TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental technology

COMPOSITION OF THE PRODUCER GAS OBTAINED FROM THE GASIFICATION OF WOOD SPECIES

ERINEVATE PUULIIKIDE GAASISTAMISEL SAADAVA GAASI KOOSTISE MÄÄRAMINE

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

Tallinn, May 26th 2020.

Author: ....

Thesis is in accordance with terms and requirements

Tallinn, May 26th 2020.

Supervisor: ….........................

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THESIS TASK

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(in English) Composition of the producer gas obtained from the gasification of wood species

(in Estonian) Erinevate puuliikide gaasistamisel saadava gaasi koostise määramine

Thesis main objectives:

1. Study the Estonian biomass context, in Estonia and for thermochemical conversion processes, specifically for biomass gasification.
2. Study the physical and chemical properties of spruce, alder and pine as biomass resources.
3. Fine-tune a prototype batch reactor to operate it in biomass gasification experiments at different operational conditions.
4. Determine and analyze the composition and energy value of the producer gas product of the gasification of spruce, alder and pine in a fixed bed reactor.

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CONTENTS

PREFACE

The following thesis was developed and based as a part of the research done by the School of Engineering: Department of Energy Technology: Research Group of sustainable Energy and fuels at the Tallinn University of Technology, under the supervision of Professor Alar Konist, with the consultancy of Oliver Järvik, Senior Researcher at the university, and assistance of other members of the Department of Energy Technology at the university. The research group provided all the required technical and theoretical assistance and guidance, as well as the required equipment to execute the research. The characterization of the biomass wood species samples was made by other members of the research group.

The thesis consisted of gasification experiments of different biomass wood species, including spruce, alder and pine, under different operational conditions, such as temperature and gasifying agent mass flow. The experiments were carried out in a prototype batch fixed bed reactor from the laboratories at the Department of Energy Technologies at the Tallinn University of Technology. The research consisted of four main stages; first a theoretical and literature overview of gasification and thermochemical conversion processes, second a set up and preparation of the experimental and measurement equipment, third the execution of the gasification experiments for spruce alder and pine under different temperature conditions, and fourth, gas measurement (using FTIR and gas chromatography), interpretation and analysis of the producer gas composition. All experimental results were analyzed and compared to understand the effect of gasification temperature in the composition of the producer gas, especially the composition of the main combustible gases, hydrogen, methane and carbon monoxide.

Keywords: Alder, biomass, fixed bed reactor, gasification, pine, spruce.

List of abbreviations and symbols

CCE	Carbon Conversion Efficiency
CGE	Cold Gas Efficiency
CHP	Combined heat and power
ER	Equivalence ratio
FTIR	Fourier Transform infrared Spectroscopy
GC	Gas Chromatography
HHV	High heating value
LHV	Low heating value
Mtoe	Millions of tons of oil equivalent
n.d.	Not detected
SGP	Specific Gas Production
SV	Superficial velocity
TOC	Total Organic Carbon
TPES	Total Primary Energy Supply
LPM	Liters per minute
SLPM	Standard liters per minute

INTRODUCTION

The planet and its population is going through a growing consumption of energy for domestic and industrial applications, combined with the scarcity of natural resources, population growth and a global environmental crisis, caused among other factors by fossil fuel emissions, which have contributed to climate change. All these global issues have encouraged the research of efficient and cleaner energy solutions, through the development of generation technologies using renewable energy resources [1], [2].

Countries such as Estonia largely depend on fossil fuels for its energy consumption needs, where the use of oil shale contributes to carbon dioxide emissions [3]. Estonia has committed to shift into efficient, renewable and sustainable energy solutions, planning to produce 50 % of the country's electricity from renewable sources by 2030, limiting the emission of pollutants and keeping emissions of greenhouse gases below 11 % by 2020, and achieving 10 % of energy from renewable sources in the transport sector by 2020. Evidence of this is the National Renewable Energy Action Plan, where Estonia aimed and achieved to produce 25 % of the total energy from renewable sources [4].

For Estonia and other countries characterized with having a large percentage of its area covered in forest, biomass as a renewable energy source is possibly one of the most economic and technologically feasible alternatives to shift into renewable energies, and combined with efficient and clean methods of transforming oil shale into energy, will lead the path to decrease carbon dioxide emissions, without compromising the country's economic growth. In Estonia the shift into sustainability has already started, where currently around 54 % of the heat generation and 7 % of electricity generation are being produced using biomass resources, such as wood and wood residues [3].

Different methods to use biomass to produce heat and electricity include pyrolysis, combustion and gasification, each one presents its advantages and its specific field of application in the energy sector. The current research studies biomass gasification, as an alternative method for thermochemical conversion of biomass, into producer gas, used for different energy generation applications such as transportation and as a resource for chemicals production. Gasification uses low cost biomass and wood residues, to produce a gas rich in hydrogen, methane and carbon monoxide, obtained through the controlled reaction of a gasifying agent and biomass feedstock.

The present research uses Scots Pine, Grey Alder and Norway Spruce samples from Estonian forests, considering that from all the wood resources in the country, around 32.57 % are pines, 29.97 % birch, 17.35 % spruce, 5.78 % aspen, 3.50 % Common Alder and 9.15 % Grey Alder [5]. The gasification experiments are done using a prototype batch fixed bed reactor, with a constant flow of gasifying agent (oxygen plus nitrogen) at different gasification temperatures (750, 850 and 950 °C). Gas analyzing equipment is used to determine the composition of the producer gas at different gasification temperatures and for the three biomass species (alder, spruce and pine), the results are compared and analyzed, taking into special consideration the concentration of hydrogen, carbon monoxide and methane in the composition of the producer gas. The research analyzes the effect of different biomass species in the production of producer gas, as well as the effect of gasification temperature and flow rate of gasifying agent in the production of producer gas.

The document consists of three main parts; first, an overview of biomass and thermochemical conversion and its context in Estonia. The overview also describes all the relevant studies and experiments to characterize biomass, an overview of biomass gasification, including gasification processes, parameters, indicators and challenges, and an overview of the biomass species used during the experiments (spruce, alder and pine).

The second part of this document includes the results of the characterization of the spruce, alder and pine biomass samples, including results of the ultimate and proximate analysis, and the calorific value. Moreover, this chapter describes all the procedures used to fine tune and operate the batch reactor that was used for the experiments, including maintenance, calibration of gas analysis equipment, and set up of the system. This section also describes the calculations used to determine the proper air to fuel ratio needed to achieve gasification at the required temperatures with the required amount of gasifying agent.

The third part of this document includes all the results from the experimental gasification of spruce, alder and pine at different gasification temperatures and gasifying agent ratios, describing and analyzing the gas chromatography readings, the producer gas composition, the total organic carbon, and the gasification residues. This section compares and analyzes the gasification experiments at different temperatures of the three biomass species, comparing specially the concentration of hydrogen, methane and carbon dioxide in the producer gas.

1. LITERATURE OVERVIEW

The world is facing a large scale transition in the energy sector in the latest years, with a growing energy demand and an increasing production of greenhouse gases. The total energy demand in the world is higher than ever before and carbon dioxide emissions are expected to increase to up to 35000 Mt by the year 2040 [6]. At the moment from the total electricity generation, over 65 % of the world's electricity generation is produced by conventional resources, such as Coal, gas and oil, and less than 25 % of the electricity being generated from renewable energies. Nevertheless, the continuous efforts to create and incorporate renewable and clean energy policies worldwide will contribute to increasing the share of electricity produced by renewable energies to 37 % when incorporating existing energy policies or 60 % when achieving internationally agreed objectives on climate change [7].

The European Union has targeted to decarbonize the energy system, prioritize energy efficiency, secure energy supply, and interconnect the energy market. Among the European Union goals for the year 2030, the top priority goals for the energy framework are to cut 40 % in greenhouse gas emissions compared to 1990 levels, produce at least 32 % of the energy demand from renewable energies, and increase energy efficiency by at least 32.5 % [8]. For transportation the European Union has goals to shift toward sustainable mobility, by reducing greenhouse gas emissions in transport by 90 % [9], including air, road, railway and sea transport, by increasing the use of clean vehicles, and vehicles using alternative fuels, improving efficiency in the transport system, implementing multimodal transport and improving public transport in cities among other measures [10].

1.1. Thermochemical conversion in Estonia

The energy sector in Estonia is unique among other countries in the world, mostly due to the large dependence of the country on fossil fuels, more specifically in oil shale used in power plants, consuming over 12 million tons of oil shale per year and producing over 90 % of the electric power demand, and over 70 % of the energy demand [11]. Biofuels and waste are the second largest energy source, with about 13 % of the Total Primary Energy Supply (TPES) [12]. At the moment the energy demand in Estonia is greatly affected by the need of liquid fuels, especially for transportation, requiring one third of the overall energy demand in liquid fuels. Solid and gaseous fuels make almost one fourth of the energy demand (24 %), while the requirements for heating and electricity are over 45 % (23 % for heating and 22 % for electricity) [13].

Estonia has reduced carbon monoxide emissions by 50 % compared to the emissions in the year 1990 [14]. To mitigate pollution and emissions and to increase energy efficiency, the country has set different goals such as [3], [15]:

- Ensuring fuel and energy supply and local generating power, with a power network modernized every 30 years.
- Preserving the competitiveness of the domestic market, especially for oil shale production, while increasing the efficiency and reducing environmental harms.
- Limiting the emission of pollutants such as sulfur dioxide, nitrogen oxide and volatile organic compounds, and keeping emissions of greenhouse gases below 11 % by 2020.
- Achieving 10 % of energy from renewable sources in the transport sector by 2020.
- Ensuring a 20 % energy share produced from CHP by 2020.
- 50 % of electricity generated from renewable sources by 2030.
- A transition to 80 % renewable energies in electricity and heat by 2030.

The main renewable energy resource in Estonia is biomass in the form of wood, bio residues and biofuels, having more than 54 % of the heat generation produced from biofuels in boiler houses and distributed through district heating, and 7 % of electricity produced from biofuels and biomass. Wood resources from forest are the most used and available type of biomass resource in Estonia, with around 2.3 million Ha of forest in the country, covering over 50 % of Estonia's territory [16], with pine, spruce, birch, aspen and alders among the most common type of tree species in Estonia (Figure 1). These tree species are not only wide available, but are increasing on average 55 m^3/ha per year [16].

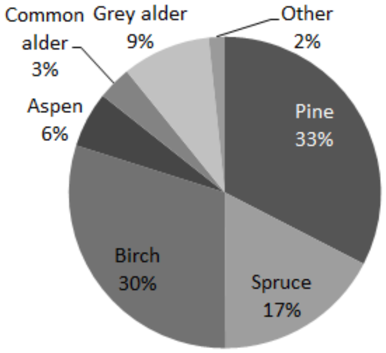


Figure 1. Forest resources in Estonia, most common types of tree species (Adapted from [17])

Estonia has used thermochemical conversion processes for energy generation since the early 20th century, as oil shale has been the main energy source through combustion, since 1923 Estonia has built oil shale combustion power plants. Other than oil shale, biomass is seen as an alternative fuel for thermochemical conversion processes in Estonia, considering its potential and availability and considering that at the current consumption the active supplies of Estonian oil shale will last for about 10 years or less and the total supplies will not last more than 60 years [18].

Alternative technologies such as wood gasification, combustion or cogeneration present a potential role in supplying energy to the Estonian energy market, especially biomass thermochemical conversion processes. At the moment district heating provides most of the heat demand of the country (more than 70 % [19]), through thermochemical conversion processes using central boiler plants or combined heat and power stations. Thermochemical conversion processes such as biomass gasification are presented as one of the relevant technologies to be researched and implemented in Estonia, to provide cleaner and renewable solutions for energy production for transportation and heat and power generation.

1.2. Biomass gasification

Biomass conversion technologies are divided in four main categories; direct combustion, agrochemical processes, biochemical processes and thermochemical processes [20]. Thermochemical conversion processes such as pyrolysis and gasification use low moisture biomass and biowaste to produce electricity, heavy oil or gas fuels [21]. This overview is focused on thermochemical conversion processes, specifically gasification.

Gasification is a low oxygen environment thermochemical conversion process for the production of syngas or producer gas, by converting organic stock such as carbon biomass, coal, natural gas, petroleum and industrial waste into flammable and combustible gas. Gasification is carried out at temperatures ranging from 500 to 1400 °C, in pressurized or atmospheric reactors, with a gasifying agent flow [21]. In the chemical industry gasification processes are used for the syntheses of chemicals and fuels like methanol and ammonia. In the energy generation industry gasification processes are used for the generation of combustible gases, especially for the generation of hydrogen, carbon monoxide and methane, used for energy generation in internal combustion engines, gas engines, gas turbines and fuel cells [22]. Gasification is chosen as the technology to study due to its high potential of producing producer gas with hydrogen and carbon monoxide concentration and its applications for alternative energy generation solutions, especially in transportation and combined heat and power.

1.2.1. Thermochemical gasification

Among the different thermochemical conversion processes for solid biomass, biomass gasification is a process that transforms solid organic materials into producer or syngas by using controlled environment, high temperature reaction processes in the presence of a limited supply of oxidants as a gasifying agent. The producer gas product of gasification usually consists of hydrogen (12 - 20 %), carbon monoxide (17 - 22 %), methane (2 - 3 %), carbon dioxide (9 - 15 %), water vapor, nitrogen and different impurities [23], the composition of the produced gas depends on the type of fuel used, the gasifier type and design, the gasifying agent and the operational conditions. Biomass gasification has different applications for CHP, especially for small to medium scale generation (up to 10 MW), having biomass to power efficiency potential between 35 – 40 % [24]. The produced gas is considered a renewable energy source if obtained from biomass, and presents several applications, such as fueling internal combustion engines and gas turbines, providing heating for CHP applications or using it to produce methanol or hydrogen [25].

Gasification as a thermochemical conversion process was first discovered at the end of the 18th century in countries such as France and England, and was implemented over half a decade later, using gas produced from coal gasification for district and housing lighting. The combustible fuel product of biomass gasification was actively used in the 19th century and early 20th century, where in countries such as the United States, cities were supplied with gas produced from gasification for cooking and lightning applications. France played a major role in the development of gasification systems, and contributed to the implementation of coal and peat gasification in European gas systems, before liquid fuels took over the market [26]. During the Second World War, the oil crisis re-introduced gasification, using producer gas as transportation and industry fuel. Likewise, gasifiers were installed during the 1973 oil crisis, while in the last decades the awareness of climate change led to a new stage of biomass gasification technologies, being mostly developed by Sweden, Finland, Estonia, China, Germany and the United States [23].

1.2.2. Gasification zones and chemical reactions

Biomass thermochemical gasification occurs through a set of stages where different thermochemical reactions take place, starting from the drying of the biomass raw feedstock, followed by the pyrolysis where biomass is transformed into char and volatiles, a partial oxidation or combustion where exothermic reactions take place, generating heat and different gaseous species, and followed by reduction, the last stage where gases and char are transformed into producer gas. During gasification different stages occur at the same time, and therefore interact with each other through heat transfer (See Figure 2).

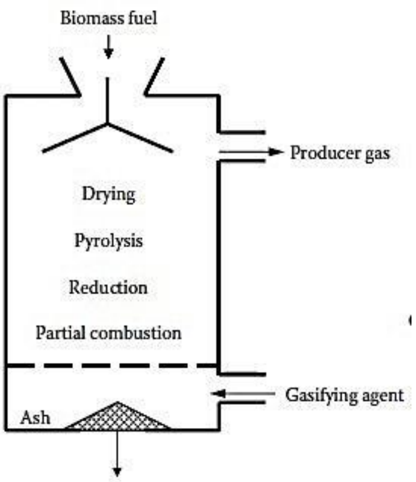


Figure 2. Gasification stages occurring in an updraft fixed bed reactor. (Taken from [23])

1.2.2.1. Drying

Biomass that presents average moisture content from 5 % up to 35 % [23] is used in gasification processes, biomass with moisture contents above 35 % and up to 60 % is not suitable for gasification as the energy losses are greater and the efficiency is severely decreased [27]. As biomass is fed into a gasifier, the heat transfer from the partial combustion raises the drying stage temperature to about 100 °C – 200 °C, thus reducing the moisture content and producing water vapor (Equation 1). Pretreatment of biomass (pre-drying to reduce moisture content to 10 % - 20 % and densification) [21] increases the efficiency of the gasification process and improves the quality of the producer gas, as the latent heat of vaporization requires a substantial amount of energy that affects the efficiency of the gasification process. During the drying stage biomass does not experience thermal decomposition of volatiles but rather loss of moisture content.

$$Biomass_{wet} \xrightarrow[heat]{} Biomass_{dry} + H_2O \ [28]$$

Equation 1

1.2.2.2. Pyrolysis

Biomass is expressed by its main elements that compose it $(C_aH_bO_cN_dS_e)$, and once the gasifier reaches temperatures over 200 °C, pyrolysis stage occurs at temperatures from 200 °C to 700 °C in the absence of air. During pyrolysis, organic compounds such as cellulose, hemicellulose and lignin break into char and gas molecules such as hydrogen, carbon dioxide, carbon monoxide and methane among others (Equation 2). At 300 °C cellulose forms into carbonyl and carboxyl radicals, at temperatures over 300 °C cellulose gets decomposed into chars, tar and different gas species, and at temperatures between 300 °C to 500 °C lignin is decomposed to form methanol, water and acetone [26]. During pyrolysis, the reactions with temperatures lower than 300 °C are exothermic, therefore to convert biomass into char with pyrolysis at temperatures lower than 300 °C external heating is not required. On the other hand for pyrolysis at temperatures over 300 °C external heating is used as the reactions are endothermic. For biomass pyrolysis in gasification, external heating is used, to reach higher temperatures and achieve a higher production of gases.

$$C_aH_bO_cN_dS_e \xrightarrow[heat]{} Char + tar + aCO + bCO_2 + dH_2 + eH_2O,\ etc.\ [23] \qquad \text{Equation 2}$$

1.2.2.3. Combustion

The combustion stage occurs when tars, char, gaseous molecules react in exothermic reactions with the gasifying agent of the process. The combustion stage reaches high temperatures starting from 900 °C and reaching 1500 °C or even up to 1800 °C depending on the gasifier conditions. The combustion stage is relevant to determine the type and quality of the producer gas and to determine different parameters such as internal pressure and temperature, type of gasifying agent and type of reactor. These parameters also affect the output producer gas. The main oxidation reactions in the combustion stage are shown in the following Equations 3, 4, 5, 6 and 7[29].

$$C + O_2 \leftrightarrow CO_2 \qquad \text{Equation 3}$$

$$C + \frac{1}{2}O_2 \leftrightarrow CO \qquad \text{Equation 4}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \text{Equation 5}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \text{Equation 6}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{Equation 7}$$

The oxidation reactions produce mostly carbon dioxide, carbon monoxide and water vapor, during combustion heterogeneous and homogeneous reactions occur, exothermic heterogeneous reactions occur within the char produced during pyrolysis and oxygen present in the process to produce carbon dioxide and heat. Both heterogeneous and homogeneous reactions are all exothermic and produce a significant amount of heat that is used as a heat source in other gasification stages such as drying, pyrolysis and reduction [26]. During combustion, a steam atmosphere increases the production of light gases such as hydrogen and carbon monoxide, therefore steam has been considered one of most best options to be implemented as a gasifying/oxidation agent as it contributes the most to the gas reforming process in the combustion reactions [30].

1.2.2.4. Reduction

The reduction zone, also known as the gasification stage, is the stage where all the gas species that compose the producer gas are produced, during this stage, carbon dioxide and water vapor are transformed into carbon monoxide and hydrogen, as the sensible heat of different gas species and char produced during pyrolysis and combustion is transformed into producer gas with high chemical energy properties [23]. The gasifying agent such as steam and carbon dioxide is also present and relevant during the reduction reactions; this agent reacts with char, gases and tars. On the other hand, if the gasifying agent is oxygen, this agent reacts within the combustion stage [31]. The main reduction reactions are shown in Equations 8, 9, 10, 11 and 12 [21], [28], [29], [32]:

Methane formation	$C + 2H_2 \rightarrow CH_4$ (-75 MJ/kmol)	Equation 8
Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$ (-41 MJ/kmol)	Equation 9
Boudouard	$C + CO_2 \leftrightarrow 2CO$ (+172 MJ/kmol)	Equation 10
Methane reforming	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$ (+206 MJ/kmol)	Equation 11
Char reforming	$C + H_2O \rightarrow H_2 + CO$ (+131 MJ/kmol)	Equation 12

The reduction reactions produce mostly methane, hydrogen, carbon monoxide, and carbon dioxide. The main reduction reactions are Boudouard and char reforming reactions [23]. At low gasification temperatures (above 700 °C and below 1000 °C) the Boudouard reaction is the controlling reaction in the reduction stage, with the heterogeneous reaction of char and carbon dioxide, producing the most significant amount of carbon monoxide [33]. The Boudouard and char reforming endothermic reactions together are responsible of the production of hydrogen at high temperatures (also produced by the water gas shift reaction) and carbon monoxide, and the decrease of the producer gas temperature during the reduction process. The water-gas shift reaction increases the H_2/CO ratio but does not affect directly the heating value of the producer gas [31].

Nevertheless, the overall gasification process also produces by-products such as nitrous oxides, sulfur dioxide and tars. Tar is the highest obstacle in biomass gasification and its utilization for energy generation applications, as tar particles in the producer gas reduces the gasification process efficiency. Tar formation can be controlled or reduced with an adequate temperature operating conditions; temperatures of 900 °C in the reduction zone reduce the production of tar particles [26]

The reactions stated above are the main reactions that produce the most significant amount of carbon monoxide, carbon dioxide, methane and hydrogen, however, there are more than fifty gasification reactions in a gasification process due presence of other species and elements in the raw biomass and the gasifying agent, such as nitrous oxides, sulfur oxides, considering that nitrous and sulfur oxides are strong air pollutants [34].

1.2.3. Gasification parameters

Biomass gasification and the properties and quality of the produced gas highly depends on the operational conditions of the gasification process, the main parameters that affect the gasification process are; the type and characteristics of the biomass, gasification temperature, gasifying agent, equivalence ratio, reactors pressure, particle size and superficial velocity [23].

1.2.3.1. Effect of temperature

Temperature affects the production rate of char, tar, and gases in the gasification process, as temperature directly affects the equilibrium reactions, it has been shown that an increase in the gasification temperature increases the producer gas yield and decreases the tar production [22]. Taking into account the impact of the gasification temperature in the producer gas, the first requirement to take into account is an accurate control to keep a constant and stable gasification temperature during the whole process [35].

Lower or higher gasification temperatures have different inputs in the gasification process, if the objective of the process is to reach higher efficiency, lower temperatures (600 – 700 °C) favor the systems efficiency, but high temperatures favor the gas yield (increasing mostly the hydrogen production) and reduce the tar and char production. Increasing the systems temperature favors the products in the endothermic reactions (Boudouard, Methane reforming, Char reforming), resulting in a higher production of hydrogen and carbon monoxide [31].

Gasification with air at temperatures from 700 °C to 900 °C promote hydrogen and carbon monoxide production and decrease methane and carbon dioxide production, biomass gasification with steam at temperatures from 700 °C to 850 °C increase the hydrogen and carbon dioxide yield [36], while decreasing the carbon monoxide and heating value of the producer gas. Air-steam gasification has shown in some researches a decrease in the gas heating value when temperature is increased over 800 °C [23] and below 1000 °C. The H_2/CO increases for air steam gasification, while the CO/CO_2 ratio decreases. Compared to gasification at temperatures higher than 1000 °C, at lower temperatures the reaction rate is slower and the residence time is longer [31], while at the same time tar and volatiles may condense and deposit and clog in the pipelines [37].

Different research has shown that increasing the gasification temperature to 1000 °C increases the hydrogen, carbon monoxide and methane concentration, hydrogen increased from 10 vol% to up to 38 vol%, methane increased from 5 vol% to up to 14 vol% and carbon dioxide decreased [21]. As endothermic reactions products increase with temperature, carbon monoxide and hydrogen production keeps increasing while thermal cracking and steam reforming decrease tar production [37]. At temperatures higher than 1200 °C gasification produces almost no methane and the reactions shift to combustion reactions.

1.2.3.2. Effect of gasifying agent

The most common gasifying agents used in gasification are air, oxygen, steam, carbon dioxide and mixtures, which directly affect the heating value of the producer gas. From all the gasifying agents, air is the most widely used, as it is the less expensive and does not produce high concentrations of tars and chars, nevertheless, the heating value is considerable low (4 – 7 MJ/kg) and the producer gas has a high concentration of nitrogen (over 50 vol%) and therefore lower concentration of the other species (hydrogen 11-17 vol%, carbon monoxide 21-24 vol%, up to 13 vol% of carbon dioxide and up to 3 vol% of methane [22], [38], [39] .

Steam is also often used as a gasifying agent, contributing to three of the most relevant reduction reactions and to a higher production of hydrogen and a high heating value producer gas (10 – 18 MJ/kg). Gasification with steam requires an external heat supply (or to be mixed with oxygen) and can increase the production of tars.

Using pure oxygen as the gasifying agent is rather expensive and requires higher safety precautions, even though this gasifying agent achieves higher temperature gasification and a high heating value producer gas (12 – 28 MJ/kg). Using carbon dioxide produces high concentrations of hydrogen and carbon monoxide but also requires an external heat supply [23].

It has been observed that gasification with gasifying agent mixtures such as air and steam can significantly increase the concentration of hydrogen and carbon monoxide in the producer gas, reaching from 63-72 % of H_2 and CO with air- steam gasification, compared to 52-63 % with only air [40]. Even though steam contributes to the production of hydrogen and carbon monoxide in the producer gas, an excessive supply of steam can produce losses in energy due to external heating requirements and lower the reaction temperatures, favoring the reactants in the main endothermic reduction reactions [21].

1.2.3.3. Equivalence ratio

The equivalence ratio (ER) is one of the most important parameters in gasification, which affects the gasification performance, the producer gas composition, heating value and efficiency. The equivalence ratio represents the ratio between gasifying agent and biomass under the gasifier operation conditions compared to the same ratio under stoichiometric conditions (complete combustion). The equivalence ratio determines the temperature of the system, the availability of oxygen, the producer gas yield and the tar content. A high equivalence ratio results in a higher gas production yield and a lower low heating value in the producer gas [22], making it necessary to search for the most adequate equivalence ratio for each gasification system, as the gas production and the heating low value are inversely affect by the equivalence ratio. An equivalence ratio close to 1 is closer to a combustion process and produces then a product with high carbon dioxide concentration, while a low equivalence (lower than 0.1) is similar to a pyrolysis process and produces hydrogen and carbon monoxide and char and a low gas yield [23]. Increasing the equivalence ratio decreases the system's efficiency, as more gasifying agent will be used for the same amount of fuel [41].

The equivalence ratio ER is expressed as (Equation 13 and Equation 14):

$$ER = \frac{r_{air-fuel\,(operational)}}{r_{air-fuel\,(stoichiometric-complete\,combustion)}} \text{ [35]} \qquad \text{Equation 13}$$

$$r_{air-fuel} = \frac{mol\ of\ gasifying\ agent}{mol\ of\ fuel} \text{ [35]} \qquad \text{Equation 14}$$

The equivalence ratio has been proved to affect the char and tar production. When increasing the ER in air gasification, the hydrogen concentration increases, while the production of methane and carbon monoxide decreases and the total gas production increases [21].

1.2.3.4. Pressure

Gasification can be operated at atmospheric pressure or as a pressurized system. The reaction rate and the composition of the producer gas are affected by the gasifiers' operational pressure. While high pressure reduces tar formation and favors the production of some gas species such as methane, the gasification cost is negatively affected [23]. Having a pressurized gasification allows having a pressurized producer gas which favors future energy production applications in internal combustion equipment such as gas engines and turbines [35]. Some research has found that gasification with pressurized cycles combined with producer gas cleaning record efficiencies higher than 40 %, which makes the technology commercially competitive compared to other energy conversion technologies [42].

1.2.3.5. Superficial velocity and residence time

Superficial velocity directly affects the time for reactions to occur, the producer gas energy content, the biomass consumption and the yield of producer gas and other products (tar, char) [23]. Superficial velocity can be defined as the producer gas flow rate divided by the internal cross sectional area of the reactor (Equation 15).

$$SV\left(\frac{m}{s}\right) = \frac{producer\ gas\ flow\ rate\left(\frac{m^3}{s}\right)}{gasifier's\ internal\ area\ (m^2)} \qquad \text{Equation 15}$$

Low superficial velocity values in biomass gasification result in a slow pyrolysis process and thus a high production of unburned chars and tars. On the other hand, high superficial velocities produce a fast pyrolysis which decreases the residence time of the producer gas in the reactor and affect the tar cracking process [22].

The reactor's superficial velocity and residence time measure the same parameter, which is the period of time that the biomass particles stay in the gasifier. The residence time is related with the superficial velocity and the reactor's height (internal height where the reactions occur). The residence time must assure that the gasification reactions occur, which depends on the type of gasifier, considering fixed bed gasifiers the ones with the longest residence times, while entrained flow gasifiers have the shortest residence times (1-2 s) [35].

1.2.3.6. Particle size

Biomass samples to be gasified must be within the proper size to achieve the fullest reactions possible and maintain a constant consumption rate in the reactor. The biomass particle size affects the producer gas composition and quality. Biomass with considerably small particle size (<0.3 mm) can cause blockage in the reactor's feeder, moreover, small particles have higher heat transfer with the reactor, causing faster reactions with lower temperatures [22]. Bigger size particles present slower reactions increasing the reaction time and requiring higher temperature reactions. The sphericity parameter has been used in biomass gasification to describe the shape of the biomass particles, considering spheres of the same volume of the particle and its similarity to a perfect sphere. Particles with similar shapes to spheres have the greatest heating transfer with the reactor. Some studies have found ratios of particle size and reactor internal diameter, such as Dogru [43], which considers a particle size of one eight of the reactor's internal diameter.

Some studies [44] have shown that small particle sizes produce more carbon monoxide, hydrogen and methane. The hydrogen yield has shown a decrease when particle size increases (>0.5 mm), causing a decrease higher than 20 vol% in hydrogen production. Nevertheless the relationship between low heating value *(LHV*) of the producer gas and particle size is not certain, as the highest *LHV* have not been correlated to particle size in all studies, some show a greater heating value with medium particle size (0,3-0,5 mm) while others found an increase in the *LHV* when increasing the particle size [45]. Smaller particles have a greater contact area with the gasifying agent and produce higher producer gas yields and lower char and tar production [21]. Large particles produce more char and tar, as the surface temperature of the particle is higher than the core temperature affecting the gasification reactions.

1.2.4. Indicators

The efficiency of a gasifier and a gasification process depends on the conversion of biomass to producer gas. To evaluate a gasifier and the biomass conversion process there are different parameters to take into account, including the Specific Gas Production (*SGP*), the Carbon Conversion Efficiency (*CCE*) and the Cold Gas Efficiency (*CGE*) [22]. The *SGP* rates the syngas flow *(Q_{gas})* at wet gas, dry gas or dry ash free gas and the biomass fed to the reactor as following (Equation 16):

$$SGP\left(\frac{Nm^3}{kg}\right) = \frac{Q_{gas}\left(\frac{Nm^3}{h}\right)}{m_{biomass}\left(\frac{kg}{h}\right)}\ \text{[22]}$$

Equation 16

The *CCE* rates the gas species containing carbon leaving the gasifier *(CO, CO_2, CH_4*, etc.) and the carbon entering the system (Equation 17), where *xi* is the mole fraction of products containing carbon and y_c is the carbon mass fraction of the biomass.

$$CCE = \frac{Q_{gas}\,\Sigma_{i=1}^{n} x_i}{m_{biomass}\,y_c}\ \text{[22]}$$

Equation 17

The *CGE* is used to express the chemical energy leaving the reactor and the chemical energy entering the system. The energy content of the producer gas (energy leaving the system) is expressed with the low heating value (*LVH*), while the energy entering the system is related to the biomass *LHV* (Equation 18).

$$CGE = \frac{Q_{gas}\,LHV_{gas}}{m_{biomass}\,LHV_{biomass}}\ \text{[22]}$$

Equation 18

An important indicator is the contaminants present in the producer gas, such as tars, heavy metals, particulate matter and other gases such as hydrogen sulfide, sulfur dioxide, nitrogen oxides and hydrogen chloride.

1.2.5. Types of gasifiers

There are different ways to classify gasifiers (Figure 3) based on parameters such as gasifying agent, heat source, design and pressure. Based on the gasifying agent, a gasifier is classified by the type of gas species that uses in the different stages, the main gasifying agents are mentioned before. Auto-thermal gasifiers involve exothermic chemical reaction as heat sources for the process, while Allo-thermal gasifiers involve heat transfer from an external source to the reactor. Based on design, there are fixed bed, fluidized bed and entrained flow gasifiers, each type having subtypes of designs. Gasifiers are also classified on the operational pressure conditions inside the reactor, having atmospheric of pressurized gasifiers [22].

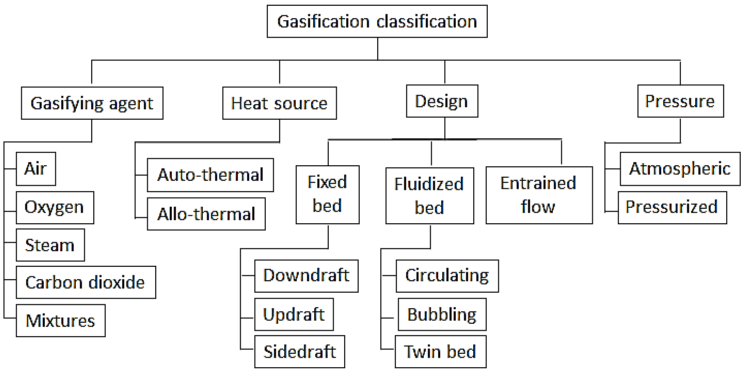


Figure 3. Classification of biomass gasification technologies based on gasifying agent, heat source, design and pressure (Based on [22])

1.2.5.1. Fixed bed

Fixed bed gasifiers are the most simple in design and among the most common used type of gasifiers, operating at temperatures of 1000 °C or lower. The simple design of fixed bed gasifiers consists of a bed of solid fuel particles reacting with a fed-in gasifying agent, an exhaust outlet for producer gas, and a unit for ash collection and filtering systems for the producer gas. Fixed bed gasifiers operate at atmospheric or pressurized conditions (2.5-3.0 MPa), have the most simple construction, made of concrete or steel, operate at low superficial velocities, therefore with long residence times, but produce a high carbon conversion. Nevertheless, fixed bed gasifiers produce high amounts of tars and are more suitable for small scale power generation. There are three types of fixed bed gasifiers, downdraft, updraft and sidedraft [23], [26] .

Updraft gasifiers (Figure 4), also known as countercurrent gasifiers are among the oldest design used in gasification reactors. In these types of reactors the biomass is fed from the top of the reactor and the gasifying is fed at the bottom of the reactor through a grate. Biomass and gasifying agent interact in a countercurrent direction. Biomass (as tar, ashes and char) reaches the bottom of the gasifier and is held by a grate (grill), where due to the reaction with the gasifying agent, biomass is ignited and generates an increase of temperature, this is considered as the combustion or oxidation zone. The gasifying agent moves updraft transferring heat from the combustion zone and interacting with biomass in a way that the biomass entering the reactor gets dried (drying zone), the devolatilized (pyrolysis zone) and then reduced (reduction zone). Updraft gasifiers accept biomass with considerably high moisture content (up to 60 %) and high ash contents (up to 25 %).

In updraft gasifiers the producer gas comes out of the gasifier at a low temperature and therefore does not take much heat from the process, increasing the efficiency of these reactors, moreover, updraft gasifiers present a small pressure drop. Nevertheless as it is a fixed bed reactor the tar production is high, the moisture content is high, the startup time is high, and it can present a poor reaction capability. These types of gasifiers are suitable for applications where high flame temperature is required and a moderate amount of dust in the producer gas is allowed [23], [26], [22], [35], [46].

Downdraft gasifiers (Figure 4), also known as co-current gasifiers are gasifiers in which the gasifying agent and the solid fuel interact in the same direction. There are two types of downdraft gasifiers, open and close top design. Open top gasifiers or stratified gasifiers present an open top where air is forced to move downwards with a homogeneous air flow through the reactor, increasing the thermochemical conversion efficiency. Open top gasifiers are convenient for small particle size and low density solid materials. Closed top gasifiers have either a straight cylindrical reactor or a throated section in the reactor core. In straight cylindrical closed top gasifiers all the reactor zones present the same internal diameters, while for throated closed top gasifiers, the throat located in the combustion zone presents nozzles around its smaller diameter where the gasifying agent is supplied. Throated gasifiers present the advantage of decreasing tar production and are suitable in small scale applications, as for larger scales the temperature and flow is not uniform in these gasifiers [23], [22], [35], [47].

Downdraft gasifiers produce producer gas at high temperature (between 900 °C and 1000°C) which reduces the thermal efficiency of the process. Moreover, the suitable types of biomass for downdraft gasifiers must contain 25 % of moisture or lower, likewise for ash contents, as downdraft gasifiers operate with difficulties with high ash content solid fuels [23]. In small scale generation applications, the gases obtained present low particulate and tar content, as the main gas species produced are carbon dioxide, water, carbon monoxide and hydrogen [26]. An advantage of downdraft gasifiers is the possibility of eliminating up to 90 % of the tars produced and removing ashes and dust with the unreacted char located in the lower end of the reactor [46]. Downdraft gasifiers present shorter residence times as particles move faster due to gravity, but a lower carbon conversion is achieved compared to updraft gasifiers [31].

Sidedraft gasifiers (Figure 4), also known as cross-flow or crossdraft gasifiers have a different configuration from downdraft and updraft gasifiers, as biomass is introduced at the top of the gasifier and falls downwards, while the gasifying agent enters from one side and the producer gas exits form the opposite side. This special arrangement causes the gasification zones to be in a different configuration, where drying occurs the on the side, partial combustion occurs in front of the gasifying agent feed area, while pyrolysis occurs around the combustion zone and reduction occurs after the combustion zone, close to the producer gas exit area. Partial combustion occurs at considerably higher temperatures (>1500 °C) than combustion in downdraft and updraft gasifiers. Sidedraft gasifiers present optimal operation conditions, producing high temperatures in small volumes, with low ash content solid fuels and low tar producer gas, present a fast response, meaning a short start up time. Nevertheless, in sidedraft gasifiers the producer gas exits at temperatures between 800 °C and 900 °C, reducing the thermal efficiency, while the gasifier is not capable of operating with small particle side solid fuels. These types of gasifiers have few applications and are not commonly used [23], [26], [22].

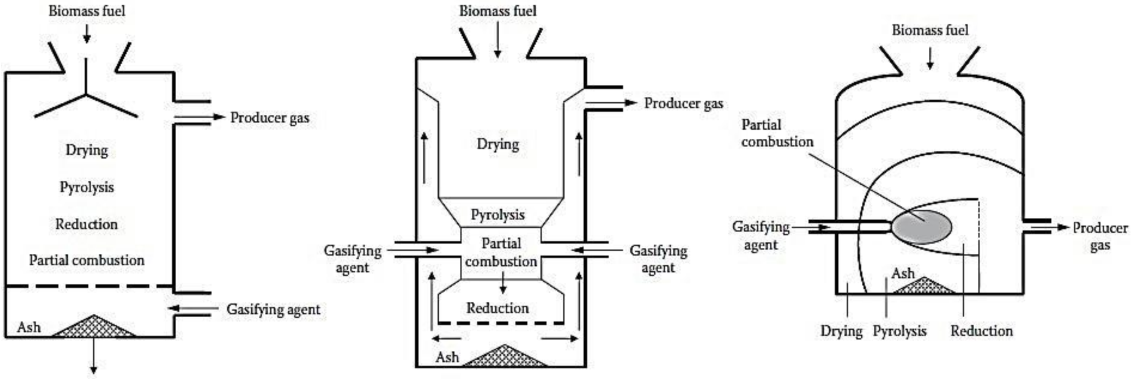


Figure 4. Fixed bed gasifiers; (Left) Updraft, (Center) Downdraft, (Right) Sidedraft. (Taken from [23])

1.2.5.2. Fluidized bed

Fluidized bed gasifiers are used in biomass and coal gasification, operating based on the principle of fluidization, where the solid fuel and a bed made of an inert solid behave as a fluid when the gasifying agent is forced through the solid particles inside the reactor and gets mixed with the feedstock particles, suspending the bed and fuel particles as the gasifying agent flows from the bottom of the reactor. The fluidization and the high temperature of the inert bed enhances the heat transfer between the fuel particles and the reactor, rapidly increasing the temperature of the solid fuel and enabling the gasification process to operate at isothermal conditions for medium to large scale generation, having operating temperatures from 800 °C to 900 °C [21], [23], [26], [48].

The relatively low operating temperature and short residence time cause gasification reactions to not achieve chemical equilibrium, decreasing the hydrocarbon production, but having up to 95 % carbon conversion. Silica, sand, and glass beads are the most commonly used inert beds in fluidized bed gasifiers. Nevertheless the inert particles are likely to react with inorganic components of the solid fuel and form adhesive layers that bind the fuel particles and causes agglomerates which stop the fluidization process. Moreover, char and tar reduce the quality of the producer gas and leads to malfunctioning of the reactor. There are three main types of fluidized bed reactors, bubbling bed gasifier, circulating bed gasifier, and twin bed gasifier [35], [46].

Bubbling bed gasifiers (Figure 5) present solid fuel gasification under high pressure with fluidized gasifying agents as a medium, which pass through the reactor and its inert bed. There are two different phases present in this type of reactors, a dense phase in the bottom of the reactor, consisting of a high solid content (inert bed and solid fuel), and a dilute phase in the top of the reactor. The solid fuel particles are fed, and at a certain point the friction between the particles and the gasifying agent counterbalances the solids weight causing bubbling of particles, the solid fuel goes through drying, pyrolysis, partial combustion and reduction stages rapidly and simultaneously, having short residence times and low temperatures (700-900 °C). This type of reactors present a lower carbon conversion efficiency than circulating bed gasifiers, as the particles tend to stick and oxygen is trapped in the bubbles and reduces the gasifiers efficiency. Bubbling fluidized bed reactors have cyclones attached at the exit of the reactor to recycle the inert bed material particles and collect char and ashes [2], [23], [6], [11], [14], [27].

Circulating fluidized bed gasifiers (Figure 5) are a modification of the bubbling fluidized bed gasifiers, where the solids (inert bed + char) and a high velocity gasifying agent are recycled back to the reactor through a cyclone, which separates them from ashes and tars, which are extracted from the reactor. Circulating bed gasifiers operate at higher gas velocities in a turbulent fluidization mode, reaching operation temperatures from 800 °C to 1000 °C. Compared to bubbling bed reactors, circulating bed reactors have a higher energy throughput, higher carbon conversion efficiency and a higher feed capacity. Moreover, there is no formation of bubbles, thus not trapping oxygen and having a higher efficiency than bubbling bed reactors. The exhaust gas temperature is as high as the bed temperature avoiding a high tar production, but the operational difficulty is related to low temperatures applications, such as biomass gasification, as the biomass' ashes melt at temperatures below 1000 °C, causing slagging in the reactor [21]–[23], [26], [31], [35].

Twin-bed gasification consists of two fluidized bed reactors, where solid fuels enter the first reactor and all the gasification stages occur (drying, pyrolysis, partial combustion and reduction), and the remaining unburned char is transported to a second reactor, where it reacts with air to produce heat, which is transported to the first reactor. Twin bed reactors (Figure 5) are usually composed by a bubbling bed reactor, where the main gasification takes places and a circulating fluidized bed reactor known as combustor, where unburned char is transformed into heat and supplied to the bubbling bed reactor. The heat carrier is the inert bed material, which circulates between the circulating bed and bubbling bed reactors. The gasifying agent for the bubbling bed is preheated steam at 700 °C to 900 °C, while the circulating bed reactor uses air as the gasifying agent.

These types of reactors produce a higher heat of calorific value producer gas, with negligible contents of tar and nitrogen, but with higher dust content.

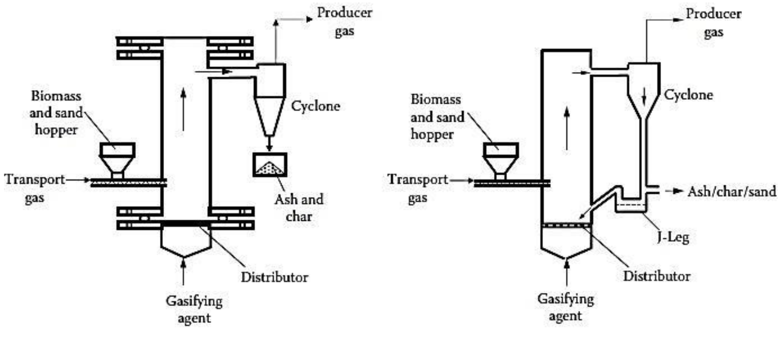


Figure 5. Fluidized bed gasifiers; (Left) Bubbling bed, (Center) Circulating bed, (Right) Twin bed. (Taken from [23])

1.2.5.3. Entrained flow

Entrained flow gasifiers (Figure 6) are reactors with large scale generation capacities, operating mostly at high pressures (2–10 MPa), using oxygen as the gasifying agent, co-currently fed with small size particles of solid fuel (<0.1-0.4 mm, or even less than 75 µm), at high temperature operation conditions (1200–1600 °C) [23]. As fuel and gasifying agent are fed co-currently, the gasifying agent entrains the fine solid particles, making a dense cloud flow through the gasifier. The high velocity of the gasifying agent entrains the particles at turbulent flows, increasing the heat transfer and rate of reactions and thus increasing the fuel to producer gas conversion rate and allowing very short residence times (of the order of a few seconds).

The high velocities, small particle size, and high temperatures produce high carbon conversion efficiencies (98-99.5 %). For these types of gasifiers, ashes and tar production are considerably low, as tars oils and other devolatilization liquids are decomposed into hydrogen and as the reactions reach temperatures above the melting point of ashes. Concerning the producer gas, it presents almost no methane or other hydrocarbons, while having high hydrogen and carbon monoxide concentrations, but low thermal efficiencies, as the producer gas exits at high temperatures. At the moment entrained flow gasifiers are most widely used especially for coal gasification, as these reactors don’t operate properly with biomass solid fuels, considering the difficulty of preparing such small size particles for fibrous woods [31], [22], [35].

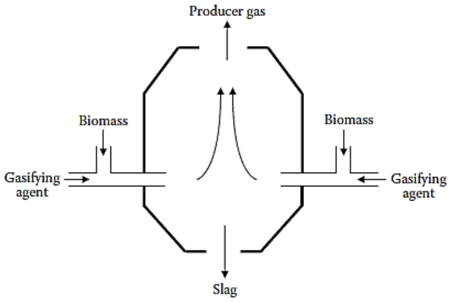


Figure 6. Entrained flow gasifier structure. (Taken from [23])

1.2.6. Challenges

Even though biomass and solid fuel gasification is well-known and used for industrial purposes, there are still some challenges required to optimize the process, decrease losses, clean the producer gas from contaminants and prevent environmental pollution. The most relevant challenges are technological barriers, producer gas impurities, biomass pretreatment and secondary equipment.

1.2.6.1. Technology and economic barriers;

Despite the existence of different types of gasifiers suitable for different solid fuels and energy requirements, more efficient gasification methods are required to increase the commercialization of the technology for industrial applications. The advantage of low cost fuel might be countered by the high initial investments, the few amount of gasification technology users, lack of standardization and proper infrastructure for the process, and lack of government policies and promotion of the technology [26]. The progress of biomass gasification and the technology related to the process depends considerably on the gasification parameters, and the characteristics and handling of the solid fuel.

1.2.6.2. Biomass moisture

Solid fuel moisture content directly affects the gasification process and the quality and composition of the producer gas. Removing excess moisture in solid fuels, especially biomass, requires a considerable amount of energy from the whole gasification process, requiring in some cases to pre-dry the fuel, which implies a reduction in the process efficiency and an increase in operation costs. Regarding the quality and composition of the producer gas, the carbon monoxide content is higher in drier biomass, while the carbon dioxide content increases with higher moisture content biomass. Biomass with higher moisture content produce a gas with a lower *LHV* [50].

1.2.6.3. Particulate matter

Solid fuels and biomass contain different minerals, some of these minerals are converted into micron size ash during gasification, and some unburned char is also converted into micron sizes. The fineness of these particles makes the separation process of producer gas and impurities more difficult, as conventional cyclones might not be able to separate particles with such a small size. Particles that are not separated into the producer gas are then present in the gas when is used for generation purposes, causing clogging and blockage if used in internal combustion engines or affecting blades if used in gas turbines. A high particle matter concentration in the exhaust gas used for energy generation might exceed the particulate matter limit in environmental regulations related to emissions [51].

1.2.6.4. Tar

Tar formation is one of the main and most challenging problems of biomass and solid fuel gasification. Tar formation is related to different gasification parameters, such as temperature, gasifying agent, and equivalence ratio and residence time. Tar formation is also affected by the type of gasifier and the secondary cleaning equipment in the gasification process. As tar as a mixture of aromatic hydrocarbons is condensable at ambient temperature, it condenses at low temperature streams of the gasifier, such as pipes and tubes. Tar causes interruptions in the gasification and generation processes, and is moreover a source of carcinogenic elements. A proper selection of the type of gasifier, configuration of the gasifier, gas cleaning and addition of catalyst, are essential to reduce and remove tar contents present in the producer gas, or to transform tar produced during gasification [35], [50], [51].

1.2.6.5. Other impurities

Ammonia is formed from the protein material plant based biomass and nitrogen containing fuels. This causes a concentration of ammonia in the producer gas, pressurized gasifiers may also facilitate the production of ammonia, which may violate environmental regulations and also be converted into nitrogen oxides, which also violate environmental regulations. Biomass also contains sulfur, which during gasification is converted into hydrogen sulfide and sulfur dioxide, which may interact with catalyst and affect processes such as tar removal. Chloride is also present in biomass, which are then converted into hydrogen chloride and are present in the producer gas, which at levels higher than 200 ppm can corrode gasification equipment. Alkali metals such as potassium and sodium are present in biomass and vaporize during gasification, these metals can deposit or adhere to different parts of the gasifier and energy generation equipment [51].

1.3. Biomass Characterization

Biomass is characterized by its physical, chemical and thermodynamic properties, which vary from difference sources and types of biomass, are measured by experimentation and calculations and affect their behavior during gasification.

1.3.1. Physical properties

Density; for solid biomass there are four different characteristic densities, true, apparent, bulk and biomass growth [52]. True density is defined as the weight per unit volume of the biomass. Apparent density is measured using the apparent volume of the biomass (porosity ε_p), including pores and internal solids. Bulk density is the density of the overall space occupied by the biomass particles as a group; it includes interstitial volume between particles, having an interstitial volume known as bulk porosity (porosity ε_b) which can be expressed as a function of the total packed volume. Biomass growth density expresses the availability of biomass per unit area of land; it is the total amount of oven-dry tons per unit area of all the above-ground organic matter of the biomass plant, including leaves, branches, bark, etc. [52].

Particle size; shape and porosity, particle size, shape of the biomass particles and porosity are among the most relevant physical properties of biomass. Particle size considerably affects the performance of the gasification process, using sizes from 10^{-6} m to 10^{-2} m, biomass is usually ground to the desired size, prior to gasification, and the particle size distribution is determined to know the distribution of particle sizes within the biomass to be gasified, the usual particle size presents a normal probabilistic curve distribution [34].

1.3.2. Chemical properties

Biomass is composed by organic and inorganic compounds, having a complex composition and molecular structure. Two main types of compositions are used to chemically characterize biomass properties; ultimate composition and proximate composition.

Ultimate analysis; the ultimate analysis or elemental analysis determines the composition of biomass from its basic elements, including carbon, hydrogen, oxygen, nitrogen and sulfur. Moisture content is not included in this analysis, meaning that the hydrogen and oxygen from moisture are not part of the composition of the ultimate analysis. Usually the sulfur content is close to zero or zero [53].

Proximate analysis; the proximate analysis gives biomass composition in other terms, including moisture content, volatile matter, ash content and fixed carbon. Volatile matter of biomass is measured when the biomass is heated as the condensable and non-condensable vapors [34].

Biomass usually presents high moisture contents, having biomass types with moisture as high as 90 %. Nevertheless for gasification, the biomass used has 35 % or lower moisture contents, as high moistures severely affect gasification efficiencies due to all the energy used for evaporation of moisture [53].

1.3.3. Calorific value

Biomass usually has a low heating value due to its low density compared to other solid fuels such as coal. For biomass, the gross calorific value *(HHV*) is defined as the amount that is released by a unit of mass or volume once it is completely combusted and the products have reached back ambient temperature (25 °C). Net calorific value (*LHV*) in biomass is defined as the heat released in a full combustion of biomass without considering the heat of vaporization of water which is not recovered. In gasification, the producer gas exits at high temperatures, where condensation processes don’t occur and the heating value of vaporization of water vapor is not recovered. Low and high heating values are related through moisture content*,* hydrogen percentage and latent heat of steam [52], [53].

1.4. Wood species available for thermochemical conversion

Estonia is a country with over 50 % of the territory covered with forest (2.3 million hectares), having pine, birch spruce and alder as the most common tree species [54]. The Estonian forestry Development Program sets the goals for protecting and safeguarding the productivity and viability for forests, stating that 74.4 % of the available forest is considered commercial, while the remaining 25.6 % is protected forest [55]. From the 2.3 million forest hectares, around 32.57 % are pine, 29.97 % Birch, 17.35 % spruce, 5.78 % aspen, 3.50 % Common Alder and 9.15 % Grey Alder [5]. The woody biomasses used and studied in this thesis are spruce, alder and pine

Norway spruce (Picea abies) is a tree species of the pine family (Pinaceae), characterized by being large trees, from 20 to 60 m high, with a conical form. This tree species is found in the northern latitudes of the world and boreal ecosystems with subarctic climates, including Estonia, with over 399 thousand hectares of Spruce.

Grey Alder (Alnus Incana) is a tree species of the Birch family (Betulaceae), characterized by being medium sized trees with heights of up to 30 m. This tree species is found in most of Europe, but also southwest Asia and northern Africa, it grows in wet environments, including around 210 thousand hectares of alder in Estonia.

Scots pine (Pinus sylvestris) is a tree species of the pine family (Pinaceae), characterized by being medium sized trees with heights of up to 35 m and 1 m trunk diameter. This tree species is found in western Eurasia, Western Europe and eastern Siberia. There are around 749 thousand hectares of pine in Estonia. Table 1 shows the main composition on dry basis for spruce, alder and pine and the calorific value based on previous research, while Table 2 shows the biochemical composition.

Table 1. Ultimate, proximate analysis and calorific value overview for spruce alder and pine [60-62]

Biomass	Ultimate analysis [wt%]					Proximate analysis [wt%]			Calorific value [MJ/kg]	
	C	H	N	S	O	Ash content	Fixed carbon	Volatile matter	LHV	HHV
Spruce [56], [57], [58]	47.31-48.25	5.87-6.30	0.07-0.35	0.04-0.05	44.55-46.20	0.20	10.20	89.60	17.51-17.93	18.80-19.26
Alder [56], [59]	48.27-49.55	6.02-6.06	0.13-0.30	0.05-0.07	43.78-45.11	0.40	12.55	87.10	17.98	19.30
Pine [60]	50.87-51.58	5.78-6.27	0.06-0.18	0.01-0.04	51.58-42.32	0.23-1.03	14.07-17.14	81.83-85.70	19.10-19.30	20.47-20.56

Table 2. Biochemical composition overview for spruce, alder and pine

Biomass	Cellulose [wt%]	Hemicellulose [wt%]	Lignin [wt%]
Spruce [56], [61], [62]	41.10-52.00	8.00-26.50	26.00-28.00
Alder [56], [62]	32.20-38.60	23.50-33.10	24.80-28.10
Pine [62]	42.00-45.00	23.50-27.50	25.00-27.80

2. MATERIALS AND METHODS

This section includes all the methodology followed to carry out the experiments, including the biomass characterization, a description of the gasification system used and the fine-tuning done before experiments, the calibration of the gas analysis systems, the calculations required for the air to fuel ratio and producer gas sample concentrations, and lastly, the parameters and experimental methodology followed during the experiments.

2.1. Biomass characterization

Samples of Norway Spruce, Grey Alder and Scots Pine were collected to be characterized through ultimate analysis, proximate analysis and calorific value as a part of a collaborative project of the Fuel and Air Analysis (Stationary Sources of Air Emissions) and Thermal Testing Research Group of the Department of Energy Technology at the Tallinn University of Technology. The characterization experiments were executed by members of the research group following the ISO standards stated in the Estonian Centre for Standardization [63]. For this purpose, the wood samples were separated into bark and wood for further analysis and ground, as can be seen in Figure 7.

Figure 7. Ground Grey Alder Sample

The elemental analysis was made according to the EVS-EN ISO 16948:2015 standard for Solid Biofuels Determination of total content of carbon, hydrogen and nitrogen, using a Vario Macro elemental analyzer. Sulfur and Chlorine were determined using the EVS-EN ISO 16994:2015 for Determination of total content of sulfur and chlorine (ISO 16994:2015) with a Dionex ICS-1000 Ion Chromatography System. Table 3 shows the results for the ultimate analysis for the three biomass samples. As seen on Table 3, there is no significant variation in the elemental composition of the biomass samples studied.

The proximate analysis for analytical moisture content was made according to the EVS-EN ISO 18134 standard for the determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method (ISO 18134-2:2017), using Memmert and Nabertherm RT120 drying ovens. To determine the ash content the EVS-EN ISO 18122 standards for Solid biofuels - Determination of ash content (ISO 18122:2015) was implemented, using a Nabertherm L9 Muffle furnace. The results for the three biomass samples can be seen on Table 3. The moisture content is lower than 25 % for all the samples, making them proper for gasification experiments [23], so are the low ash content levels.

The calorific values determined were gross calorific value in dry basis and net calorific value. These properties were determined using the EVS-EN ISO 18125 for Solid biofuels - Determination of calorific value (ISO 18125:2017), using IKA 2000C and IKA 5000C Calorimetric systems. Table 3 shows the results for the three biomass samples. There are also no significant variations in the calorific value of the biomass samples studied.

Table 3. Ultimate, proximate analysis and calorific value overview for spruce alder and pine results

Biomass	Ultimate analysis [wt%]					Proximate analysis [wt%]		Calorific value [MJ/kg]	
	C	H	N	S	O	Analytical moisture	Ash content	LHV	HHV
Norway Spruce	50.33	6.62	0.06	n.d.	42.69	6.87	0.29	18.61	20.04
Grey Alder	49.89	6.55	0.21	n.d.	42.99	7.59	0.35	18.52	19.95
Scots Pine	50.12	6.59	0.19	n.d.	43.09	8.47	0.33	18.35	19.79

2.2. Batch reactor set up

2.2.1. Batch reactor

For the gasification experiments with spruce, alder and pine a prototype fixed bed reactor was used from the laboratories at the Department of Energy Technologies at the Tallinn University of Technology. The gasification system was fine-tuned and modified for gasification experiments. As seen in Figure 8 and 9 the system is composed by a reactor, gasifying agent supply and mass flow and temperature controllers, gas cleaning and cooling system, and a gas analysis system, composed by Fourier Transform infrared Spectroscopy (FTIR) equipment, and Gas Chromatography (GC) equipment.

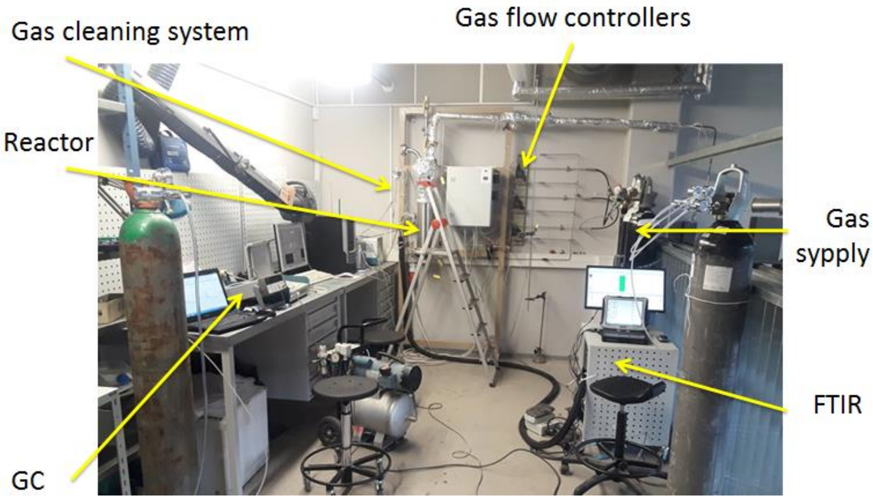


Figure 8. Fixed bed gasifier system arrangement

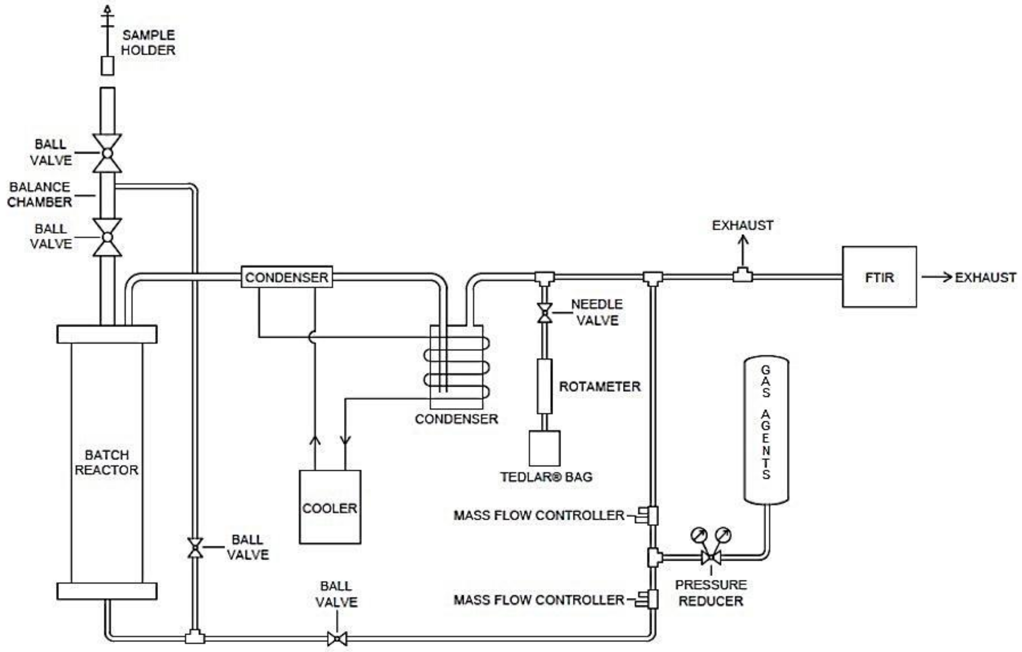


Figure 9. Gasification system set up (Modified from [64])

2.2.1.1. Reactor

A batch reactor was used (Figure 10), which consists of a quartz glass covered by a cylindrical internal heater, covered with thermal insulation and the reactor main body. A sample of biomass (around 1.5 g) is placed in a sample holder (Figure 11), which is introduced into the reactor through the top, which has two valves that create an equilibrium chamber before the sample enters the reactor. Once the sample is inside the reactor, it its heated with the internal heating system, while the gas agent (N_2+O_2) is fed at the bottom of the reactor, and the producer gas exits the reactor at the top exhaust. The reactor exhaust, the gas input and the reactor covering lids are heated with external heating tapes (150 °C) to avoid condensation inside the reactor. The reactor's diagrams can be seen on Figure 10.

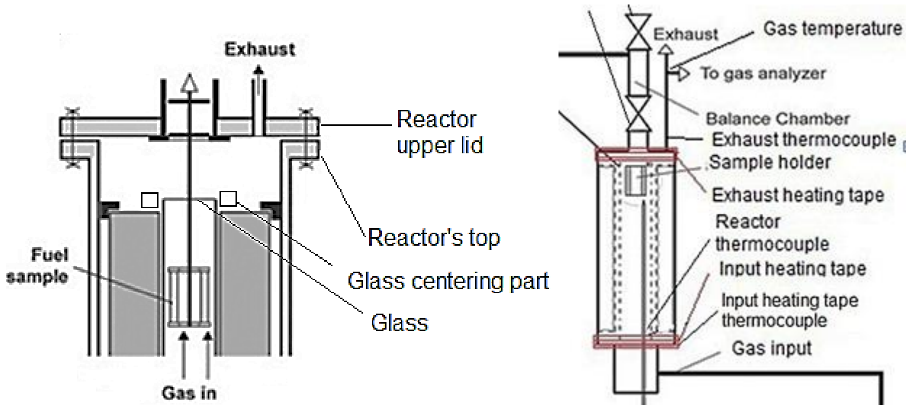
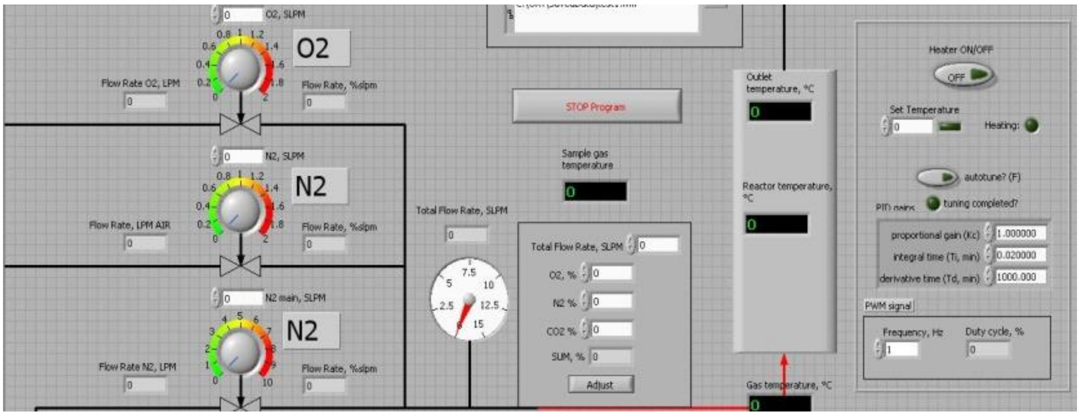


Figure 10. (Left) Top of the reactor configuration. (Right) General Reactor configuration

Figure 11. Biomass ample holder fed into the reactor

2.2.1.2. Controlling

The overall controlling of the system is done using LabView software, a set of thermocouples and mass flow controllers for the gas agent flow. The system has 4 type K thermocouples measuring; room temperature, reactor's internal heater (internal temperature) and upper and low heating tapes. Each heating element has a thermocouple that is set so that LabView reads the temperature measurements and controls the heat supply to keep a constant temperature in the system. The interface (Figure 12) allows choosing a set temperature for the internal heater, and a set temperature for the heating tapes.



O2, SLPM 0
Flow Rate O2, LPM 0
Flow Rate, %slpm 0
N2, SLPM 0
Flow Rate, LPM AIR 0
Flow Rate, %slpm 0
N2 main, SLPM 0
Flow Rate N2, LPM 0
Flow Rate, %slpm 0
Total Flow Rate, SLPM 0
Sample gas temperature 0
Total Flow Rate, SLPM 0
O2, % 0
N2 % 0
CO2 % 0
SUM, % 0
Outlet temperature, °C 0
Reactor temperature, °C 0
Gas temperature, °C 0
Set Temperature 0
Heating:
autotune? (F)
tuning completed?
proportional gain (Kc) 1.000000
integral time (Ti, min) 0.020000
derivative time (Td, min) 1000.000
Frequency, Hz 1
Duty cycle, % 0

Figure 12. LabView interface for controlling reactor's temperature and gas agent flow

There are two gases supplied to the gasifier, nitrogen and oxygen, the mass flow of these gases is controlled by three Alicat Scientific Mass Flow controllers, with an output voltage of from 0-5 V AC and a gas flow control from 0 to 5 SLPM. One flow controller for oxygen and one for nitrogen that are supplied to the reactor gas input, and one mass flow controller for nitrogen, supplied before the FTIR input, to dilute the producer gas with nitrogen so that the FTIR can measure properly. High concentrations of some gases can affect the performance of the FTIR, plus the FTIR needs a gas supply of 3 SLPM or higher. For this reason the FTIR gets a mix of the gas produced in the reactor (0.3 SLPM) and a nitrogen dilution of 3.3 SLPM. The gas agent mass flow is set through the LabView interface, which controls the mass flow controllers output with a precision of ±0.8 %.

2.2.1.3. Gas cleaning and cooling;

The liquid and gaseous products of the gasification process exit the gasifier through the reactor's gas output. This output is connected to a cooling system (Figure 13), which condenses and removes the volatile components (tars and oils) from the producer gas. The cooling system consists of 2 condensers, which are cooled down with a CoolCare refrigeration system that supplies cold water (4 to 6 °C) that cools down the producer gas through heat exchange. The gas passes through the condensers, which also have wool inside that absorbs the volatiles; this wool is constantly replaced after every experiment. After the gas is cleaned, one part of the gas goes to a rotameter, which can be connected to Tedlar bags to get gas samples for the Gas Chromatography. Another part of the gas is diluted with nitrogen and goes through a heating hose to the FTIR for its analysis.

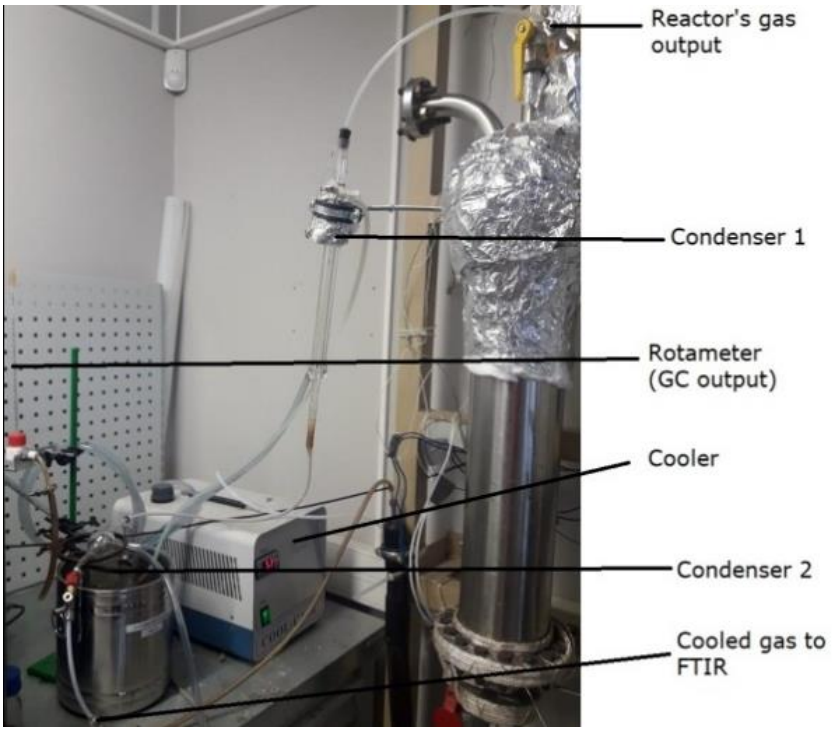


Figure 13. Cooling system

2.2.1.4. Gas analysis system;

The system counts with two gas analysis devices, a Gas Chromatography (GC) analyzer and a Fourier transform Infrared Spectroscopy (FTIR) analyzer. The producer gas is supplied to the GC through Tedlar bags that can be connected to the rotameter located after the cooling system, for each experiment the Tedlar bag is connected once gasification starts, and disconnected once its finished, having then a gas sample of the overall gasification process. For the FTIR, the gas diluted with nitrogen is constantly fed during the experiment through the cooling system output, once the gas exits the cooling system and its diluted, it enters a heating hose that heats the gas to 180 °C, which is the set temperature required for the gas to enter the FTIR.

The FTIR equipment installed was a Calcmet DX4000 gas analyzer, which measures in real time the absorption spectrum of H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, CH_4, HCl, HF and other organic compounds. The measurement time was set for every 5 s. The FTIR was used to control the overall progress of the reactions by checking the concentration of Total Organic Carbon (*TOC*), O_2 and CO. The analyzer displays the results in the Calcmet software for further analysis.

The GC equipment installed was a Gazohrom 3101 gas analyzer that measures the thermal conductivity of H_2, CO, CH_4, CO_2 *and* O_2. The gas sample from the Tedlar bag is supplied through syringes to the GC. The GC uses two carrier gases air and argon; air is used to detect H_2, CO and CH_4, which is supplied by a compressor (6 – 7 SLPM). For detecting CO_2 and O_2 the GC uses an argon canister which supplies 4 SLPM of carrier gas. The changes in the thermal conductivity of the carrier gases display the concentration of each gas species. This conductivity change (current change) over time is displayed in the Keysight Benchview software, and the area under the curve is the analyzed gas composition. Each carrier gas requires separate samples and measurements with the syringe.

2.2.2. Maintenance and set up

In order to start gasification experiments with the reactor, an overall maintenance and set up was done, which included modifications in the reactor, sensors and controlling, heating tapes and thermal insulation and condensation equipment.

Reactor; The reactor major modifications were as following:

- Installation of the heating tapes to avoid condensation on the reactor and reactor exhaust; a 3 m, 15 mm, 126.6 Ω heating tape and a 2.4 m, 18 mm, 112.9 Ω heating tape, to operate at 150 °C.
- Thermal insulation covering for the top of the reactor end exhaust pipes
- The reactor’s cleaning included; heating to 1000 °C using oxygen to remove remaining volatiles, removal of oil tars and chars from the top of the reactor and the exhaust pipes and the bottom of the reactor.
- A new quartz glass and a new sample holder replaced the previous ones.
- The internal heater was disassembled, and the connections were replaced. The thermal insulation covering the internal heater was replaced. The heater connections were insulated with ceramic tubing to avoid short circuits.

Controlling and LabView software; the reactor's temperature controlling was checked with a different thermocouple, the temperature was correct with an error of around ±10 °C at 750 °C.

- The gas flow rate was checked with a rotameter, while also verifying the conditions of the input gas delivered by the flow controllers.

Tars and oil condensation equipment; the cooling equipment as well as the rotameter were disassembled and cleaned with acetone until there were no remains of oils in the inner walls. This cooling system was designed and installed by another member from the Energy Department [64].

2.2.3. Gas analysis and calibration

For the FTIR, the equipment was installed but had been already calibrated before, the background of the FTIR was checked every day there were experiments, with a 3 SLPM flow of N_2. As for the GC equipment, it was installed and calibrated for the detection of H_2, CO, CH_4, CO_2 and O_2. The GC calibrations were done separately for the gases that are detected using air as a carrier (H_2, CO and CH_4) and the ones that use argon as a carrier (CO_2 and O_2). The calibration conditions were the following:

- Sample size in GC → 2 ml (maximum sample size in the GC for detection), inserted with a syringe.
- Gases calibrated → H_2, CO, CH_4, O_2, CO_2.
- H_2, CO and CH_4 were calibrated individually with air at 6 – 7 SLPM.
- O_2 and CO_2 were calibrated together with argon at 4 SLPM.
- The calibrations were done by inserting different concentrations of each gas.
- Each gas concentration for the calibration was measured 3 times with a different syringe sample.
- The concentrations for H_2 and CH_4 were 100, 25, 10, 5 and 1 vol% (2, 0.5, 0.2, 0.1 and 0.02 ml samples).
- The concentrations for CO were 25, 12, 3, 1.5 and 0.05 vol% (0.5, 0.24, 0.059 0.029 and 0.001 ml samples).
- The concentrations for O_2 and CO_2 were 75, 50, 25, 12.5, 5, 2.5 and 1 vol% (1.5, 1, 0.5, 0.25, 0.1, 0.05 and 0.02 ml samples).
- The Keysight Benchview software displays the changes in thermal conductivity over time in the carrier gases air and argon, which are delivered to the software as current changes over time. These data was stored in excel for the calibration. Figure 14 shows the peaks detected for the different gases.

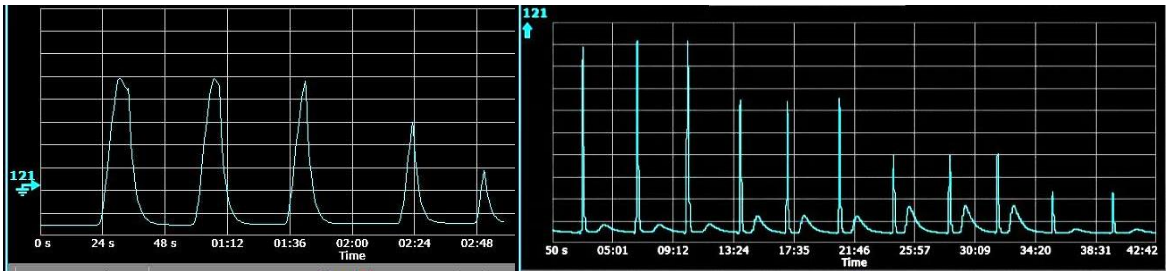


Figure 14. (Left) Detection chart for independent samples of H_2, CO and CH_4. (Right) Detection chart for O_2 and CO_2 samples, high slim peaks for O_2, and low wider peaks for CO_2

- Once the calibration data was transferred to excel, the area under the curve of each peak detected was calculated.
- A linear relation was established between area under the detected peaks and the gas composition (composition in vol% as a function of the area under the peak). See Table 4 for the calibration of CH_4 as an example.
- These calibration relations were done for each gas (H_2, CO, CH_4, CO_2 and O_2) and used to measure producer gas composition during the experiments.

Table 4. CH_4 calibration using a linear relation between area under the peak and gas concentration

Gas: CH_4		Area			Average Area
vol (ml)	vol%	Sample 1	Sample 2	Sample 3	
2.0	100	0.297	0.282	0.260	0.280
0.5	25	0.103	0.102	0.099	0.101
0.2	10	0.039	0.040	0.041	0.040
0.1	5	0.019	0.018	0.018	0.018
0.02	1	0.003	0.003	0.003	0.003
0	0	0			
Linear relation		area=0.004concentration[vol%], y=0.004x			R^2=0.999

2.3. Biomass gasification experiments

2.3.1. Air to fuel ratio, equivalence ratio and gas composition

2.3.1.1. Air to fuel ratio and equivalence ratio

Among the most important parameters to set and calculate are the Air to Fuel ratio (stoichiometric and operational) and the equivalence ratio, in order to establish the proportion of gas agent supplied to the biomass during the gasification process. In order to do so, the stoichiometric air to fuel ratio as well as the operational air to fuel ratio have to be calculated for each biomass (spruce, alder and pine) and gas agent setting. These ratios are calculated as stated in Equation 14, so that the equivalence ratio (ER) can be calculated using Equation 13.

To calculate the stoichiometric air to fuel ratio it is necessary to calculate the amount of gasifying agent (oxidizer) required to achieve a stoichiometric combustion with the biomass sample used. This is calculated by balancing the stoichiometric reaction for the combustion of biomass, where biomass reacting with oxygen transforms into carbon dioxide, water and nitrogen (Equation 19).

$$C_aH_bO_cN_d + wO_2 -> xCO_2 + yH_2O + zN_2 \quad \text{Equation 19}$$

This equation can be balanced to establish the amount of oxygen required for the complete combustion of one mole of biomass. The stoichiometric reactions for spruce, alder and pine were calculated using the elemental analysis results. These reactions are shown in Equations 20, 21 and 22.

Spruce $$CH_{1.567}O_{0.637}N_{0.004} + 1.073O_2 -> CO_2 + 0.784H_2O + 0.0005N_2$$ Equation 20

Alder $$CH_{1.430}O_{0.659}N_{0.002} + 1.068O_2 -> CO_2 + 0.782H_2O + 0.002N_2$$ Equation 21

Pine $$CH_{1.567}O_{0.645}N_{0.003} + 1.069O_2 -> CO_2 + 0.783H_2O + 0.002N_2$$ Equation 22

After determining the reactions, the stoichiometric air/fuel and oxy/fuel ratios are calculated for each biomass. The stoichiometric air to fuel ratio are shown in Table 5.

Table 5. Stoichiometric oxy/fuel and air/fuel ratio for the biomass samples

Spruce	Oxy/fuel (sto)	1.444	g of O2 per g biomass
	Air/fuel (sto)	6.874	g of air per g of biomass
Alder	Oxy/fuel (sto)	1.424	g of O2 per g biomass
	Air/fuel (sto)	6.782	g of air per g of biomass
Pine	Oxy/fuel (sto)	1.427	g of O2 per g biomass
	Air/fuel (sto)	6.797	g of air per g of biomass

The operational (*op*) air to fuel ratio was calculated using the operational conditions for the gasification experiments and Equation 14. The fuel (biomass) mass was determined as the average mass held by the sample holder (1.5 g), while there were two different settings of gasifying agent supplied. The first one was flow of 0.063 SLPM of oxygen and 0.237 SLPM of nitrogen (0.3 SLPM 21 vol% O_2, 79 vol% N_2), while the second one was a flow of 0.0315 SLPM of oxygen and 0.2685 SLPM of nitrogen (0.3 SLPM 10.5 vol% O_2, 89.5 vol% N_2).

The first setting (0.063 SLPM O_2), which simulates the air composition was used in experiments with spruce, alder and pine. The second setting (0.0315 SLPM O_2), which has half the concentration of oxygen than in air, was used in experiments with alder. Having the flow rate in SLPM of gasifying agent and having the experiments length (10 min), this rate is converted to mass units under the conditions which the gases are supplied by the gas flow controllers (25 °C and 1 bar). Table 6 shows the operational air to fuel ratios for each gas agent setting.

Table 6. Operational oxy/fuel and air/fuel ratio for the gas agent settings

Gas agent setting	Biomass	Ratio		
Setting 1 0.063 SLPM O_2	Spruce, alder and pine	Oxy/fuel ratio (op)	0.542	g of O2 per g biomass
		Air/fuel (op)	2.582	g of air per g of biomass
Setting 2 0.0315 SLPM O_2	Alder	Oxy/fuel ratio (op)	0.271	g of O2 per g biomass
		Air/fuel (op)	1.291	g of air per g of biomass

The (ER) equivalence ratio (See Table 7) for each biomass and gas agent setting was calculating using the stoichiometric and operational air/fuel from Table 5.

Table 7. Equivalence ratio for each biomass and gas agent setting

Gas agent setting	Biomass	ER
Setting 1, 0.063 SLPM O_2	Spruce	0.376
	Alder	0.381
	Pine	0.380
Setting 2, 0.0315 SLPM O_2	Alder	0.190

2.3.1.2. Tedlar gas samples composition

The composition of the gas samples contained in the Tedlar bags for each gasification experiment has to be calculated considering the main components that are required for the gasification reaction and the ones that are produced in the gasification reaction. Equation 23 shows the main components of the gasification process in the experiments.

$$Biomass(C_aH_bO_cN_d) + gas\ agent\ (O_2 + N_2\ ) -> \ Producer\ gas + N_2 + tars + ashes \qquad \text{Equation 23}$$

To calculate the amount of producer gas for each experiment it is necessary to know the amount of biomass and gas agent supplied. Nitrogen is considered as a gas that does not react, so the amount of nitrogen supplied is the same as the amount of nitrogen after gasification. As for ashes and tars, these cannot be measured in the gasification system, so it is assumed and average production of 10 % (ashes+tars+unburned char) considering the data available from other researches [28], [43] and the biomass characterization results that indicate a small difference in the ash content and elemental composition of the biomasses used. The amount of producer gas is calculated for the gas agent settings (Table 8).

Table 8. Producer gas and nitrogen concentration in the Tedlar sample bags

Gas agent setting	Reactives		Products		Tedlar bag concentration [vol%]
0.063 SLPM O_2 (21 vol% O_2 79 vol% N_2)	Biomass [g]	1.500	Tar+ashes [g]	0.150	
	Gas agent (O_2+N_2) [g]	3.872	N_2 [g]	3.059	58.6
			Producer gas [g]	2.163	41.4
0.0315 SLPM O_2 (10.5 vol% O_2 89.5 vol% N_2)	Biomass [g]	1.500	Tar+ashes [g]	0.150	Tedlar bag concentration [vol%]
	Gas agent (O_2+N_2) [g]	3.872	N_2 [g]	3.465	66.4
			Producer gas [g]	1.757	33.6

2.3.2. Experiment parameters and methodology

2.3.2.1. Parameters

The following parameters were defined for all the gasification experiments:

- Biomass sample mass ≅ 1.5 g.
- 3 Temperatures: 750, 850 and 950 °C.
- 3 biomasses: Alder, spruce and pine.
- 2 Gas agent settings.
- Total parameters: 8 (3 temperatures, 3 biomasses, 2 gas agents).
- Total experiments: 30 (3 repetitions per parameter).
- Total gas agent flow: 3 SLPM (O_2+ N_2).
- Gas agent setting 1: 0.063 SLPM O_2 (21 vol% O_2, 79 vol% N_2).
- Gas agent setting 1 is used in alder, spruce and pine at all 3 temperatures.
- Gas agent setting 2: 0.0315 SLPM O_2 (10.5 vol% O_2, 89.5 vol% N_2).
- Gas agent setting 2 is used in alder at 850 and 950 °C.
- Gas dilution to FTIR: 3.3 SLPM N_2.

The reactor set up and maintenance was done in the months of November and December 2018, and June, July, September and August 2019. The experiments were done from 14.08.2019 - 29.08.2019 for alder and spruce, and from 01.09.2019 – 12.09.2019 for pine. Table 9 shows the experiment test plan.

Table 9. Test plan for the gasification experiments

Experiment	Biomass	Temperature	Gas agent flow (SLPM O2)
1	Alder	750 °C	0.063
2	Spruce	750 °C	0.063
3	Alder	850 °C	0.063
4	Spruce	850 °C	0.063
5	Alder	950 °C	0.063
6	Spruce	950 °C	0.063
7	Alder	850 °C	0.0315
8	Alder	950 °C	0.0315
9	Pine	750 °C	0.063
10	Pine	850 °C	0.063
11	Pine	950 °C	0.063

2.3.2.2. Methodology

The following procedures were done before, during and after every gasification experiment

These procedures were followed before each experiment was started:

1. Background measurement of FTIR with N_2 environment, the room air composition is verified with FTIR.
2. Carrier flow of air is set in GC.

3. Reactor and heating tapes are heated to desired temperature.
4. Gas flow is introduced in the reactor and the flow rate is verified.
5. N_2 flow of 3.3 SLPM is introduced before the FTIR for dilution.
6. The biomass sample is introduced in the sample holder.

The steps followed during each experiment were the following:

Total experiment time: 18 minutes

1. The biomass sample is introduced in the reactor.
2. 2 minutes in the balance chamber with N_2 environment.
3. 1 minute in the reactor with N_2 flow (0.3 SLPM).
4. 10 minutes in the reactor with gas agent (0.3 SLPM O_2+N_2) (Gasification).
5. 2 minutes in the reactor with N_2 flow (0.3 SLPM).
6. 2 minutes in the balance chamber with N_2 environment.

These procedures were followed after each experiment was finished:

1. The sample holder is removed from the reactor and residues are collected for each experiment setting.
2. The producer gas is collected in a Tedlar sample bag.
3. GC measurements of H_2, CO and CH_4 (3 per experiment) with air as carrier gas.
4. GC measurements of O_2 and CO_2 (3 per experiment) with argon as carrier gas.
5. The gas agent flow is closed and the reactor is opened until FTIR measures low organic compounds and room air conditions.
6. The condensation system is cleaned with acetone and compressed air and the wool is replaced.
7. All the equipment is shut down.

3. RESULTS AND ANALYSIS

This section shows the results for the gasification experiments at different parameters including; biomass species, reactor temperature and gasifying agent. The first part shows the readings from the gas chromatography system for the gases detected with air as a gas carrier and oxygen as a gas carrier. The following section shows the results and analysis of the producer gas composition at the different temperatures and biomass species, using a constant gasifying agent flow rate. The effect of varying the gasifying agent configuration is shown for alder at two different temperatures. The behavior of the gasification process during experiments is shown by the results obtained from the FTIR under different experimental parameters. Lastly, the char and ashes residues from the experiments are shown.

3.1. Gas composition

3.1.1. Gas chromatography readings

A gas chromatography system was used during the experiments to detect H_2, CO, CH_4, CO_2 and O_2 gases from the Tedlar gas sample bag. H_2, CO and CH_4 were detected with air as the carrier gas, and CO_2 and O_2 were detected with argon as a carrier gas. For each experiment the data obtained from the GC was adjusted, and the area under every peak was calculated to compare it with the calibration curves and calculate the gas species concentration.

Figure 15 shows the data obtained from the GC for the H_2, CO and CH_4 gases, and the data after being processed and adjusted to the baseline. This figure shows three peaks for three different samples from the Tedlar bag, as for every experiment there were three gas samples introduced in the GC to reduce measurement errors. The gas composition was calculated as the average area of the three samples. The first peak in every sample is H_2, the second is CO and the third is CH_4.

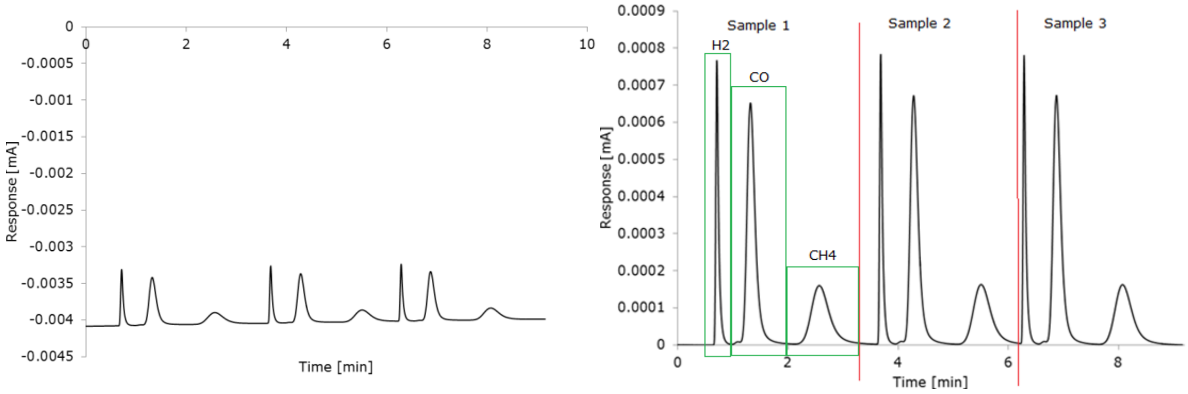


Figure 15. (Left) GC data obtained with air as carrier gas. (Right) Processed data

Figure 16 shows the data obtained from the GC for the CO_2 and O_2 gases, and the data after being processed and adjusted to the baseline. The gas composition was calculated as the average area of three samples. The calculation and interpretation of this data was more complicated, as for oxygen the peaks did not show the same behavior as during the calibration. In processed results O_2 is represented by the first series of peaks and CO_2 is the last and lower peak detected for every sample.

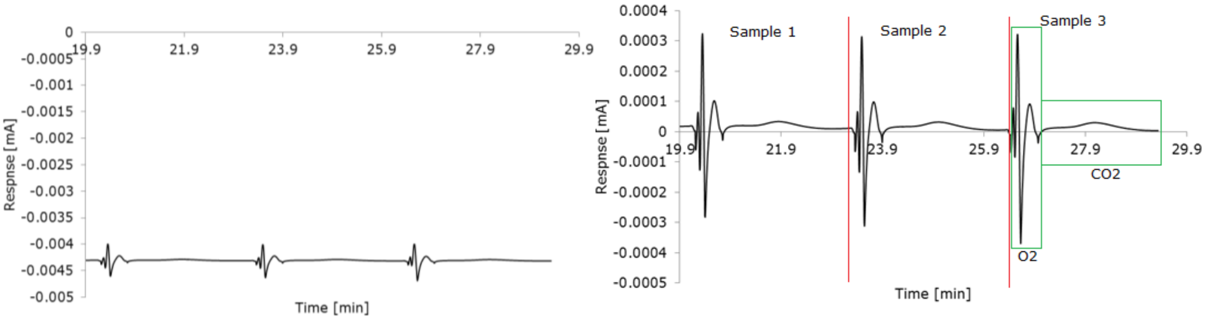


Figure 16. (Left)GC data obtained from with argon as carrier gas. (Right) Processed data

The measurement of CO_2 and O_2 gases from the Tedlar bag were more difficult to process, as the presence of other gases affected the GC detection of CO_2 and O_2. As it can be seen in the peaks of the gases during the calibration have a different behavior than the peaks during experiments (Figure 17), which increased the error when calculating the area and calculating the gas species concentration, special for oxygen, which presented several peaks and a different behavior even from one experiment to another.

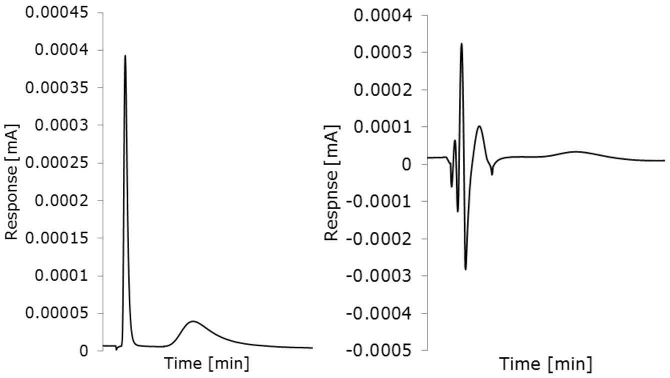


Figure 17. CO2 and O2 readings during calibration (left) and during experiments (right)

3.1.2. Producer gas composition at different temperatures

The gasification experiments were done at three different temperatures (750, 850 and 950 °C) for three biomass samples (Spruce, pine and alder). Each experimental condition (temperature and biomass type) had three repetitions and for each repetition the producer gas was measured with three samples in the GC for gas analysis. The N_2 concentration supplied to the reactor is assumed to be the same concentration after the gasification process, thus the calculations for the producer gas compositions are done following this assumed condition. The producer gas composition results displayed for the experiments show the composition of H_2, CO, CH_4, O_2, CO_2 and N_2, as these are the ones measured by the equipment. The remaining gases consist of H_2O, sulfur dioxide SO_2, Ethane C_2H_6, Ethylene C_2H_4, Propane C_3H_8, Hexane C_6H_{14}, Benzene C_6H_6, Toluene C_7H_8 and other hydrocarbons, which are detected by the FTIR but were not considered for analysis, as the N_2 dilution to the FTIR is considerable higher than the producer gas entering the FTIR, making the detected gases as low as the measurement error provided by the FTIR.

3.1.2.1. Spruce

For spruce, the results obtained from the GC gas samples show the produced gas composition from gasification at 750, 850 and 950 °C and a gas agent flow of 0.063 SLPM of O_2 and 0.237 SLPM of N_2. Table 10 shows the composition of the producer gas and Figure 18 shows the main combustible gases (H_2, CO and CH_4) composition at different gasification temperatures.

Table 10. Producer gas composition from spruce gasification at different temperatures

Temperature [°C]	Gas composition [vol%]							
	H_2	CO	CH_4	O_2	CO_2	N_2	Total	Total + N_2
750	1.1	9.0	2.1	4.1	3.7	58.6	19.9	78.5
850	2.6	14.6	3.3	3.9	3.0	58.6	27.4	86.0
950	4.2	19.6	4.1	4.5	2.8	58.6	35.3	93.8

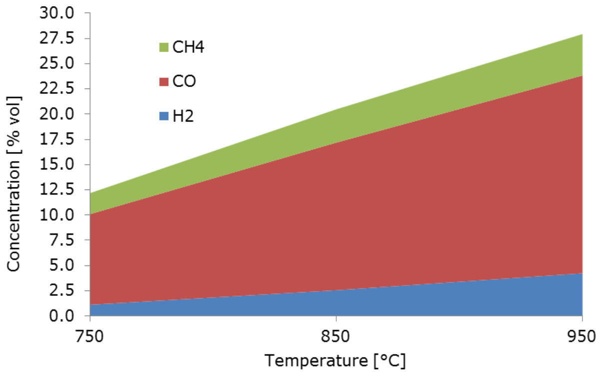


Figure 18. Comparison of producer gas species for spruce at three different temperatures

From the experiments of gasification from spruce, it can be seen how the composition of the producer gas changes with the gasification temperature, having a total of 19.94 vol% of H_2, CO, CH_4, O_2 and CO_2 gases at 750 °C, which increased to 27.21 vol% and 35.25 vol% with experiments at 850 and 950 °C. H_2, CO and CH_4 as main combustible gases made together 12.17 vol%, 20.48 vol% and 27.93 vol% of the producer gas at gasification at 750 °C, 850 and 950 °C respectively.

H_2 production increased over 128.3 % % and 278.1 % at gasification at 850 and 950 °C compared to gasification at 750 °C. The same behavior can be seen for CO, which increased 63.0 % and 118.5 % at experiments with 850 and 950 °C compared to gasification at 750 °C. For CH_4, 58.9 % and 97.3 % more gas was produced at 850 and 950 °C compared to the CH_4 at 750 °C. Table 11 shows the composition of the combustible part of the producer gas at 750, 850 and 950 °C.

Table 11. Combustible gas composition from spruce gasification

Temperature [°C]	Combustible gas [vol%] (from total producer gas)	Combustible gas composition [vol%]		
		H_2	CO	CH_4
750	12.2	9.2	73.7	17.1
850	20.5	12.5	71.4	16.1
950	27.9	15.2	70.2	14.7

3.1.2.2. Alder

Alder gasification was done at 750, 850 and 950 °C and a gas agent flow of 0.063 SLPM of O_2 and 0.237 SLPM of N_2. Table 12 shows the composition of the producer gas and Figure 19 shows the main combustible gases (H_2, CO and CH_4) composition at different gasification temperatures.

Table 12. Producer gas composition from alder gasification at different temperatures

Temperature [°C]	Gas composition [vol%]							
	H_2	CO	CH_4	O_2	CO_2	N_2	Total	Total + N_2
750	1.3	8.6	2.3	5.3	3.3	58.6	20.8	79.4
850	2.2	13.3	3.2	3.5	3.2	58.6	25.4	84.0
950	4.0	20.3	5.1	4.4	1.9	58.6	35.7	94.3

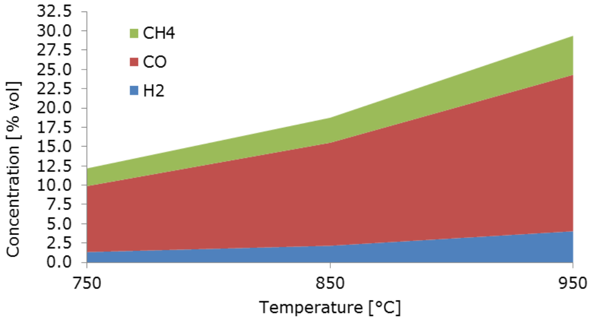


Figure 19. Comparison of producer gas species for alder at three different temperatures

For alder gasification, there was a total of 20.80 vol% of H_2, CO, CH_4, O_2 and CO_2 gases at 750 °C, which increased to 25.40 vol% and 35.70 vol% with experiments at 850 and 950 °C. The three main combustible gases of the producer gas; H_2, CO and CH_4 made together 12.18 vol%, 18.74 vol% and 29.36 vol% of the gas at 750 °C, 850 and 950 °C respectively.

H_2 production increased over 61.4 % and 201.8 % at gasification at 850 and 950 °C compared to gasification at 750 °C. For CO, concentration increased 56.0 % and 136.9 % at experiments with 850 and 950 °C compared to gasification at 750 °C. For CH_4, 41.41

% and 120.8 % more gas was produced at 850 and 950 °C compared to the CH_4 at 750 °C. Table 13 shows the composition of the combustible part of the producer gas at 750, 850 and 950 °C.

Table 13. Combustible gas composition from alder gasification

Temperature [°C]	Combustible gas [vol%] (from total producer gas)	Combustible gas composition [vol%]		
		H_2	CO	CH_4
750	12.2	11.0	70.2	18.8
850	18.7	11.5	71.2	17.3
950	29.4	13.7	69.1	17.2

3.1.2.3. Pine

Pine gasification experiments were done at 750, 850 and 950 °C and a gas agent flow of 0.063 SLPM of O_2 and 0.237 SLPM of N_2. Table 14 shows the composition of the producer gas and Figure 20 shows the main combustible gases (H_2, CO and CH_4) composition at different gasification temperatures.

Table 14. Producer gas composition from pine gasification at different temperatures

Temperature [°C]	Gas composition [vol%]							
	H_2	CO	CH_4	O_2	CO_2	N_2	Total	Total + N_2
750	0.8	8.9	2.2	7.5	5.8	58.6	25.1	83.7
850	2.7	18.0	4.6	4.3	5.3	58.6	34.8	93.4
950	5.1	23.4	5.9	3.1	3.9	58.6	41.4	100.0

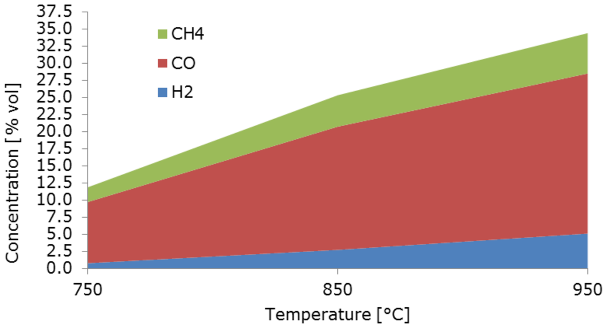


Figure 20. Comparison of producer gas species for pine at three different temperatures

During the gasification experiments of pine a total of 25.14 vol% of H_2, CO, CH_4, O_2 and CO_2 gases was obtained at 750 °C, which increased to 34.83 vol% and 41.39 vol% at 850 and 950 °C. The three combustible gases H_2, CO and CH_4 made together 11.86 vol%, 25.30 vol% and 34.36 vol% of the producer gas at 750 °C, 850 and 950 °C respectively. H_2 production increased over 258.2 % and 573.2 % at gasification at 850 and 950 °C compared to gasification at 750 °C. The same behavior can be seen for CO, which increased 101.3 % and 161.5 % at experiments with 850 and 950 °C compared to gasification at 750 °C. For CH_4, 112.8 % and 173.2 % more gas was produced at 850 and 950 °C compared to the CH_4 at 750 °C. Table 15 shows the composition of the combustible part of the producer gas at 750, 850 and 950 °C.

Table 15. Combustible gas composition from pine gasification

Temperature [°C]	Combustible gas [vol%] (from total producer gas)	Combustible gas composition [vol%]		
		H_2	CO	CH_4
750	11.9	6.4	75.5	18.2
850	25.3	10.7	71.2	18.1
950	34.4	14.8	68.1	17.1

3.1.2.4. Comparison between biomass species

Figure 21 shows a comparison of the concentration of the main combustible gases (H_2, CO and CH_4) in the producer gas measured from the gasification of spruce, alder and pine at the three experimental temperatures

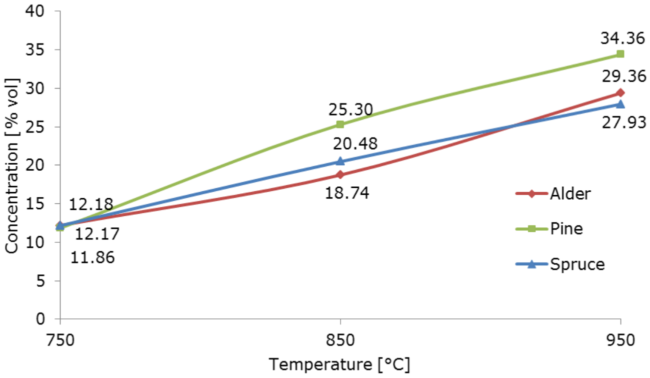


Figure 21. Combustible gases in the producer gas for spruce, alder and pine at gasification at 750, 850 and 950 °C

Overall, the three biomass species showed a similar behavior during the gasification process. As seen in Figure 21 for the experiments made, the higher the gasification temperature, the higher the concentration of all the three main combustible gases and the total combustible gas. The total main combustible gas increased by 68.3 %, 53.8 % and 113,0 % for spruce, alder and pine respectively during gasification at 850 °C compared to 750 °C. At 950 °C gasification the total main combustible gas increased by 129.6 %, 141.0 % and 189.8% for spruce, alder and pine respectively compared to 750 °C.

Pine samples showed the highest increase in combustible gas when increasing the gasification temperature, having a similar concentration of combustible gases at 750 °C, but producing a higher yield of combustible gas at 850 and 950 °C compared to spruce and alder. Pine produced 36.0 % and 23.5 % more combustible gases at 850 °C compared to alder and spruce respectively. At 950 °C, pine produced 17.0 % and 23.0 % more combustible gases than alder and spruce respectively. Alder and spruce did not show considerable differences, with spruce producing 9.3 % more combustible gases at 850 °C and alder producing 5.1 % more combustible gases at 950 °C.

The average composition of the three main combustible gases present in the producer gas was similar for all the experiments, including the experiments at different temperatures and with the different biomass species. Table 16 shows the average composition of the combustible part of the producer gas from the gasification experiments.

Table 16. Average composition of combustible gas in the producer gas

Parameter		Average main combustible gas species [vol%]		
		H_2	CO	CH_4
Biomass type	Spruce	12.3	71.8	15.9
	Alder	12.1	70.2	17.8
	Pine	10.6	71.6	17.8
Temperature [°C]	750	8.8	73.1	18.0
	850	11.6	71.3	17.2
	950	14.6	69.1	16.3
Total average		11.7	71.2	17.2

Overall the combustible part of the producer gas was composed on average by 11.6 % H_2, 71.2 % CO and 17.2 % CH_4, this composition can be compared to the average composition for spruce, alder and pine, as shown in Table 16, as well as the average composition of the combustible gas at different temperatures, which shows higher percentage of H_2 when increasing the temperature.

Figure 22 shows a more detailed comparison for each combustible gas separately; hydrogen, carbon monoxide and methane at different gasification temperatures.

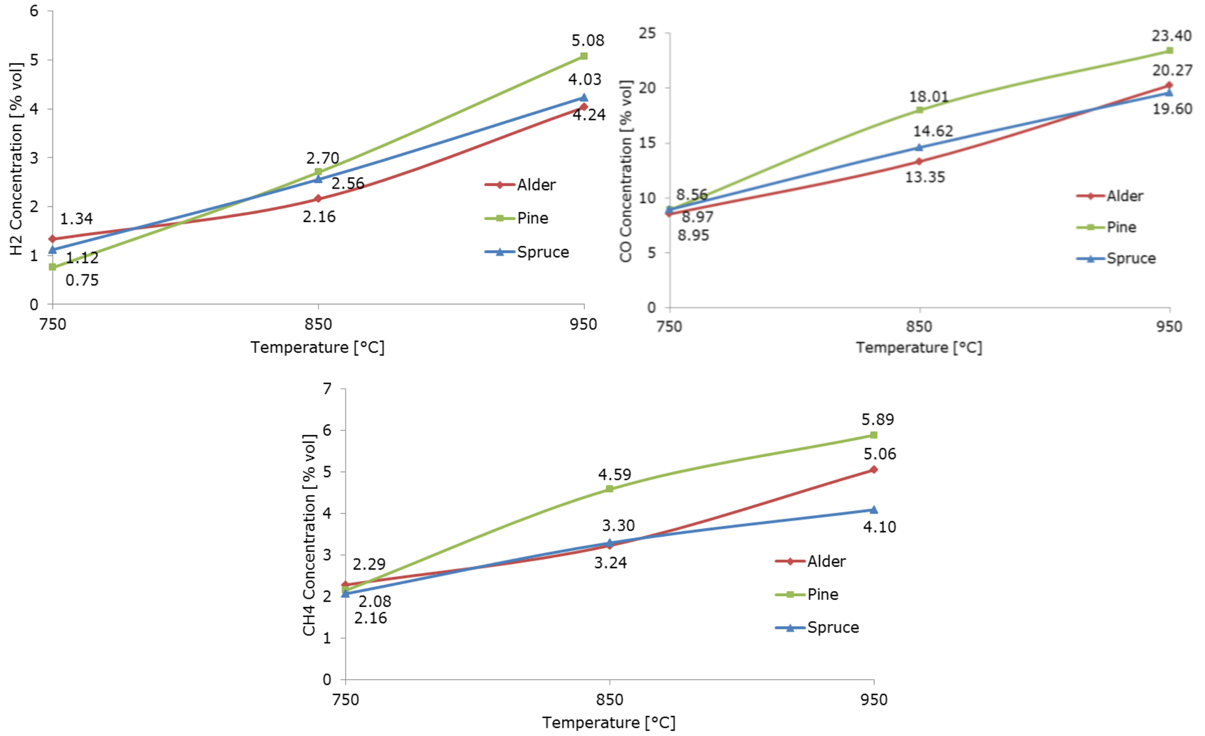


Figure 22. H_2 (left), CO (right) and CH_4 (bottom) concentration in the producer gas for spruce, alder and pine at gasification at 750, 850 and 950 °C

The producer gas from the three biomass species presented a similar concentration of H_2, CO and $CH4$ at 750 °C, but the H_2 production was lower for pine compared to spruce and alder. At 850 and 950 °C pine showed the highest yield of H_2, CO and CH_4. At 850 °C pine produced 25.3 and 5.7 % more H_2, 34.9 and 23.1 % more CO, and 41.7 and 39.1 % more CH_4 compared to alder and spruce respectively. At 950 °C pine produced 25.9 and 19.9 % more H_2, 15.4 and 19.4 % more CO, and 16.5 and 43.8 % more CH_4 compared to alder and spruce respectively.

The concentration of O_2 and CO_2 was also affected by the gasification temperature, where the concentration of both gas species in the producer gas decreases at 850 °C and at 950 °C compared to gasification at 750 °C for all the three biomass species. These changes of concentration from biomass species and temperatures are not further analyzed considering the higher measurement error delivered by the gas chromatography system.

Different studies have been made to analyze the effect of temperature, gas agent ratio and different parameters on biomass gasification for fixed bed updraft and downdraft reactors, considering mainly the composition of the producer gas, as well as sub products such as tar, ashes and unburned char. Some studies have been experimental, while others have been mathematical models, based on experimental and theoretical data. Some studies have been made with wood residues, such as rice husks, empty fruit bunch and hazelnut shells. Table 17 shows the main parameters and results of different gasification models and experiments from different researches.

Table 17. Comparison of gas composition for different experiments and models (Spruce, alder and pine at 950 °C, and results from other researchers.

Biomass	Gasification temperature [°C]	Gasifier type	Gas composition [vol%]			
			H_2	CO	CH_4	N_2
Spruce	950	Batch updraft fixed bed reactor	4.2	19.6	4.1	58.6
Alder			4.0	20.3	5.1	58.6
Pine			5.1	23.4	5.9	58.6
Rice husks [28]	955	Fixed bed downdraft reactor	9.8	29.3	3.0	42.1
Wood from short rotation forests [65]	955	Fixed bed downdraft reactor	12.9	24.3	2.9	50.5
Woodchips [66]	n.d.	Fixed bed downdraft reactor	14.3	23.3	2.4	47.6
Hazelnut shells[43]	700-950	Fixed bed downdraft reactor	13.4	16.1	2.0	56.1
Empty fruit bunch [44]	700-1000	Fluidized bed reactor	10.0-35.0	20.0-35.0	5.0-12.0	n.d.

Biomass	Gasification temperature [°C]	Gasifier type	Gas composition [vol%]			
			H_2	CO	CH_4	N_2
Pine pellets[67]	870-940	Fixed bed reactor	5.0-6.00	17.0-27.0	5.0-10.0	n.d.
Charcoal[68]	n.d.	Updraft reactor	19.7	30	n.d.	46.0
Charcoal[68]	n.d.	Downdraft reactor	5.0-10.0	28.0-31-0	1.0-2.0	55.0-60.0
Wood with 12-20 % moisture content[68]	n.d.	Downdraft reactor	16.0-20.0	17.0-22.0	2.0-3.0	55.0-60.0
Coconut husks[68]	n.d.	Downdraft reactor	16.0-20.0	17.0-19.5	n.d.	n.d.

3.1.3. Gas composition at different gas agent ratios

Other gasification experiments were done at 850 and 950 °C for alder, with a lower mass flow of oxidizing agent, of 0.0315 SLPM O_2 and 0.2685 SLPM N_2 (10.5 vol% O_2, 89.5 vol% *N2)* in order to compare it to the experiments of alder gasification with a gasifying agent flow of 0.063 SLPM O_2 and 0.237 SLPM of N_2 (21 vol% O_2, 79 vol% N_2). Each experimental condition (at 850 and 950 °C) had three repetitions and for each repetition the producer gas was measured with three samples in the GC for gas analysis.

The producer gas composition results displayed for this experiment show the composition of H_2, CO, CH_4, O_2, CO_2 and N_2. The remaining gases consist of H_2O, SO_2, C_2H_6, C_2H_4, C_3H_8, C_6H_{14}, C_6H_6, C_7H_8 and other hydrocarbons. Table 18 shows the results obtained from the composition of the producer gas from gasification of alder at the two gas agent conditions and the two gasification temperatures. Figure 23 shows a comparison of the producer gas composition for both gas agent settings.

Table 18. Producer gas composition from alder at two different gas agent settings

Temperature [°C]	Gas agent setting		Gas species composition [vol%]							
	[SLPM O_2]	[vol%]	H_2	CO	CH_4	O_2	CO_2	N_2	Total	Total + N_2
850	0.0315	21 vol% O_2 79 vol% N_2	1.8	11.7	2.7	4.1	2.6	66.4	22.9	89.3
	0.063	10.5 vol% O_2 89.5 vol% N_2	2.2	13.3	3.2	3.5	3.2	58.6	25.4	84.0
950	0.0315	21 vol% O_2 79 vol% N_2	3.6	19.1	4.4	3.4	2.1	66.4	32.6	99.0
	0.063	10.5 % O_2 89.5 % N_2	4.0	20.3	5.1	4.4	1.9	58.6	35.7	94.3

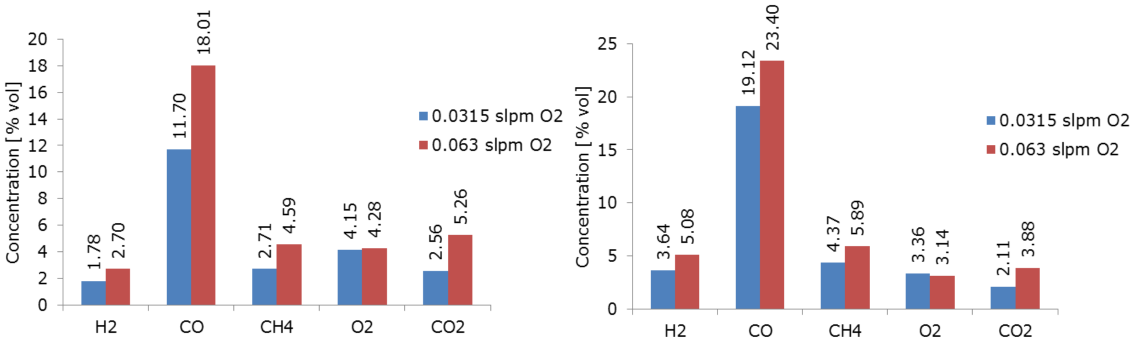


Figure 23. Comparison of producer gas species for alder at 850 °C (left) and 950 °C (right) with two different gas agent settings

For alder gasification with 0.063 SLPM the O_2, H_2, CO, CH_4, O_2 and CO_2 gases together made 25.40 and 35.70 vol% of the producer gas at 850 °C and 950 °C respectively. For alder gasification with 0.0315 SLPM these gases together made 22.89 and 32.60 vol% of the producer gas at 850 °C and 950 °C respectively. With the first gas agent setting (0.063 SLPM O_2) the three main combustible gases of the producer gas; H_2, CO and CH_4 made together 18.74 vol% and 29.36 vol% of the gas at 850 and 950 °C respectively. For the second gas agent setting (0.0315 SLPM O_2) the main combustible gases made together 16.18 vol% and 27.13 vol% of the gas at 850 and 950 °C respectively. The 0.063 SLPM O_2 gas agent setting produced 15.8 and 8.2 % more combustible gases than the 0.0315 SLPM O_2 gas agent at 850 and 950 °C respectively

The H_2 yield was 21.1 % and 10.6 % higher at gasification at 850 and 950 °C for the 0.063 SLPM O_2 compared to the 0.0315 SLPM O_2 gasifying agent setting. The same behavior was observed for CO, where the concentration was 14.1 % and 6.1 % for the 0.063 SLPM O_2 setting compared to the 0.0315 SLPM O_2 setting at 850 and 950 °C respectively. The CH_4 yield was also higher for the 0.063 SLPM O_2 compared to the 0.0315 SLPM O_2 setting, with 19.6 and 15.8 % more CH_4 at 850 and 950 °C respectively.

From these experiments it can be observed how the higher concentration of O_2 in the gasifying agent increased the yield of combustible gases, especially at 850 °C, where the gases presented concentrations from 14 to 21 % higher than the concentrations at a lower O_2 mass flow in the gasifying agent. Moreover it can be seen, how establishing a proper equivalence ratio can affect the producer gas yield, as for the 0.063 SLPM O_2 setting the ER was 0.381, while the ER for the 0.0315 SLPM O_2 setting 0.190, which led to a lower yield of combustible gases in the producer gas.

3.1.4. Total organic Carbon

The FTIR equipment recorded in real time the absorption spectrum of H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, HCl, HF, C_2H_6, C_2H_4, C_3H_8, C_6H_{14}, C_6H_6, C_7H_8 and other organic compounds. This data gave information related to the evolution of the reactions during the gasification experiments, as it showed the constant change of the composition of the gas species. The FTIR was used to control the overall progress of the reactions by checking the concentration of Total Organic Carbon (TOC), O_2 and CO. The results were adjusted considering the N_2 dilution to the FTIR and the N_2 entering and leaving the reactor. After the adjustments the results were organized in graphs to compare the evolution of the total organic carbon at the three gasification temperatures and with the three biomass species. Figure 24 shows how gasification proceeds when using spruce, alder and pine at different temperatures.

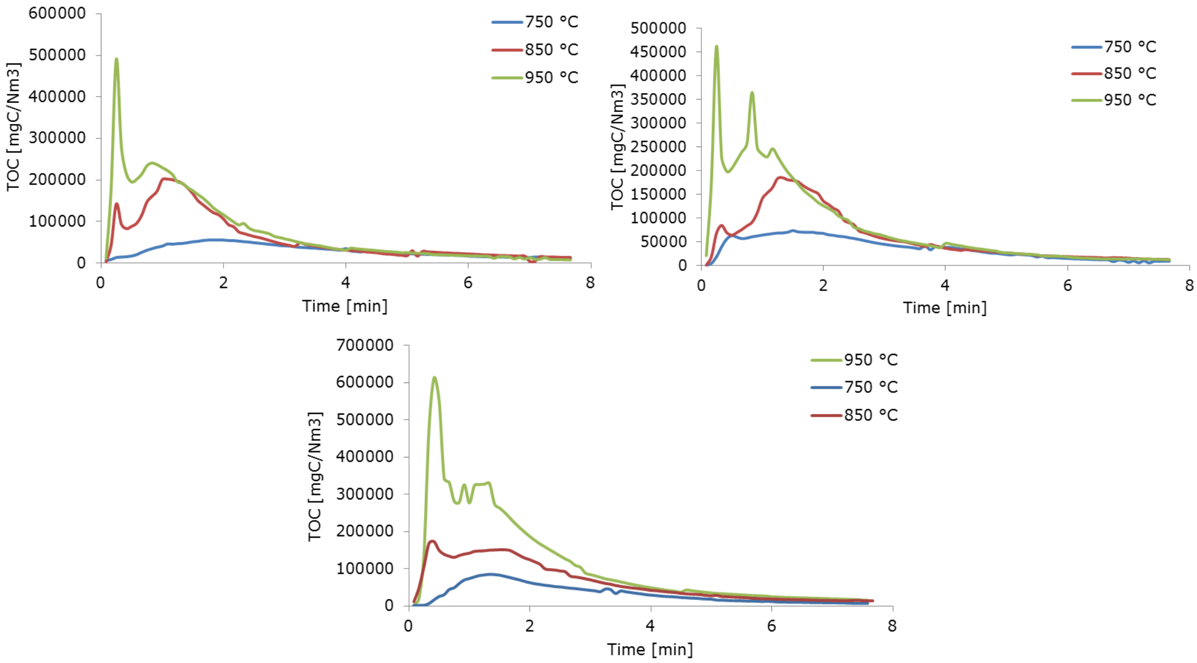


Figure 24. Gasification process for spruce (left), alder (right) and pine (bottom) at three different temperatures

It can be observed how the highest amount of TOC are produced at the beginning of the gasification process for all the three biomass species, having a very fast increase in the TOC, that reaches its highest value during the first 30 s of the gasification, as the biomass starts the pyrolysis process, followed by a constant decrease in TOC production during the rest of the process until all the gasification reactions are almost finished, the majority of the TOC compounds are produced within the first 4 minutes of gasification.

Figure 24 also shows the TOC production for the biomass species at different temperatures, where it can be observed that the total TOC products are higher with higher gasification temperatures, especially at the beginning of the reactions, where the highest TOC are close to 5 times higher at 950 °C compared to 750 °C for all the three biomass species. The two high TOC peaks in the beginning of the gasification processes were observed to be the start of the pyrolysis reactions for the first peak, when there was only N_2 as a gas agent, and later the start of the oxidation and reduction reactions for the second peak, where oxygen is introduced with nitrogen as gasifying agent. Figure 25 shows how gasification proceeds when using spruce, alder and pine.

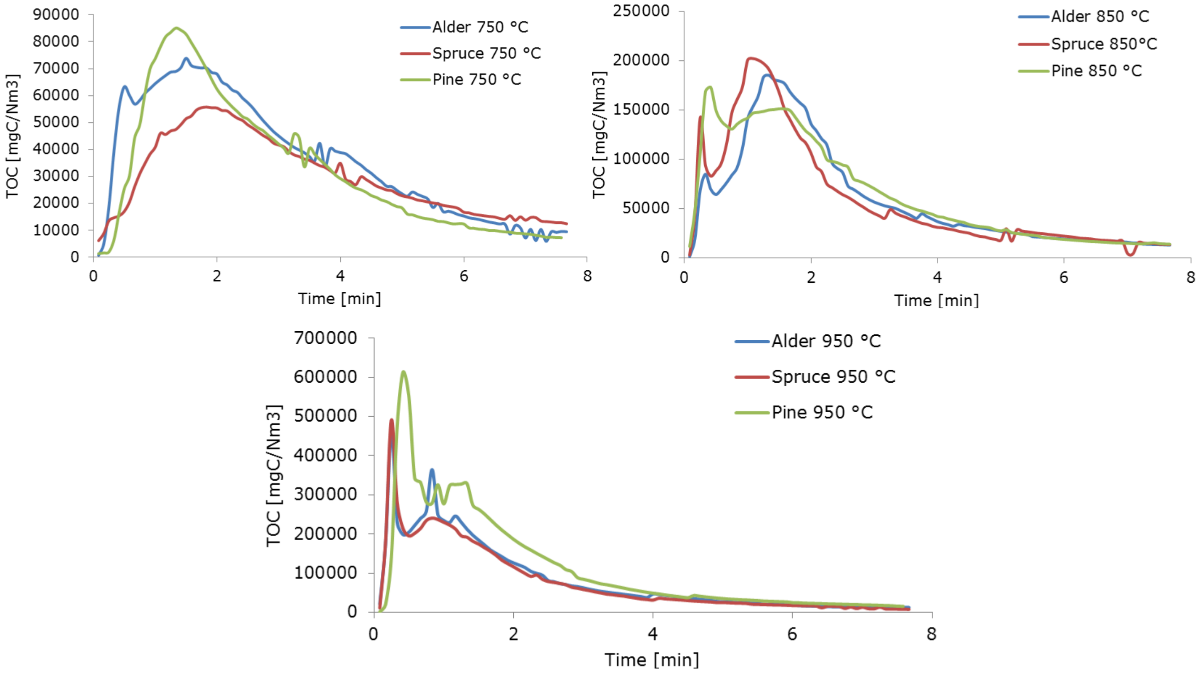


Figure 25. Gasification process at 750, 850 and 950 °C for spruce, alder and pine

Figure 25 shows how the overall behavior of the gasification process is similar for the three biomass species at the same temperatures. The data was compared for the same amount of biomass sample for each one of the three wood species. It can be observed how the TOC [mgC/Nm^3] has a similar behavior for spruce alder and pine, at 750 °C, even though spruce presents a lower TOC, and a similar behavior for all the biomass species at 850°C, and at 950 °C, with pine having higher TOC at 950 °C compared to the two other biomass species. This higher TOC for pine at 950 °C matches the results of the CO and CH_4 concentration in the producer gas, obtained from the gas chromatography.

3.2. Ashes and unburned char

Figures 26, 27, 28 and 29, show the unburned char and ashes and all solid residues collected from the sample holder after experiments. The mass of these residues was not measured, as the residues could be lost when removing the sample and could also fall to the bottom of the reactor. Overall there was a lower production of residues at higher gasification temperatures.

Figure 26. Solid residues from spruce at 750 °C (left), 850 °C (center) and 950 °C (right)

Figure 27. Ashes and unburned char from alder gasification at 750 °C (left), 850 °C (center) and 950 °C (right)

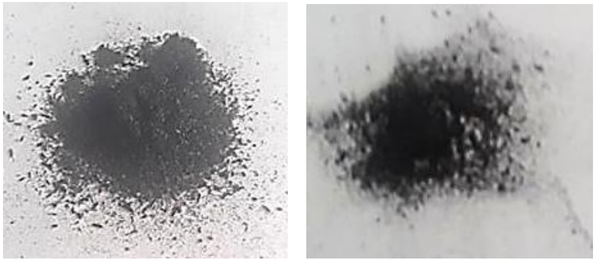


Figure 28. Ashes and unburned char from alder gasification with lower gas agent flow (0.0315 SLPM O2) at 850 °C (left) and 950 °C (right)

Figure 29.Ashes and unburned char from pine gasification at 750 °C (left), 850 °C (center) and 950 °C (right)

4. CONCLUSIONS

The present thesis carried out different experiments to study and analyze the composition of the producer gas produced in the gasification of three different biomass species (Spruce, alder and pine) at three different gasification temperatures (750, 850, 950 °C), using a mixture of oxygen and nitrogen as a gasifying agent (and two different gas agent flows for alder) in a prototype fixed bed reactor, connected to a gas cleaning system and a Fourier-transform Infrared equipment and Gas Chromatography equipment, to determine the concentration of H_2, CO and CH_4 in the producer gas.

The overall energetic structure and types of resources available in Estonia, provides suitable possibilities to integrate gasification technologies (fixed bed or fluidized bed) for heat and power generation, considering that biomass is already used for heat generation, and considering the country's renewable energies targets. A transition to more efficient and cleaner methods of using oil shale, combined with co-combustion, co-pyrolysis or/and co-gasification of oil shale-biomass mixtures would present a suitable path to achieve the energy goals, as the country has well developed the knowledge and technical capabilities in fixed and fluidized bed technologies and thermochemical conversion processes for energy generation.

From the chemical composition analysis, it was observed that overall spruce, alder and pine present very similar characteristics, with a composition within 49.89 to 50.33, 6.55 to 6.62 and 42-69 to 43.09 wt% of Carbon, Hydrogen and Oxygen respectively, as well as analytical moistures from 6.87 to 8.47 wt% and ash contents from 0.29 to 0.35 wt%. The similarities were presented also in the gross calorific values, which ranged from 18.35 to 18.43 MJ/ kg and a net calorific value from 18.35 to 18.61 MJ/kg. Comparable values were found in literature. The composition similarities plus the same particle size used in the experiments, resulted in a producer gas with a similar composition for the three biomass species.

From the actual gasification system used, it was observed that multiple gas cleaning stages are necessary to condensate the produced tars and volatiles, so that the gas sample and the gas analysis equipment are not contaminated. Moreover, the producer gas exhaust requires additional heating to avoid condensation of volatiles inside the reactor, which can produce clogging and affect the experiments. For future experiments it is recommended to implement a system to fully condensate all volatiles, in order to have a complete mass balance of the process. These improvements would help to understand the reaction evolution in the gasification process.

There was a similar composition of the producer gas at different temperatures during the gasification of each one of the wood species. For all three biomass the gasification temperature increased the yield of the main combustible gases (H_2, CO and CH_4). Overall, spruce, alder and pine presented a total of 11.9 to 12.2 vol% of main combustible gases at gasification temperatures of 750 °C, which increased to concentration ranging from 18.7 to 25.3 vol% at 850 °C, and from 27.9 to 34.4 vol% at 950 °C. Pine presented the highest concentration of combustible gases. However, considering the wide availability of these three wood species in Estonia, and the similarities in composition, it would be suitable to use biomass mixtures of these wood species for gasification, including mixtures obtained from biomass residues, including birch and aspen which are also widely available. Further as gasification of wood biomass mixtures and wood-oil shale mixtures is a possible next step for future research.

The composition and yield of the main combustible gases is directly affected by the gasification temperature. A considerable increase in the concentration of H_2, CO and CH_4 was observed when gasifying at 750 °C, compared to 850 °C and 950 °C. On average the hydrogen concentration increased from 1.1 to 2.5 to 4.5 vol% at 750, 850 and 950 °C respectively. For carbon monoxide, the concentration increased from 8.8 to 15.3 to 21.1 vol% at 750, 850 and 950 °C respectively, and for methane the concentration increased from 2.2 to 3.7 to 5.0 vol% at 750, 850 and 950 °C respectively. Based on these results, literature overviews and external experiments, a gasification temperature close to 950 °C would be the most suitable temperature to obtain a higher yield of producer gas with a higher concentration of the main combustible gases.

Compared to experiments done by other researchers in similar gasification conditions, the producer gas obtained from the experiments at 950 °C shown in this document presented a comparable concentration of carbon monoxide, ranging from 20.0-30.0 vol% in other experiments compared to 19.6 to 23.4 vol% in the presented experiments. The methane concentration is also comparable in the presented experiments, from 4.1 to 5.1 vol% compared to values from 2.0 to 10.0 % in other experiments. For hydrogen, the concentration obtained was lower on average than other research done, with values obtained from 4.0 to 5.1 vol% compared to concentrations ranging from 5.0 to 15.0 vol% in other experiments. Overall these results show that the process done in the experiments was indeed a gasification process.

Measuring the composition of the gas as well as the evolution of the gasification process with two measurement equipment was an effective way to control the gasification process, as the Total Organic Compounds allowed comparing the evolution of the process for experiments ran under the same conditions, as well as comparing the reaction process for experiments under different conditions. It was observed how the higher temperatures in the gasification experiments increased the speed of reactions and resulted in a higher yield of producer gas, as well less production of tars and ashes. Moreover, for future experiments it is recommended to analyze the effect of different gas agents, such as pure oxygen, steam, steam and air mixtures, and carbon dioxide among others. Experiments in a fluidized bed reactor controlling the particle size, would also be suitable to obtain a more extensive analysis of gasification processes.

5. SUMMARY

Biomass gasification as a thermochemical conversion process for the production of syngas or producer gas provides an alternative solution for renewable and decentralized technologies for energy generation. The present research was executed to determine the difference in the composition of the producer gas obtained from gasification, when using different types of Estonian wood biomass species and different gasification temperatures, as the composition of the producer gas highly depends on the gasification parameters. The experiments were made in a prototype fixed bed batch reactor, which was fine-tuned and adjusted, the reactor was connected to a gas cleaning system, a Fourier-transform Infrared Spectroscopy equipment and a Gas Chromatography equipment to determine the composition of the producer gas as well as the evolution of the gasification process. The biomass samples used were Estonian Scots Pine, Grey Alder and Norway Spruce samples from Estonian forests, which were gasified at 750, 850 and 950 °C, under a flow O_2+N_2 as the gasifying agent (Equivalence ratio of 0.379 on average). Overall it could be observed an increase on the main combustible gases in the producer gas when increasing the gasification temperature, going from 0.7, 8.6 and 2.1 vol% of H_2, CO and CH_4 respectively in gasification at 750 °C, to 5.1, 23.4 and 5.9 vol% of H_2, CO and CH_4 respectively in gasification at 950 °C. There was not a significant difference between the gas compositions for the three biomass species; however, pine gasification produced the highest yields of H_2, CO and CH_4 at 850 °c and 950 °C. Regarding the evolution of the reactions, at 950 °C the reduction reactions happened at a faster rate, observed by the concentration of Total Organic Carbon over time, as well as the amount of ashes and tars were reduced at the highest gasification temperature. Overall, using alder, spruce and pine for biomass gasification present an alternative for producer gas production, when gasifying at 950 °C, with air. Future experiments with gasification using steam as a gas agent or carbon dioxide would be adequate to determine the increase on the yield production of H_2, and CH_4, as well as experiments with fluidized bed gasification, studying the effect of the particle size.

6. REFERENCES

[1] United Nations, "Sustainable Development Goal 13 Climate Action," 2020.

[2] U. Nations, "Sustainable Development Goal 7- Renewables," 2020. [Online]. Available: https://sustainabledevelopment.un.org/sdg7. [Accessed: 14-May-2020].

[3] Republic of Estonia Ministry of Economic Affairs and Communications, "National Development Plan of the Energy Sector until 2030," no. 285, 2017.

[4] International Energy Agency, "National Renewable Energy Action Plan (NREAP)," 2016. [Online]. Available: https://www.iea.org/policiesandmeasures/pams/estonia/name-36461-en.php. [Accessed: 01-Apr-2019].

[5] "Forestry - Statistics Estonia." [Online]. Available: https://www.stat.ee/forestry. [Accessed: 07-Oct-2019].

[6] International Energy Agency, "World Energy Outlook 2017," 2017. [Online]. Available: https://www.iea.org/weo2017/. [Accessed: 02-Oct-2019].

[7] IRENA, *Rethinking Energy 2017*, vol. 55, no. July. 2017.

[8] European Comission, "2030 climate & energy framework," *European Commission*, 2019. [Online]. Available: https://ec.europa.eu/clima/policies/strategies/2030_en. [Accessed: 14-May-2020].

[9] European Comission, "Sustainable mobility," 2019.

[10] European Commission, "Mobility and Transport - Sustainable transport," 2020. [Online]. Available: https://ec.europa.eu/transport/themes/sustainable_en. [Accessed: 14-May-2020].

[11] S. Liive, "Oil shale energetics in Estonia," *Oil Shale*, vol. 24, no. 1, pp. 1–4, 2007.

[12] International Energy Agency, *Estonia 2013*. 2013.

[13] International Energy Agency, "Estonia - Energy system Overview," 2018.

[14] Eesti Energia, "Environment." [Online]. Available: https://www.energia.ee/en/keskkond. [Accessed: 01-Apr-2019].

[15] Republic of Estonia Ministry of Economic Affairs and Communication, "Energy sector." [Online]. Available: https://www.mkm.ee/en/objectives-activities/energy-sector. [Accessed: 01-Apr-2019].

[16] "Energy- Estonia Statistics," 2018. [Online]. Available: https://www.stat.ee/68027. [Accessed: 11-Nov-2018].

[17] International Energy Agency, "Statistics: Global Energy data at your fingerprints. Estonia," 2016. [Online]. Available: https://www.iea.org/statistics/?country=ESTONIA&year=2016. [Accessed: 11-Nov-2018].

[18] A. Paist *et al.*, "Potential of biomass fuels to substitute for oil shale in energy balance in estonian energy sector," *Oil Shale*, vol. 22, no. 4, pp. 369–379, 2006.

[19] M. of E. and C. Republic of Estonia, "Heating sector | Ministry of Economic Affairs and Communications," 2015. [Online]. Available: https://www.mkm.ee/en/objectives-activities/energy-sector/heating-sector. [Accessed: 02-Oct-2019].

[20] R. P. Overend, "Renewable energy sources charged with energy from the sun and originated from earth-moon interaction," *Direct Combust. biomass*, vol. I.

[21] A. A. Ahmad, N. A. Zawawi, F. H. Kasim, A. Inayat, and A. Khasri, "Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation," *Renew. Sustain. Energy Rev.*, vol. 53, pp. 1333–1347, 2016.

[22] M. La Villeta, M. Costa, and N. Massarotti, "Modelling approaches to biomass gasification-review," *Renew. Sustain. Energy Rev.*, no. 74, pp. 71–88, 2017.

[23] V. Strezov and T. J. Evans, *Biomass Processing Technologies*. Boca Raton: CRC Press, 2014.

[24] J. Ahrenfeldt, T. P. Thomsen, U. Henriksen, and L. R. Clausen, "Biomass gasification cogeneration - A review of state of the art technology and near future perspectives," *Appl. Therm. Eng.*, vol. 50, no. 2, pp. 1407–1417, 2013.

[25] C. Higman and M. van der. Burgt, *Gasification*, Gulf Profe. Gulf Professional Pub./Elsevier Science, 2008.

[26] S. K. Sansaniwal, K. Pal, M. A. Rosen, and S. K. Tyagi, "Recent advances in the development of biomass gasification technology: A comprehensive review," *Renew. Sustain. Energy Rev.*, vol. 72, no. December 2015, pp. 363–384, 2017.

[27] A. P. G. Peres, B. H. Lunelli, and R. Maciel FIlho, "Application of Biomass to Hydrogen and Syngas Production," *Chem. Eng. Trans.*, vol. 32, no. 2011, pp. 589–594, 2013.

[28] A. Chaurasia, "Modeling simulation and optimization of downdraft gasifier: Studies on chemical kinetics and operating conditions on the performance of the biomass gasification process," *Energy*, no. 116, pp. 1065–1076, 2016.

[29] A. M. Sepe, J. Li, and M. C. Paul, "Assessing biomass steam gasification technologies using a multipurpose model," *Energy Convers. Manag.*, no. 128, pp. 216–226, 2016.

[30] A. Kumar, D. Jones, and M. Hanna, "Thermochemical Biomass Gasification: A Review of the Current Status of the Technology," *Energies*, vol. 2, no. 3, pp. 556–581, Jul. 2009.

[31] N. Mahinpey and A. Gomez, "Review of gasification fundamentals and new findings: Reactors, feedstock, and kinetic studies," *Chem. Eng. Sci.*, vol. 148, pp. 14–31, 2016.

[32] T. K. Patra and P. N. Sheth, "Biomass gasification models for downdraft gasifier--A state of teh art review," *Renew. Sustain. Energy Rev.*, no. 50, pp. 583–593, 2015.

[33] I. I. Ahmed and A. K. Gupta, "Kinetics of woodchips char gasification with steam and carbon dioxide," *Appl. Energy*, vol. 88, no. 5, pp. 1613–1619, May 2011.

[34] M. L. de Souza-Santos, *Solid Fuels Combustion and Gasification*-. Columbus: Marcel Dekkeer Inc, 2004.

[35] J. A. Ruiz, M. C. Juárez, M. P. Morales, P. Muñoz, and M. A. Mendívil, "Biomass gasification for electricity generation: Review of current technology barriers," *Renew. Sustain. Energy Rev.*, vol. 18, pp. 174–183, 2013.

[36] Y. Chhiti, S. Salvador, J. Commandré, F. Broust, and C. Couhert, "Wood Bio-Oil Noncatalytic Gasification: Influence of Temperature, Dilution by an Alcohol and Ash Content," *Energy & Fuels*, vol. 25, no. 1, pp. 345–351, Jan. 2011.

[37] J. J. Hernández, R. Ballesteros, and G. Aranda, "Characterisation of tars from biomass gasification: Effect of the operating conditions," *Energy*, vol. 50, pp. 333–342, Feb. 2013.

[38] L. Wang, C. L. Weller, D. D. Jones, and M. A. Hanna, "Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production," *Biomass and Bioenergy*, vol. 32, no. 7, pp. 573–581, Jul. 2008.

[39] N. Couto, A. Rouboa, V. Silva, E. Monteiro, and K. Bouziane, "Influence of the Biomass Gasification Processes on the Final Composition of Syngas," *Energy Procedia*, vol. 36, pp. 596–606, Jan. 2013.

[40] P. Lv, Z. Yuan, L. Ma, C. Wu, Y. Chen, and J. Zhu, "Hydrogen-rich gas production from biomass air and oxygen/steam gasification in a downdraft gasifier," *Renew. Energy*, vol. 32, no. 13, pp. 2173–2185, Oct. 2007.

[41] M. Hosseini, I. Dincer, and M. A. Rosen, "Steam and air fed biomass gasification:

Comparisons based on energy and exergy," *Int. J. Hydrogen Energy*, vol. 37, no. 21, pp. 16446–16452, Nov. 2012.

[42] P. Klimantos, N. Koukouzas, A. Katsiadakis, and E. Kakaras, "Air-blown biomass gasification combined cycles (BGCC): System analysis and economic assessment," *Energy*, vol. 34, no. 5, pp. 708–714, May 2009.

[43] M. Dogru, C. R. Howarth, G. Akay, B. Keskinler, and A. A. Malik, "Gasification of hazelnut shells in a downdraft gasifier," *Energy*, vol. 27, no. 5, pp. 415–427, 2002.

[44] M. A. A. Mohammed, A. Salmiaton, W. A. K. G. Wan Azlina, M. S. Mohammad Amran, and A. Fakhru'L-Razi, "Air gasification of empty fruit bunch for hydrogen-rich gas production in a fluidized-bed reactor," *Energy Convers. Manag.*, vol. 52, no. 2, pp. 1555–1561, 2011.

[45] J. Li, Y. Yin, X. Zhang, J. Liu, and R. Yan, "Hydrogen-rich gas production by steam gasification of palm oil wastes over supported tri-metallic catalyst," *Int. J. Hydrogen Energy*, vol. 34, no. 22, pp. 9108–9115, 2009.

[46] W. Lan, G. Chen, X. Zhu, X. Wang, and B. Xu, "Progress in techniques of biomass conversion into syngas," *J. energy Inst.*, no. 88, pp. 151–156, 2015.

[47] A. A. C. . Beenackers, "Biomass gasification in moving beds, a review of european technologies," *Renew. energy*, no. 16, pp. 1180–1186, 1999.

[48] tigadwa y Ahmed, murni m Ahmad, S. Yusup, A. Inayat, and Z. Khan, "Mathematical and computational approaches for design of biomass gasification," *Renew. Sustain. Energy Rev.*, no. 16, pp. 2034–2315, 2012.

[49] M. M. Ruiz Esparza, "Simulación del proceso de gasificación termoquímica para la obtención de gas combustible, aplicado a la cascarilla de café," Universidad Veracruzana, 2007.

[50] E. G. Pereira, J. N. Da Silva, J. L. De Oliveira, and C. S. MacHado, "Sustainable energy: A review of gasification technologies," *Renew. Sustain. Energy Rev.*, vol. 16, no. 7, pp. 4753–4762, 2012.

[51] M. Asadullah, "Biomass gasification gas cleaning for downstream applications--A comparative critical review," *Renew. Sustain. Energy Rev.*, no. 40, pp. 118–132, 2014.

[52] P. Basu, *Biomass Gasification and Pyrolysis : Practical Design and Theory*. Elsevier Science & Technology Books, 2010.

[53] P. Basu, *Biomass Gasification, Pyrolysis and Torrefaction : Practical Design and Theory,*. Elsevier Science & Technology Books, 2013.

[54] Republic of Estonia - Ministry of the Environment, “Forestry | Ministry of the Environment,” 2019. [Online]. Available: https://www.envir.ee/en/forestry. [Accessed: 07-Oct-2019].

[55] Statistics Estonia, “Eesti Statistika Kvartalikiri. 2/18. Quarterly Bulletin of Statistics Estonia - Statistics Estonia,” 2018.

[56] M. J. Antal, S. G. Allen, X. Dai, B. Shimizu, M. S. Tam, and M. Grønli, “Attainment of the theoretical yield of carbon from biomass,” *Ind. Eng. Chem. Res.*, vol. 39, no. 11, pp. 4024–4031, 2000.

[57] L. Sørum, M. . Grønli, and J. . Hustad, “Pyrolysis characteristics and kinetics of municipal solid wastes,” *Fuel*, vol. 80, no. 9, pp. 1217–1227, Jul. 2001.

[58] ECN (Netherlands), “Phyllis2 - ECN Phyllis classification, wood, spruce (#176),” 1997. [Online]. Available: https://phyllis.nl/Browse/Standard/ECN-Phyllis#spruce. [Accessed: 07-Oct-2019].

[59] O. Kitani and C. W. Hall, *Biomass Handbook*. New Yorl: Gordon and Breach science publishers, 1989.

[60] H. F. Feldmann, “Conversion of Forest Residues To a Methane-Rich Gas.,” pp. 537–556, 1978.

[61] T. Richard and N. Trautmann, “Substrate Composition Table - Cornell University,” 2002. [Online]. Available: http://compost.css.cornell.edu/calc/lignin.noframes.html#Sources. [Accessed: 07-Oct-2019].

[62] R. J. Leemhuis and R. M. de Jong, “Biomassa: biochemische samenstelling en conversiemethoden (confidential report,” *ECN*, vol. 7, 1997.

[63] “Esileht - Eesti Standardikeskus. Estonian Centre for Standarisation.” [Online]. Available: https://www.evs.ee/. [Accessed: 12-Nov-2019].

[64] P. Cascante Cirici, “Biomass and Oil shale Co-pyrolysis,” Tallinn Univeristy of Technology, 2019.

[65] K. Senelwa, “The air gasification of woody biomass from short rotation forests-opportunities for small scale biomass-electricity systems,” Massey University, 1997.

[66] C. Chee, “The air gasification of woodchips in a downdrat gasifier,” Kansas State University, 1987.

[67] S. Poskrobko, D. Król, and A. Borsukiewicz Gozdur, “Gasification of waste wood

biomass," *Drewno*, vol. 59, no. 197, pp. 241–248, 2016.

[68] S. C. Bhatia, "17 - Biogas," in *Advanced Renewable Energy Systems*, S. C. Bhatia, Ed. Woodhead Publishing India, 2014, pp. 426–472.