poland, i.e. 21 Nm^3/h, taking oxygen content in the air as 21 vol.% and nitrogen content as 78%, and examined biomass material, also with flow being the same as while running experiment in Institute in Poland, i.e. ca. 15 kg/h. Oxygen and nitrogen joint flow stream was set to be at the room temperature, i.e. 298 K and 101325 Pa pressure at the beginning. Before reaching mixer by oxygen flow, it passed through compressor to increase pressure of gas flow and simultaneously its temperature. Compression was done according to adiabatic (isentropic) model. Pressure at the outlet has been set 10 bar with efficiency of the device being 90%. Stream temperature increased to 596,9 K and enthalpy carried with it was 8,3 MJ/h. Biomass feed was at the room temperature, i.e. 298 K and carried enthalpy -87,7 MJ/h. Both streams were directed to mixer with output pressure 10 bar. After mixing, joint stream had 596,9 K and enthalpy - 79,4 MJ/h.

Next step was to set data for Gibbs reactor itself. It required thermal mode specification, where specified heat duty has been chosen. Calculated by software heat duty was 9.2 MJ/h. Reaction phase was chosen as vapor or mixed phase. Moving to optional specifications pressure in the reactor was chosen 10 bar. Lambda factor for air flow specified as 0,4. In the case of convergence parameters temperature of the process range was specified, being 800-1400 K. The software calculated overall heat of reaction, being -33.4 MJ/h. Char is a residue in gasification process, but as its representative in this simulation carbon was chosen, in its graphite form as modification of carbon. Below is going to be presented chart of simulation flowsheet in Chemcad software.

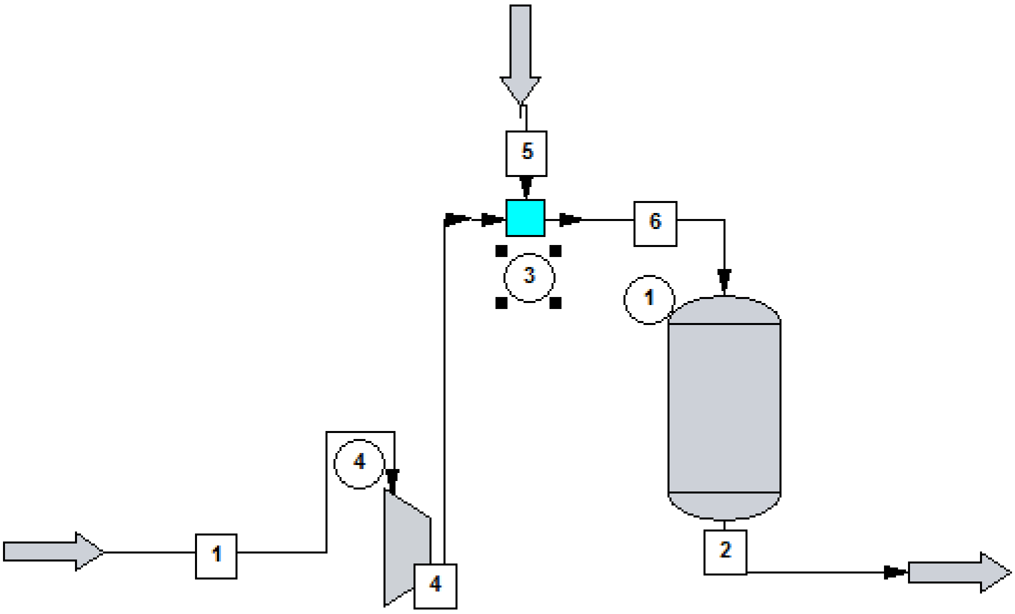


Fig. 39 Scheme of gasification process taking place in Gibbs reactor. Downstream processes were not considered. Respective streams are signed in squares: 1. Oxygen feed stream before compression, 2. Product stream, 4. Oxygen feed stream after compression, 5. Biomass feed stream 6. Mixed feed stream. Respective units are signed in circles: 1. Gibbs reactor, 3. Mixer, 4. Compressor.

Chemcad software allows to create convenient for users reports about overall process, mass and energy balances, but also detailed report on particular units. To illustrate inputs set for each unit and outputs obtained through software, report on this data is going to be presented below.

```
CHEMCAD 6.3.1                                                   Page 1

Simulation: Gibbs reactor            Date: 01/23/2017   Time: 22:32:31
EQUIPMENT SUMMARIES

                      Compressor Summary

Equip. No.                        4
       Name
Pressure out   Pa         1.0000e+006
Type of Compressor                1
Efficiency                     0.9000
Actual power   kW              2.3128
Cp/Cv                          1.4004
Theoretical power   kW         2.0815
Ideal Cp/Cv                    1.3979
Calc Pout   Pa            1.0000e+006
Calc. mass flowrate              27
 (kg/h)
```

```
                      Mixer Summary

Equip. No.                    3
       Name
Output Pressure  Pa     1.0000e+006

                      Gibbs Reactor Summary

Equip. No.                    1
       Name
Thermal mode                  2
Reaction Phase                1
Temperature  K           1190.0399
Heat duty  MJ/h             9.2422
Pressure  Pa            1.0000e+006
Overall Heat of Rxn       -33.4304
 (MJ/h)
Solid Component               7
Min Allowable Temp  K      800.0000
Max Allowable Temp  K     1400.0000
Inert Component              11 (nitrogen)
Lamda factor                0.4000
```

The notation has been left as it was transported from Chemcad to Wordpad. What is worth to notice in this case is equilibrium temperature in the reactor of the process, that is 1190,04 K.

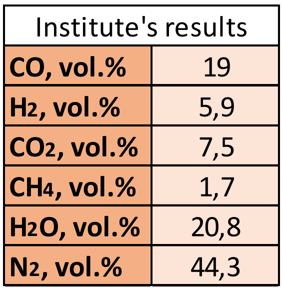
Considering mass and energy balance, the following results were obtained.

```
CHEMCAD 6.3.1                                           Page 1

Simulation: Gibbs reactor          Date: 01/23/2017  Time: 22:39:45

Calculation mode : Sequential
Flash algorithm  : Normal

Equipment Calculation Sequence
   4   3   1

No recycle loops in the flowsheet.
```

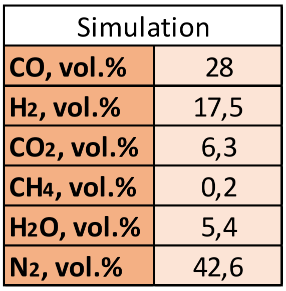
```
CHEMCAD 6.3.1                                           Page 2

Simulation: Gibbs reactor          Date: 01/23/2017  Time: 22:39:45

Overall Mass Balance       kmol/h                     kg/h
                     Input       Output        Input       Output
Oxygen               0.188        0.000        6.000        0.000
Carbon Monoxide      0.000        0.490        0.000       13.732
Carbon Dioxide       0.000        0.111        0.000        4.889
Methane              0.000        0.003        0.000        0.040
Water                0.000        0.095        0.000        1.720
Hydrogen             0.000        0.307        0.000        0.619
Carbon               0.000        0.000        0.000        0.000
biomass              0.154        0.000       15.000        0.000
Benzene              0.000        0.000        0.000        0.000
Naphthalene          0.000        0.000        0.000        0.000
Nitrogen             0.750        0.750       21.000       21.000

Total                1.091        1.756       42.000       42.000


Overall Energy Balance        MJ/h
                         Input              Output
Feed Streams            -87.7543
Product Streams                            -70.1861
Total Heating            9.24216
Total Cooling                  0
Power Added              8.32604
Power Generated                0

Total                   -70.1861           -70.1861
```

What can be noticed from the report placed above, the highest yield has carbon monoxide, being roughly 28 vol.% of output stream. The second highest yield has carbon dioxide giving around 6,3 vol.% of output. In the outlet stream there are also present water (5,4 vol.%), hydrogen (17,5 vol. %), nitrogen treated in the sumulation as an inert (42,6 vol. %) and in small amounts methane (ca. 0,2 vol. %). Shown above energy balance is a mean to obtain equilibrium conditions of the process, i.e. equilibrium temperature and equilibirum composition. As a default set, the program takes conversion as 100 %, what may be observed in outlet stream composition, since the software assumed no carbon and oxygen in the output. When compared these results to the ones obtained in the Institute of Coal Chemical Processing, it is to be noted, that there are differences in the composition.

Tab: 12 Comparison of outlet gas composition from GazEla biomass gasifier [56] and results of simulation



Institute's results	
CO, vol.%	19
H_2, vol.%	5,9
CO_2, vol.%	7,5
CH_4, vol.%	1,7
H_2O, vol.%	20,8
N_2, vol.%	44,3



Simulation	
CO, vol.%	28
H_2, vol.%	17,5
CO_2, vol.%	6,3
CH_4, vol.%	0,2
H_2O, vol.%	5,4
N_2, vol.%	42,6

This tables show, that assumption of species being present in the outlet gas was appropriate. However, the results to not match each other entirely. It may be noticed, that obtained through software yield of water is way lesser than presented in the table. The same situation is in case of methane and carbon dioxide. Hydrogen, in turn, was obtained in amount much higher than presented in the table.

5. Conclusions

To sum up all what have been presented in the report on research carried out for the purpose of this thesis so far, here will be provided brief summations on each of chapters regarding research.

Regarding biomass reactivity, it may be concluded, that higher temperature implies higher conversion of material. However, there are still some remaining volatiles in the residue of carbonization process, since the highest temperature applied was 400°C. That suggests, that to perform complete carbonization of given material, higher temperatures must be applied.

When analyzing combustion of arising after pyrolysis char, it is to be noted that it burns entirely, with registered weight being 0 mg at the end of the experiment. That means, there is no ash registered, which becomes an issue, since according to the proximate analysis, there is, 0,5 wt.% of ash in the material. Since presence of ash after combustion has not been observed in any case, that may mean the ash is not evenly distributed in the material provided, what could be explained with higher density of ash than organic material and it could have settled to the bottom of container when material was being grounded.

When it comes to char’s reactivity graph, there can be noticed two peaks: one probably referring to charring process, since some volatile matter left after pyrolysis and the second one referring to char combustion. Temperature when first peak starts to arise is 243°C and its peak temperature is 322°C with peak rate being 0,14 mg/ml. Temperature of combustion peak are 376°C and 443°C respectively with peak rate 0,43 mg/ml.

Moving to kinetic parameters and the results for rate constants at reference temperature (298 K), it can be observed, that in case of hemicellulose and lignin these parameters do not differ much among each species. However, when it comes to water there might be seen some slight differences due to its fitting sensitivity caused by relatively small amount of water as one of three pseudo-components.

Differences are also observed in case of pyrolysis mode, what is reasonable, since lack of oxygen in the environment changes rates of reaction. In this experiment mode activation energy has tendency to fall, but kinetic constant to rise when compared to modes with oxygen presence in the gas.

Regarding study of kinetic parameters with changes in heating rate, it can be noticed, that for water and hemicellulose these parameters increase with increased heating rate, but for lignin they drop. These events may indicate, that in case of hemicellulose, there are mostly occurring endothermic reactions of decomposition, but in case of lignin, there are mainly exothermic reactions of dewatering present.

There has been studied also changes in rate constant with different partial pressure of oxygen applied and heating rates. At the beginning, it should be stated, that for all three pseudo components, i.e. moisture, hemicellulose (cellulose) and lignin, at certain point of oxygen content in the gas, rate constant value increases with increased heating rate, if not constant. Just in case of water, it may be observed, that rate constant increases with partial pressure of oxygen, but around 10 % of oxygen in the gas it starts to decrease with higher heating rate. This may suggest, that adsorption of oxygen on the material’s surface speeds up the reaction.

When it comes to discussion about weight evolution, the common thing for all conditions applied in the experiment is that, there can be distinguished three pseudo components: moisture, hemicellulose (cellulose) and lignin, based on changes in slopes of curves. Depending what conditions are applied, if it is pyrolysis, partial oxidation or oxidation mode, various slopes of curves are obtained.

Kinetic parameters were obtained through the method based on curve fitting. To the experimental weight of sample curve, by changing values of kinetic parameters, modeled sample‘s weight curve was fitted. The quality of that model was checked. According to its results, the method of curve fitting appears to give reasonable results. Average of fitting quality is roughly 98 %, what shows that method may be applied as reasonable tool for kinetic parameters studies.

Regarding mass evolution, on the graph it can be noticed,that the higher oxygen content in flowing gas the higher slope of the sample‘s weight evolution curve. As stated before, oxygen may speed up the reaction and higher slope implies higher rate of reaction. In case of material‘s weight evolution with change in heating rate, it is to be noted, that slope increases with higher heating rate applied. The faster certain required temperature is obtained, the higher rate is implied.

As far as thermal analysis is concerned, from DTG curves presented for pyrolysis, partial oxidation and combustion, it can be conclude, that with lower oxygen content in the gas, second peak decreases, at the end disappearing. This shows that partial oxidation mode is combination of pyrolysis and combustion processes.

When it comed to DSC curves, there has been studied its evolution with different oxygen partial pressure applied and with different heating rates. Regarding changes with various oxygen content, it may be seen, that with higher share of oxygen in the flowing gas, the amount of heat released become bigger. That means reaction become more exothermic, since there is higher contribution of combustion process. In case of DSC curves examined for different heating rates, in heating rate 50°C/min two peaks present in lower heating rates collude into one. This may be explained by the fact, that with higher heating rate rate of reactions incease and at certain point, given reaction may coincide with each other during one process.

When it comes to performed simulation the results obtained through Chemcad do not coincide as it should with results obtained in the Institute of Coal Chemical Processing in Poland. This happens due to many reasons. In this simulation, using just one reactor it was not possible to perform calculations with regard to three air streams inlets, like it is in actual GazEla gasifier. Due to certain limitations, the simulation has been performed in the way presented in this report. However, in case of Gazela gasifier the last air inlet placed at the bottom of the reactor was added to provide complete combustion of remaining char.

5.2 Future proposals

To carry on research performed for the purpose of this thesis, it is proposed to separate components of given biomass material into cellulose, hemicellulose and lignin and carry out experiment for each of them separately. It would help to understand, what might be the composition of outlet gas, if also FTIR method could be applied to check species released and their concentration. Also, when heat released studied through DSC curves for each of components, the pattern of reactions occurring in the gasification process of this certain material could be understood. The assumptions made for the purpose of this work are burden with errors.

Simulation of given material gasification was performed for gasifier allowing to produce 60 kWt represented by Gibbs reactor. There could be performed the whole process with electricity production from arising syngas through generator to see how much electricity could be produced with gas having obtained in the simulation calorific value. Process could be scaled up as well, to check how it could perform in the industrial application, since simulated gasifier was built in the laboratory scale.

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