



UNIVERSITETET I AGDER

Future district heating plant integrated with municipal solid waste gasification for hydrogen production

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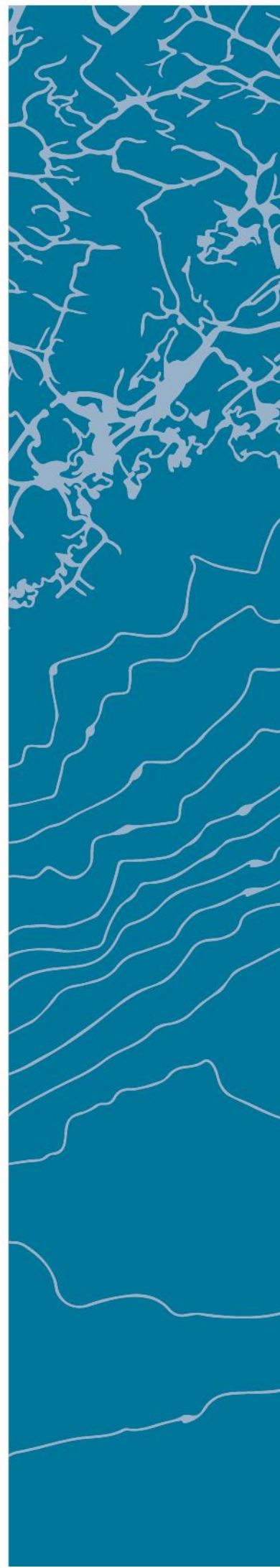
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Abstract

Nowadays energy storage in the form of electrolytic Hydrogen is a common practice for integration of intermittent renewable energy sources in the smart grid environment, utilizing it in the transportation sector and other industrial applications. Similarly, biomass and municipal solid waste (MSW) use to produce hydrogen by thermochemical processes. The characterization of MSW is a critical step in planning, designing, operating or upgrading solid waste management systems. The experimental characterization of Norwegian MSW using statistical waste data performed. The method used for sampling the MSW was economical and straightforward. The data from characterization used for a theoretical investigation of hydrogen production by gasification of MSW, and water-gas-shift reaction. Three setups were modeled for direct and indirect gasification processes using gasification agent of air, steam, and air-steam. The process models simulated using Aspen plus process simulation software to predict the hydrogen yield potential and heat production from MSW. Besides, a sensitivity analysis conducted to study the effect of operating parameters of gasification and water-gas-shift reactors on the composition of the output of the two reactors.

The result from characterization showed a reasonable agreement with the existing study in the characterization of MSW in different countries. The maximum achieved hydrogen yield from tested setups was around 222g H₂/kg of dry ash-free MSW, which is 94% of the maximum theoretical hydrogen yield from specified MSW. At specific operation condition, the hydrogen and heat produced in steam gasification per one kg of MSW were 199.6g of hydrogen, and the excess thermal energy heats 4 liters of water to 100°C. The indirect gasification with steam as gasifying medium showed the highest hydrogen production potential while the direct gasification was the lowest. From the study integrating indirect gasifier in preexisting MSW-fired plants can play a significant role in recovering energy from MSW in the form of energy carrier hydrogen. This technology can also reduce the capital cost of building new incineration to handle the increasing waste generation. However, if it is necessary to construct a new waste incinerator, from the result found in this study, it is recommended to build a direct gasification system.

Preface

This study aims to investigate hydrogen yield potential of municipal solid waste in Norway by integrating district heating plant with a gasifier. This thesis has been written to fulfill the graduation requirements for the degree of Master of Science in Renewable Energy at Faculty of Engineering and Science, University of Agder (UiA) in Grimstad, Norway. Researching and writing of this thesis performed from January to June 2018, and the work conducted under the supervision of Associate Prof. Souman Rudra.

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My sincere gratitude goes to the programme coordinator of MSc in Renewable Energy Prof. Joao Leal for his constructive suggestions and support during the project work.

I would like to thank my wife Selamawit Gebreab Tesfagiorgis for everything because none of this would ever be possible without the love and the fantastic support from her. Last but not the least my family deserve a particular note of thanks: your wise counsel and kind words have, as always, served me well.

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List of Abbreviations

| | |
|------|---|
| ASTM | American Society for the Testing of Materials |
| CHP | Combined heat and power |
| DH | District heating |
| DTG | Derivative thermogravimetry |
| FC | Fixed carbon |
| FTIR | Fourier-transform infrared spectrometer |
| GHG | Greenhouse gases |
| GTL | Gas to liquid |
| HHV | Higher heating value |
| HT | High-temperature |
| HTC | High-temperature catalyst |
| LHV | Lower heating value |
| LT | Low-temperature |
| LTC | Low-temperature catalyst |
| MC | Moisture content |
| MS | Mass spectrometer |
| MSW | Municipal solid waste |
| O&M | Operational and maintenance |
| PBP | Payback period |
| RDF | Refused derived fuel |
| SRF | Solid recovered fuel |
| SSB | Statistisk sentralbyrå |
| TGA | Thermogravimetric analysis |
| VM | Volatile matter |
| WGS | Water-gas-shift |
| WtE | Waste-to-energy |

1 Introduction

Continuous increasing of population, lifestyle behavioral change and the growth of the economy, are the critical driving force behind increasing global waste generation. Also, it leads to high demand for energy, at the same time the issue of sustainability and environmental problems come in connection to waste management and energy generation from fossil fuel-based energy sources to meet the energy demand. The absence in proper management of waste can cause severe damage on socio-economic development of a country, thus managing and using waste as a potential renewable energy source would use as waste disposal and contribute to the saving of raw materials and energy. So, identifying an optimum technology future is essential for addressing such kinds of the issue to inform management as well as decision-maker.

A technology which can help to manage the waste and at the same time contribute to the energy sector is waste-to-energy (WtE) processing unit by incineration or gasification of waste. Waste-to-energy technology is any waste treatment process that uses waste as a fuel/feedstock to produce energy in the form of electricity, heat, and energy carrier chemicals, at the same time it helps in a reduction in the waste volume and weight. Energy recovery from waste provides a double environmental benefit, the diversion of solid waste from landfill and the production of renewable energy, displace the use of fossil fuels and reducing carbon emissions. Nowadays WtE plants mostly work as combined heat and power (CHP) or district heating (DH) plant by conventional combustion of waste to meet the energy demand in the form of electricity and heat.

Gasification technology commonly used with municipal solid waste (MSW) as feedstock is very mature and commercially used in many processes. Integrating CHP/DH plants powered by MSW with gasification technology to produce energy carrier chemicals can substitute the energy carrier's production from fossil fuel-based sources. Thus, the technology plays a significant role in the reduction of greenhouse gases (GHG) emission from fossil fuel-based sources. Also, it can minimize loss of energy from the plant by converting the energy in MSW to energy carrier chemicals according to fluctuating energy demand customers.

A bunch of studies is going on to make a transition from fossil fuel-based economy to the hydrogen-oriented economy; the successful output will be a reduction in greenhouse gas emissions, increased energy security, and more significant overall efficiency. Freedonia Group reported in 2014 that, the annual world hydrogen demand is rising by 3.5% annually, and production projected to have increased to more than 300 billion m³ by 2018 out of this around 95% of the produced hydrogen is from fossil fuel-based methods [1]. Thus, using MSW as potential hydrogen source by gasification would contribute to the increasing global hydrogen demand.

Studying and identifying of potential hydrogen yield of MSW by gasification in Norwegian waste context can help in integration of MSW gasification technology with CHP/DH plants in the focus of hydrogen production. Thus, it can contribute to the increasing world hydrogen demand from a renewable source. To identify the potential hydrogen yield of an MSW, first, it is vital to study physical and thermochemical characteristics of the waste. In this work, to address the issue an experimental characterization of Norwegian MSW was performed in the University of Agder (UiA) laboratory using statistical data of the Norwegian waste fraction. With the help of waste characteristic data, the

potential hydrogen production of the waste by gasification studied using Aspen plus commercial thermochemical simulation software.

1.1 Background

The Norwegian government has a goal of developing a low-emission society and achieving carbon neutrality by 2050 [2]. The government has also implemented, through the EEA/EFTA agreement, the EU Renewable Directive with a national goal of 67.5% renewable energy sources by 2020 from a 2012 value of about 64.5% [3]. Implementation of environmental policies, especially waste policies, is one of the European Commission's key priorities, as confirmed by its proposal for a 7th Environment Action Programme (EC, 2012) and the Roadmap to a resource efficient Europe (EC, 2011) [4]. Thus, waste management policies in the European Union evolve towards waste generation minimization and promotion of recycling, reuse, and energy recovery before disposal on landfills.

The central government authorities in Norway set the general framework, gives municipalities and industry with a relatively free hand to design local collection and treatment solutions. The authorities have put in place several instruments. One of Norwegian waste policy instruments is a ban on landfilling of biodegradable waste from 1 July 2009 [5]. The report from Norwegian statistics office in July 2017 shows that the household waste generated in Norway has been steadily increasing over the last few years. The amount of household waste generated in 2016 increased by 9 percent compared to the amount produced in 2010. From this household waste sent for incineration, almost 80 percent of the waste utilized for energy recovery [6]. Generally, the waste treatment trend in Figure 1.1 shows the increase of waste treatment by incineration whereas the waste sent to landfill decreases from the year 2000.

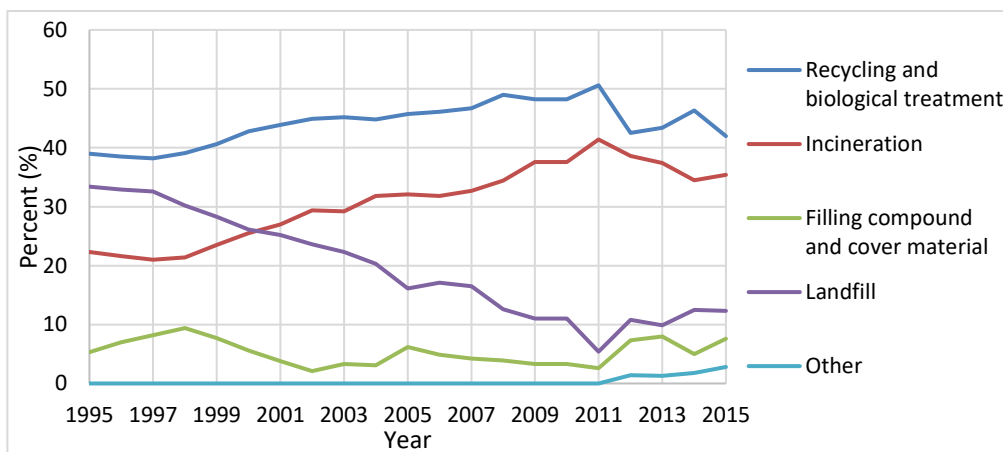


Figure 1.1 Non-hazardous waste in Norway, by the method of treatment. 1995-2015. Percent of known handling [7]

Incineration of the high volume of MSW once recyclable materials have been recovered, i.e., the reject fraction named refused derived fuel (RDF) has a dual purpose, it recovers valuable energy at the same time it reduces the waste volume. The Norwegian WtE sectors have shown growth from a total waste handling capacity of 1.3 million tonnes/year in 2010 to 1.7 million tonnes in 2016. The WtE plants currently account for 17 plants, spread all across Norway [3]. Optimizing these existing waste management infrastructures will be an economically efficient approach to tackle the continual rising of waste generation rate. Also, it can help in the optimal recovery of valuable energy exist in the waste.

In Norway electricity accounts for a significantly higher share of energy consumption. Although the district heating still comprises a small percentage of the total energy consumption in Norway, the consumption trend shows a growing pattern in last 25 years (Figure 1.2) District heating consumption increased by 8.6 percent in 2016 compared to the year before and amounted to a record high 5.2 TWh. Investment in district heating production and the further expansion of the district heating net has pushed up consumption over time [8].

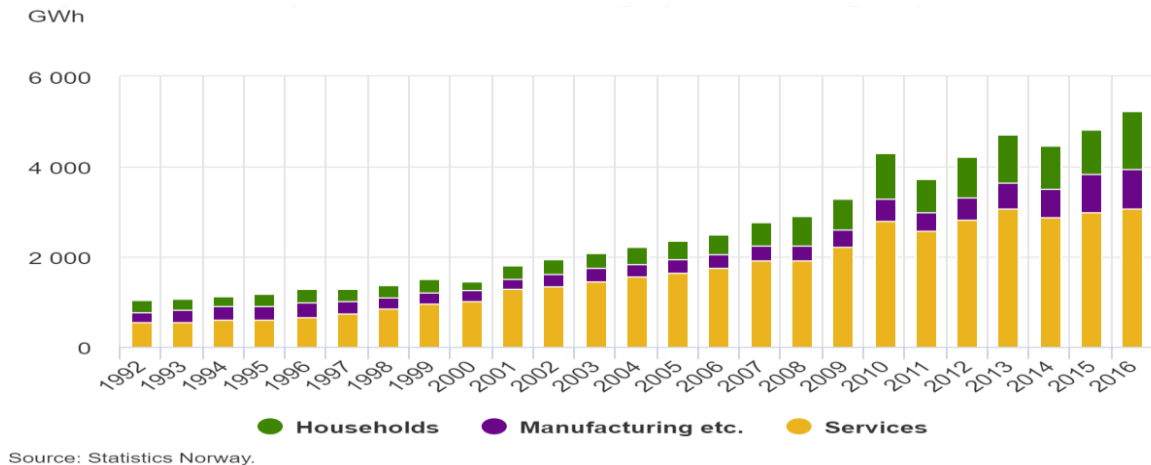


Figure 1.2 Consumption of district heating in Norway by consumer group [8]

Waste incineration is an alternative energy source for district heating system. In 2016, about 50 percent of district heating, or 2.8 TWh, was produced from waste in Norway. In addition to district heating, the waste incineration plants utilized in the production of electricity and district cooling systems. Figure 1.3 shows the development in the amount of energy generated from waste incineration from 2003 until 2012.

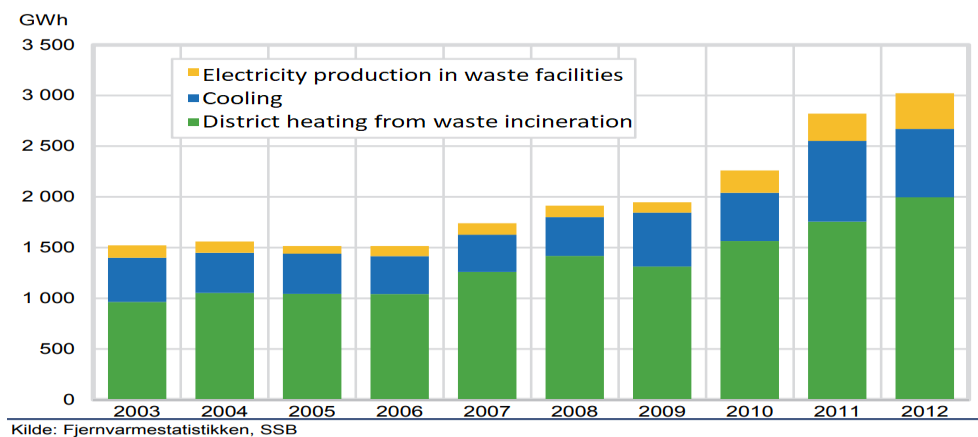


Figure 1.3 Energy production in waste incineration plants. 2003 - 2012. [9]

Gasification of the solid combustible materials is not a new idea nor a new technology; the technology has used for more than a century. ENERGOS has built eight commercially proven clean energy recoveries from waste plants and technology across Europe, out of these five plants constructed in Norway. These plants constructed in Norway works as CHP or DH plant with a fuel capacity of two 30000 tonnes per year, two 39000 tonnes per year and one 78000 tonnes per year. The thermal conversion principle in these plants is carried out in two stages; this is gasification followed by direct oxidation of producer gas produced during gasification stage[10], [11]. The product gas produced in the first stage could utilize as a feedstock for production of hydrogen or methane.

Returkraft MSW-fired CHP plant in Kristiansand is one of the WtE plants in Norway. The plant receives about 130,000 tonnes of waste per year. The energy production at the plant corresponds to the annual consumption of nearly 20,000 detached houses. The thermal conversion principle in this plant is conventional mass combustion process. The plant generates both electricity and heat.

In most incineration plants waste incineration keeps on continuous throughout the whole year since the waste could not store as a long-term energy source due to the characteristics of the waste. During excursion program in Returkraft I learned that usually, energy loss occurs from the MSW-fired CHP or DH plants due to customer energy consumption behavior and seasonal heat energy demand variation [9]. Also, the waste handle capacity of existing incineration plants compares to continue rising of waste generation will be insufficient in future. Building new incineration facility will be costly, so, modifying the existing plants is an alternative to tackle mentioned problems. Integrating gasifier with a CHP/DH plant to convert and store the waste in the form of high energy density gaseous fuel increases waste handling capacity of the plant at the same time minimize the energy loss due to the fluctuation of customer energy demand.

The number of different uses of energy carrier gases shows the flexibility of gasification process and therefore allows it to integrate with several industrial processes, transportation and power generation systems. Integration of electric, heating and transportation system gives an efficient utilization of energy and best smart energy system. For the best management, usage, and participation in greener energy carrier production of MSW, it is essential to look for the flexible technologies for this third-generation to produce energy carrier fuels like hydrogen from the sustainable primary energy source. The focus in this work is that, to evaluate gasification technology for producing gaseous energy carrier from MSW for application in the transport sector, industrial use or for distributed electricity generation.

1.2 Motivation

The background in the previous section shows that district heating by waste to energy technology attracted considerable interest in Norway the last few years. At the same time, waste generation rate shows an increasing trend. Although WtE technology by conventional combustion helps as both waste treatment system and energy recovery, some literature indicated it is less efficient and less environmentally friendly compared to gasification process.

Gasification plants could integrate with preexisting industrial and thermoelectric plants, because of their flexibility and compactness. The most significant choices of design are the reactor type and process cycle, which can conveniently adopt according to waste characteristics [12]. Due to environmental and shift in energy consumption and production situation, production of energy carrier hydrogen by integrating gasifier with CHP/DH plants considered an alternative to the conventional technology for the thermal treatment of solid wastes in future.

One of the thing that makes interesting the MSW gasification is its fuel and product gas flexibility. Since a gasifier designed for MSW gasification take in consideration of various characteristics of the waste, it can handle a diverse type of feedstock. Similarly, the output gas product of gasification can be conditioned/treat as per the necessary downstream use. The outcome of gasification plant could be pure hydrogen, syngas, methane and another type of fuel or chemical.

The other thing is that integrating a gasifier with an existing MSW-fired CHP or DH plants play a significant role in reducing the energy loss from the plant. As it was explained by plant operators

during excursion program in Returekraft in 2017, due to the intermittency of thermal energy demand energy loss occurs in the existing power plants. The reason is that WtE plants have dual purpose reducing the volume of waste and energy generation. To fulfill the purpose of the reduction of waste volume the energy will be unused during less energy demand time. So, during less energy demand period the energy could be utilized in gasification of MSW and convert the energy in MSW into the form of energy carrier fuel. At the same time, the surplus heat from gasification could be utilized to provide heat for DH instead of using direct heat from combustion of MSW. Besides this integrating gasifier could increase waste handling capacity of the plant.

From my level of knowledge, there is no published literature work on characterization of municipal solid waste in Norway. Similarly, very few publications are available on Aspen plus simulation models for MSW gasification and the subsequent syngas adjustment process using water gas shift reaction focusing on hydrogen production. This work could fill these mentioned gaps in this field.

1.3 Research Questions

The study of gasification has attracted considerable interest. The well-established gasification and pyrolysis treatment technology for a homogeneous solid fuel in industrial applications could apply to various solid fuel, by taking consideration on essential gasification related fuel characteristics.

One of the objectives of this thesis was a characterization of the Norwegian MSW using average statistical data for the primary constituent materials of the waste (paper, cardboard, plastic, and wood) in University of Agder (UiA) laboratory. The second objective is developing an integrated model for the fixed bed MSW gasification process and subsequent syngas adjustment using water gas shift reaction with the aid of commercial process simulation software Aspen Plus. The questions to be answered in this thesis are listed as follows.

- How representative is a sampling of waste for characterization using statistical data of the primary constituent materials of the MSW?
- Performing proximate, ultimate and thermogravimetric analysis of the MSW.
- How much will be the potential hydrogen yield and heat generation for district heating by direct (Auto-thermal) and indirect (Allo-thermal) gasification of MSW?
- How gasification and water-gas-shift reactor parameters affect the yield of hydrogen in direct and indirect gasification processes?

1.4 Literature Review

One of the main challenges in thermal conversion of MSW is that MSW presents different physical and chemical behaviors due to its complex heterogeneous material composition. The complexity of the waste composition makes difficult in designing of the appropriate thermal conversion system. In this section, different studies on characterization of MSW, and gasification technologies and their output gas composition analyzed.

1.4.1 Characterization of MSW

Researchers from different countries have reported their findings of physical and thermochemical characteristics of municipal solid waste by taking a sample from a specific location of study. The heterogeneity, location dependency and other factors make difficult designing international standard method for sample collection and preparation. Thus, taking out a representative sample for physical

and thermochemical characterization of MSW is a challenging task. Though estimation of the energy content of MSW using average physical compositions empirical models is a quick and inexpensive method, the type of waste in the country where the empirical model developed is likely to differ significantly from that in the country where the model is applied [13]. The reason is that the dependency of the quantity and type of waste generated in different countries on geographical, seasonal and other factors.

To analyze thermochemical characteristics of RDF preprocessing of small representative samples are very difficult due to the heterogeneity of RDF. This difficulty has limited the effectiveness of thermogravimetric analysis (TGA) for characterization of RDF [14]. Robinson et al. , [14] discussed different comminution techniques to prepare small samples and influence that grinding and sieving had on the composition of the RDF. A TGA method applied to a variety of materials from a commercially available RDF using a variety of procedures. As Robinson et al., mentioned retrieving well ground representative sample after comminution is difficult due to sieves and screens can cause massive changes in the composition of RDF sample. Plastic materials appear to be held up on sieves and screens.

The study in Australia by Hla and Roberts [14] used random sample collection method and categorized the waste sample according to the constituent material type. The study used two methods to analyze the chemical properties of the waste. The first one was examining for each category of material type individually and the second was for the entire MSW by mixing according to their initial weight ratios. The result found in [13] by calculating each category of the waste material type using their weight ratios and the individual properties of the components, and the mixed MSW measurement agreed excellently.

Baawain et al. , [15] reported the result from ultimate analyses of MSW samples with various physical and chemical characteristics for specific site location in Oman. The method they used for sampling in the study was all the fractions were hand sorted according to their waste categories and weighted according to their size fraction. The MSW characterized for each group of material type individually both for analyzing ultimate and proximate analysis of the waste.

Analysis and comparison of the essential properties from the energy standpoint investigated in Spain by Montejo et al. , [16], to prove the advantages of RDF incineration over MSW incineration in function of the composition. The method used in the study to determine the composition of the sample performed by manually sorting and weighting of the waste. The study found out that RDF was a better fuel than MSW. Eisted and Christensen [17] characterize the household waste in Greenland by sorting household waste into material fractions and by determining the composition of each material fraction by chemical analysis. The study presented that the chemical composition of the material-fractions was like the composition of material-fractions in Danish household, this result shows, the sociocultural properties and geographical dependency of MSW characteristics.

In the literature discussed above, all the authors used a method of sorting the waste by material fractions. As Hla and Roberts [13] justified the characteristics obtained by calculating each category of the material type using their weight ratios and the individual properties of the components, and the mixed MSW measurement agreed excellently. Table 1.1 shows the findings of these literature reported for the proximate, ultimate and heating value analysis result of MSW of corresponding study location.

Table 1.1 Proximate, ultimate and heating value analysis of common MSW in different study areas

| Analysis | Parameters | [13] | [15] | [16] | [17] |
|---------------------------|---------------------------|-------|-------|-------|-------|
| Proximate | Total moisture (%) | N/A | 20 | 46.46 | 43 |
| | Volatile matter (%) | 77.4 | 28-33 | N/A | N/A |
| | Fixed carbon (%db) | 15.1 | N/A | N/A | N/A |
| | Ash (%db) | 7.6 | N/A | 15.23 | 19.2 |
| | C (%db) | 52.8 | 52 | 41.37 | 47.4 |
| Ultimate | H (%db) | 6.40 | 8 | 5.36 | 6.64 |
| | N (%db) | 1.29 | 1 | 1.4 | 2.5 |
| | O (%db) | 31 | 39 | 29.01 | 24 |
| | S (%db) | 0.18 | 1 | 0.21 | N/A |
| Energy content (MJ/kg) | HHV _{db} (MJ/kg) | 22.5 | 22.2 | 18.97 | 21.2 |
| | LHV _{db} (MJ/kg) | 21.12 | 20.1 | 17.68 | 18.85 |

Different authors use a TGA to analyze essential characteristics of homogenous and heterogeneous feedstocks. Fang et al. , [18] have studied pyrolysis characteristics of MSW, paper sludge, and their blends through a thermogravimetric simultaneous thermal analyzer from room temperature to 1000°C. The pyrolysis process at the heating rate of 30°C/min shows that, two noteworthy peaks in pyrolysis of MSW, which distinguish MSW into two individual stages. The primary decomposition phase occurred at 267.2–364.1°C and the continuous slight decomposition phase occurred at 364.1–926.81°C.

Singh et al. , [19] have reported the characterization and assessment of the volatile species evolved during the thermal degradation of biomass wood waste, refuse derived fuel (RDF), waste plastic and waste tire. In their investigation they use TGA-FTIR (thermogravimetric analyzer coupled with a Fourier-transform infrared spectrometer) and TGA-MS thermogravimetric analyzer coupled with a mass spectrometer). It showed a similar trend of mass loss rates of the waste materials under the same pyrolyzing heating rates employed for both TGA-MS and TGA-FTIR. In the study, the principal thermal events occurring for the different wastes are approximately in the range of 220 and 500°C.

1.4.2 Gasification Technology

A review of the most significant applied MSW gasification technologies, processes, performance, and system are presented in this section. In thermochemical conversion system gasification of solid materials is not a new concept. Gasification systems successfully applied to the production of energy and chemicals from biomass and coal. Similarly, for the final treatment of MSW, gasification technology has emerged as an attractive alternative to the well-established thermal treatment systems for the recovery of energy from solid wastes [12]. Cost competitiveness of gasification in comparison with combustion, besides the potential for better environmental performance, makes it an attractive technology in recovering energy from solid waste [20].

Much progress achieved regarding the MSW gasification technology and many companies offer a commercially proven technology on WtE gasification-based plants around the globe. Panepinto et al., [18] investigated 100 plants around the world that use gasification systems to process MSW in 2014. Energos is one of the companies offer the commercially proven technology. The company has several

essential gasification plants in Norway and one in Germany. These gasification technologies use the product gas directly to produce heat energy. A thermal conversion that takes place in two stages: gasification of the waste in the primary chamber equipped with a fixed horizontal grate and oxidation of syngas in the secondary chamber [20].

The most stable state-of-the-art gasification technologies in combination with fundamental aspects of the process, comparative analysis of reactor configurations and environmental performance of the primary commercially available gasifiers for municipal solid wastes discussed by Arena [10]. Gasification mentioned as the accepted technology for solid waste conversion, including residual waste from a separate collection of municipal solid waste. Porteous [21] investigated emissions performance of MSW gasification in comparison with MSW incineration. They found out that gasification has the advantage of lower emissions, compared to MSW incineration. The report by Belgiorno et al. , [12] describes the state of gasification technology, pre-treatments, and perspective to syngas use with particular attention to the different process cycles and environmental impacts of solid wastes gasification.

Energy carrier hydrogen can be produced using various, domestic resources, including biomass, MSW, and other renewable sources. Much work has been done on the focus of production of chemicals and fuel by gasification of solid fuel. Kalamaras and Efstathiou [22] discussed in their conference paper different technologies used for hydrogen (H_2) production from both fossil and renewable biomass resources. Among the technologies they presented in their work, biomass gasification, pyrolysis and aqueous phase reforming are the technology's used for hydrogen production from biomass resources. Turn et al., [21] performed an experimental investigation of hydrogen production from biomass using a bench scale fluidized bed gasifier. They investigated the effects of reactor temperature, equivalence ratio, and steam to biomass ratio on hydrogen yield. They found out that, hydrogen yield potential proved to be most sensitive to equivalence ratio.

The two main MSW or biomass gasification reactors configuration used commonly are fluidized bed reactors and fixed bed reactors [24], [25]. Different others use Aspen plus thermochemical simulation software to analyze their work for different reactor configuration and pathways. Rudra et al., [24] discussed upgrading of the existing co-generation plants to quad-generation. The study examined the quad-generation processes to produce power, heating, cooling, and SNG was modeled and compared regarding design and energy efficiency analysis. The quad-generation system is simulated using Aspen plus. Chen et al. , [27] have studied the effect of flue gas on syngas composition and conversion characteristics by simulation of MSW gasification using updraft fixed bed reactor in Aspen Plus. They investigated that the improvement of the heat conversion efficiency and the lower heating value (LHV) of syngas by the introduction of flue gas into the gasification section. Regarding carbon conversion, it increases with the increase of gasification temperature and air equivalence ratio in both reactors. Pala et al. , [28] developed an integrated model for steam gasification of biomass and subsequent syngas adjustment using shift reaction based on Gibbs free energy minimization using the Aspen Plus process simulator. They studied the effect of relevant parameters such as gasification temperature, steam to biomass ratio and shift reaction temperature on hydrogen concentration, CO concentration, CO conversion, CO_2 conversion and H_2/CO ratio in the syngas. Table 1.2 summarize typical producer gas composition of different gasifiers.

Table 1.2 Typical product gas characteristics from different gasifiers [29]

| Gasifier type | Gas composition, dry, vol% | | | | | HHV (MJ m ⁻³) | Gas quality | |
|---------------------|----------------------------|----|-----------------|-----------------|----------------|------------------------------|-------------|------|
| | H ₂ | CO | CO ₂ | CH ₄ | N ₂ | | Tars | Dust |
| Fluid bed air-blown | 9 | 14 | 20 | 7 | 50 | 5.4 | Fair | Poor |
| Updraft air-blown | 11 | 24 | 9 | 3 | 53 | 5.5 | Poor | Good |
| Downdraft air-blown | 17 | 21 | 13 | 1 | 48 | 5.7 | Good | Fair |
| Downdraft oxygen | 32 | 48 | 15 | 2 | 3 | 10.4 | Good | Good |
| Twin fluid bed | 31 | 48 | 0 | 21 | 0 | 17.4 | Fair | Poor |
| Pyrolysis for | 40 | 20 | 18 | 21 | 1 | 13.3 | Poor | Good |

Mustafa et al. , [30] investigated a techno-economic feasibility study of a biomass gasification plant to produce transport biofuel for Narvik, in Norway. They performed the study depending on the demand and available feedstock (forest and MSW) in the region. The investigation carried out on 6 MW downdraft gasification plant assuming ten years of plant lifetime. The cost analysis was performed considering capital cost, operational and maintenance (O&M) costs for the biomass pre-treatment processes, the gasification plant and the gas to liquid (GTL) plant. They found out that, the Payback Period (PBP) of the gasification plant of 4 years and they concluded that downdraft gasification technology was best suited for meeting the demand for small communities. The capital cost and O and M annual cost data they used for the coast analysis listed in Table 1.3.

Table 1.3 Total capital cost for the whole system and total annual O&M cost in a million NOK [30]

| Cost category | Capital Cost (million NOK) | O&M Annual Cost (million NOK) |
|--------------------------|----------------------------|-------------------------------|
| Biomass pre-treatment | 9.50 | 8.57 |
| Gasification plant | 71.50 | 9.64 |
| GTL plant | 35.00 | 5.02 |
| Total Cost (million NOK) | 116.00 | 23.23 |

1.5 Assumptions and Limitations

For characterization of MSW, it could not find a company provides a waste sample as it planned. The attempt to get an actual representative MSW sample from Avfall Norge and the nearby CHP plant (Returkraft) which powered by MSW was not successful due to the lack of sampling technology in the plant. Manual sorting and sampling of the waste also expensive and time-consuming. Therefore, the waste sampled according to Norwegian statistic office, and Avfall Norge reports by considering only the primary constituent materials. The sample is assumed to be an average representative of Norwegian waste.

In an elemental analysis of the waste, there was some limitation in the identification of sulfur content of the sample waste due to the absence of a sulfur column in the analyzer. So, the sulfur content of the waste sample and the simulation model is based mainly on relevant literature. The other assumptions considered in Aspen plus simulation presented in section 3.4.1.

1.6 Outline of Thesis

The thesis focuses on the characterization and the process analysis of MSW gasification system with water-gas-shift reaction. The report organized into chapters and subchapters where every section presents MSW characterization part and followed by process analysis of the gasification system. The sections arranged in the following way.

Chapter 1 presents an introduction and background information on the selected problem and the motivation towards the chosen issue. Research questions and literature review followed by the assumptions and limitations also defined in this chapter.

Chapter 2 describes relevant theoretical background and components to the project. The subchapters present technical information regarding MSW, characterization of MSW, the theory of gasification and mass and energy balance.

Chapter 3 presents method and experimental setup implemented in this work. The subchapters present material and characterization procedure, MSW gasification plant design and simulation method.

Chapter 4 presents the results and discussion of the characterization and the process analysis of MSW gasification system. The subsections present experimental and simulation results.

Chapter 5 concluded with the different findings and implications. Finally, some further work suggested.

2 Theoretical Background

2.1 Introduction

Building systematic theoretical framework on the whole system and the characteristics of the feedstock (MSW) was a significant step in answering the research question. In this chapter, the theory of MSW characterization and theory of gasification system discussed. This chapter deal with brief discussion of municipal solid waste as a feedstock in the gasification process, characterization of MSW, the theory of gasification, the theory of mass and energy balance in the thermochemical conversion process.

2.2 Municipal Solid Waste (MSW)

The definition of 'municipal solid waste' used in different countries varies, reflecting diverse waste management practices. Simply a municipal solid waste can be defined as a waste type consisting of everyday items that are discarded by the public. In the EU's Landfill Directive, MSW defined as 'waste from households, as well as other waste which, because of its nature or composition, is similar to waste from households' [4]. Globally, the common municipal solid waste treatment operations categories are [31]:

- Recycling (excluding composting or fermentation)
- Incineration with and without energy recovery
- Composting/digestion
- Landfilling

Depending on the waste material composition and characteristics, waste can be treat by physical, thermal, chemical or biological processes. The combustible fraction in the municipal solid waste can be processed to manufacture refuse-derived fuel (RDF) or solid recovered fuel (SRF). This RDF or SRF has relatively stable physical and chemical characteristics. Stabilizing the characteristics of a feedstock can be achieved by application of a combination of processes which may include: sorting, shredding, hygiene, drying, and densification. Solid recovered fuel (SRF) is a waste-derived fuel made from non-hazardous household waste. It is feasible to recover energy with an important reduction in the amount of waste landfilled. The SRF is the non-recyclable fraction of municipal waste and consists of approximately 20 % of wood, 30 % of paper, 35 % plastic, and 15 % textile waste. It is a lightweight material with <20 % moisture and formed by fragments of about 4 cm [32].

Choosing a suitable waste treatment pathway depends primarily on the physical and chemical characteristic of the waste. Physical characterization of waste material composition commonly consists of three phases: first picking the waste sample, then sorting the waste according to the material fraction constitute the waste (e.g., paper, plastic, organics, combustibles), and finally handling, interpretation and application of the obtained data. The primary focus of this paper is on the gasification-related characteristics of municipal solid waste treated in waste-to-energy (thermal processes) plants, determination of material composition and distribution of wastes is out of the scope of this work.

Feedstock chemical properties and energy content are an essential data in designing and operation of any thermochemical conversion system, whether combustion or gasification-based. For a correct and efficient gasification process, a sufficiently homogeneous carbon-based material required. Therefore,

many kinds of waste cannot treat in the gasification process directly, and for some types of waste, an extensive pre-treatment required. Several types of waste are directly suitable for the process; they are paper mills waste, mixed plastic waste, forest industry waste and agricultural residues [12].

In Norway, Statistisk sentralbyrå (SSB) quantified waste streams based on three different characteristics: the source of origin, material type, and treatment method. The primary sources of origin for waste are manufacturing industries, construction, service industries, households and other or unspecified. One of the waste treatment methods SSB specified is recycling of waste before incineration. The data sources in the Waste account of SSB include both data based on reported information from businesses, enterprises or households, data from registers, and standard factors from selected studies have also employed.

Table 2.1 shows the amount and material category of waste sent to incineration in the year 2015. This data was the base for the preparation of average MSW sample for experimental characterization in this work. From the waste category which was sent to incineration, the most appropriate material category for energy recovery by thermal conversion methods and which has high percentage material composition used for characterization of the waste. Those materials used for characterization are wood waste, paper and cardboard, plastics and mixed waste.

Table 2.1 Waste in Norway by treatment and material [33]

| Waste incinerated in 2015. | |
|---------------------------------------|-------------------|
| Waste type | Amount (%) |
| Wet organic waste | 1.34 |
| Park- and gardening waste | 0.56 |
| Wood waste | 18.15 |
| Sludges | 1.23 |
| Paper and cardboard | 0.38 |
| EE-waste | 0.48 |
| Cinders, dust bottom ash, and fly ash | 0.03 |
| Plastics | 3.30 |
| Rubber | 0.05 |
| Textiles | 0.03 |
| Discarded vehicles | 0.67 |
| Hazardous waste | 8.98 |
| Mixed waste | 64.46 |
| Other | 0.35 |

2.2.1 MSW as a Fuel

The design of a process for the management of MSW and the resultant economic evaluation and development of a viable business plan requires the knowledge of the properties of the waste. Due to the heterogeneous nature of MSW, the management of MSW needed country-specific technology. In general, MSW materials which use for energy recovery can categorize into renewable and non-renewable materials. The main material categories used for energy recovery from waste are paper, cardboard, wood and wet organic wastes derived from a renewable source, while plastics are from the fossil-derived source. Figure 2.1 displayed the total household waste generated in Norwegian in

2016. In Norway, there is a good practice of sorting the waste from the primary source of the waste according to an available waste management system.

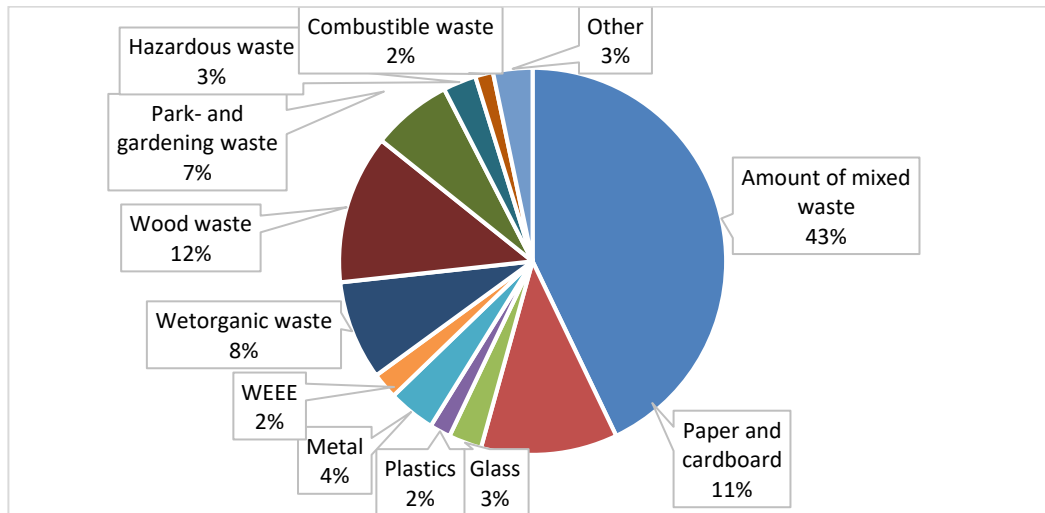


Figure 2.1 Household waste by material type in Norway in 2016 [6].

Currently, refuse disposal methods determined by cost and their effect on the environment. Intensification of environmental and health concerns, combined with the possibility of exploiting day-to-day by-products as valuable energy resources, has led to the exploration of alternative methods for waste disposal [34]. Sustainable waste management is an essential component to make countries more resource efficient by promoting waste prevention, recycling of MSW and the conversion of waste to energy and valuable chemicals. This important target is driving European environmental policies and legislation towards a more efficient waste management system [34]. Waste-to-energy is the third option of waste management and followed by landfill, waste that cannot be recycled or reused should be used for energy recovery and leaving landfill as the last option for waste disposal.

Waste to energy technologies physically converts waste matter into more useful forms of fuel that can be used to supply valuable energy. The waste to energy conversions can be performed using either biological treatments such as anaerobic digestion and fermentation, or thermal conversions such as combustion (incineration), pyrolysis, gasification. Gasification with hydrogen production performs as efficiently as incineration but is advantageous compared to landfilling [35].

Although the hydrogen content in biomass is only 6-6.5% compared to almost 25% in natural gas, the potential zero net CO₂ impact of renewable biomass makes it an attractive alternative to fossil feedstocks. Fortunately, the presence of both renewable and fossil feedstocks in MSW could give the average of the two-mentioned advantage and drawback of the two sources of feedstocks. An integrated process, in which part of the feedstock is used to produce more valuable materials or chemicals and only residual fraction are used to generate hydrogen, can be an economically viable option [36].

2.3 Characterization of MSW

Characterization of MSW is the primary and a critical step in the evaluation of waste feedstocks to choose a suitable waste treatment method. Due to the heterogeneity of the waste feedstocks, for a thermal conversion process detailed and accurate analysis is essential, to prevent operational related problems, optimize conversion processes and design conversion systems. The vital characteristic of

MSW to be analysed proposed in the different literature are the proximate analysis, ultimate analysis, calorific value, thermogravimetric analysis (TGA), ash composition and ash melting and fusion points. Except for the ash composition and ash melting, and fusion points of the MSW sample, the other characteristics investigated in this work.

The experimental determination of ultimate analysis and thermogravimetric analysis data require unique instrumentation (TGA and elemental analyzer), while proximate analysis data can be obtained easily by using conventional equipment's [37]. Similarly, the heating value of a feedstock can be readily determined using simple bomb calorimeter or by a calculation from elemental analysis data of the feedstock. MSW is like other fuel types in need for standardized methods of analysis leading to accurate and consistent evaluations of fuel properties. Standards have developed for characterization of different feedstocks. ASTM, ISO, Standard Norway and other organizations maintain standards for the determination of properties of a feedstock such as chemical composition, heating value, density and ash fusibility, and other. In Table 2.2 available RDF laboratory sample preparation and characterization standards in Standard Norwegian presented.

Table 2.2 Sample preparation and characterization of RDF standards by Standards Norway based on national, European and International standards.

| Standards | Standard description |
|---------------------|--|
| NS-EN 15413:2011 | Solid recovered fuels - Methods for the preparation of the test sample from the laboratory sample |
| NS-EN 15407:2011 | Solid recovered fuels - Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content |
| NS-EN 15408:2011 | Solid recovered fuels - Methods for the determination of Sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content |
| NS-EN 15403:2011 | Solid recovered fuels-Determination of ash content |
| CEN/TS 15414-1:2010 | Solid recovered fuels-Determination of moisture content using the oven dry method - Part 1: Determination of total moisture by a reference method |
| CEN/TS 15414-2:2010 | Solid recovered fuels-Determination of moisture content using the oven dry method - Part 2: Determination of total moisture content by a simplified method |
| NS-EN 15402:2011 | Solid recovered fuels-Determination of the content of volatile matter |
| CEN/TR 15404:2010 | Solid recovered fuels - Methods for the determination of ash melting behavior by using characteristic temperatures |

Municipal solid waste is a complex chemical mixture of biogenic and petroleum-derived materials. Van Krevelen (VK) diagrams provide an alternative way to visualize the chemical composition of complex chemical mixtures by plotting the hydrogen to carbon ratio against the oxygen to carbon ratio for every compound in the mixture [38]. Knowing the chemical composition of the chemical mixture of fuel helps in identifying the type and nature of the fuel. Using the ultimate analysis result of the MSW the plots in Figure 2.2 can provide some insight into the nature of the chemicals in the mixture.

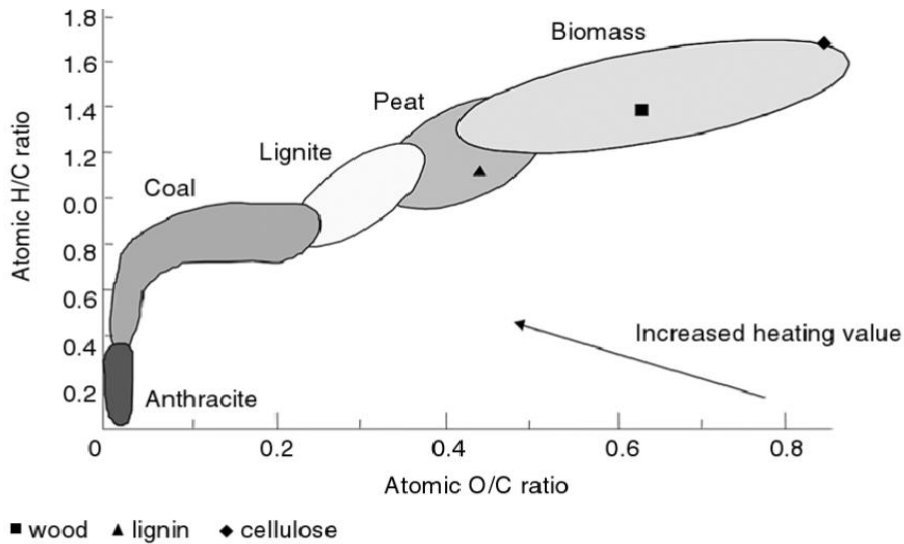


Figure 2.2 Classification of solid fuels by their H/C and O/C ratios [39]

2.3.1 MSW Sorting

Physically and chemically heterogeneity of MSW makes collecting a sample for analysis less straightforward. As only a few grams of the sample used for analysis of thermal related properties, it must be representative of the vast waste pile. Due to the heterogeneity of MSW, managing and treating waste in complying with the implementation of environmental policies, especially waste policies are a demanding task. One of the challenges in analyzing the chemical characteristics of MSW is the lack of a standard method for sample collection and preparation [13]. Most researchers categorized and analyzed the different physical components of MSW (e.g., food, paper, plastics, textiles, wood, glass, metals,) [13], [15–17], [40].

2.3.2 Bases for Expressing a Feedstock Composition

The proximate analysis and ultimate analysis values of a feedstock commonly expressed as a dry basis or wet basis depending on the situation. More specifically the bases of the two analyses' can be expressed in four bases As-received, Air-dry, Total dry and dry ash-free bases. Figure 2.3 illustrates the comparison of these bases.

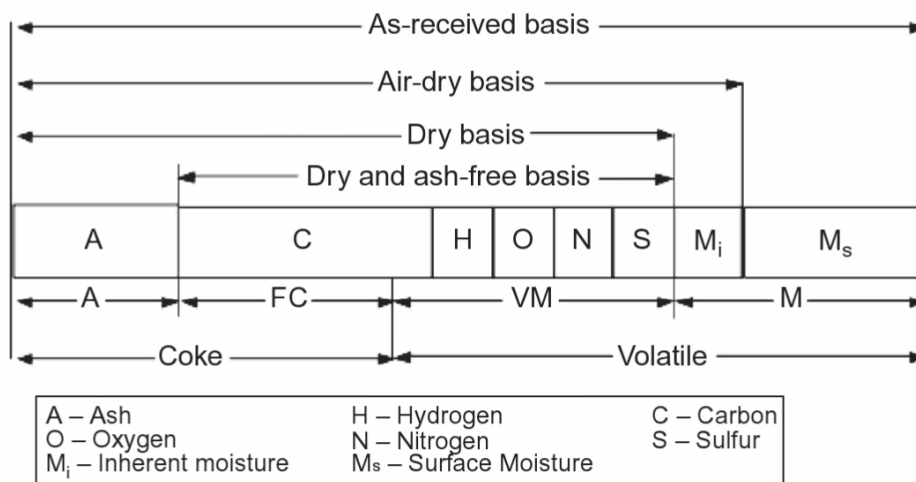


Figure 2.3 Basis of expressing fuel composition [39]

2.3.3 Proximate Analysis

Proximate analysis of a feedstock is the determination of the compounds contained in the fuel. The four major components of the fuel determined by proximate experimental analysis include the measurement of moisture content (MC), volatile matter (VM), ash content (Ash), and fixed carbon (FC), though FC is the difference of the three measurements out of 100%. Proximate analysis is relatively simple, inexpensive and can perform with a simple drying oven, a laboratory furnace, and a balance. In the determination of proximate analysis various standards can implement for the measurement of MC, VM, FC and Ash content a fuel, for example, standards given in Table 2.2.

Moisture content (MC)

The moisture content of MSW significantly influenced by various reasons, such as differences in waste content, season, geographical location and weather conditions at the time of sampling [41]. The moisture content of MSW drains much of the deliverable energy in thermochemical conversion plant, as the energy used in evaporation is not recovered [39]. In another hand for a gasifier uses steam as gasifying agent the vaporized moisture can replace or reduce the need for steam injected into the plant as a gasifying medium. Moisture content is an essential design parameter utilized for proper design and operation of the gasifier. In measuring the moisture content of a feedstock, simple gravimetric forced convection dryer with the ability to maintain the temperature within the range of 104°C to 110°C is used [42].

Different standards can implement for determination of moisture content of different feedstocks. The total moisture content of the reduced samples of refused derive fuel can determine according to American Society for the Testing of Materials (ASTM) standard method E 949-88 [39]. Hla and Roberts [13] determined the moisture content of oven-dried MSW samples using ASTM standard method E 871-82, which is a standard method for particulate wood fuels. The standards state that weighted wet samples should be placed in the oven at 103°C for at least 16 h; following drying, the samples removed from the oven and cooled in desiccators at room temperature. The dried samples then weighed immediately to avoid moisture gain from the atmosphere. A feedstock moisture content on a dry basis can express as.

$$\%MC_{dry} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (2.1)$$

Where: $\%MC_{dry}$ percentage of moisture composition on a dry basis, W_{wet} wet sample and W_{dry} dried samples.

The moisture content in a feedstock can categorize into two types which is inherent moisture and surface moisture. In the case of MSW, the surface moisture is dominant since the waste absorbs moisture from the surrounding. The relatively renewable fraction of the waste absorbs much moisture than nonrenewable fraction like plastics barely absorb moisture. Especially for unsorted MSW, the presences of the biodegradable fraction in the waste increase the moisture content of the waste highly. For high moisture containing a biodegradable fraction of waste composting/digestion is a preferred conversion method.

Volatile matter

The volatile matter of solid fuel is the condensable and no condensable vapor released when the fuel heated elevated temperature [39]. The volatile matter of solid fuel can give a useful approximation of the organic matters in the samples [15]. For MSW, volatiles represents a significant portion of the carbonaceous fuel that provides an easily ignitable atmosphere of fuel gases around the solid waste as well as part of the produced gases of the gasification process [10] with the same principle as burning a fire matches. In a common MSW sample, the mass fraction of volatile matter species is around 60–80% [13], [40], [43].

For the determination of the volatile matter fraction of a feedstock, different standards are available. The test procedures in these standards describe the determination of the percentage of gaseous products exclusive of moisture vapor. The applicable ASTM standard for determination of the volatile matter is E-872 for wood fuels it specifies that a weighted sample in the covered crucible is placed in a furnace at 950°C for 7min [39]. EN 15148 standard specifies the temperature setting is 900 °C ± 10 °C, for 7min [44]. The mass loss after heating the sample represents the VM and MC for a sample tested on a wet basis. The percentage of volatile matter on a dry bass ($\%VM_{dry}$) is calculated from the loss in mass of the test portion after deducting the loss in mass due to moisture content as shown in eqs.(2.2) and (2.3).

$$VM = W_{loss} - MC \quad (2.2)$$

$$\%VM_{dry} = \frac{VM}{W_{dry}} \times 100 \quad (2.3)$$

Where: W_{loss} is a mass loss, W_{dry} is the dried weight of the sample from MC test.

Ash content

Ash is an inorganic, noncombustible component left in the form of soft gray powder after complete combustion of a feedstock. Similarly, for determination of ash content of a feedstock different standards can be implemented. Standard test method for ash in biomass (ASTM E1755) covers the determination of ash, expressed as the mass percent of residue remaining after dry oxidation (oxidation at 575 ± 25°C). The standard can apply for hard and soft woods, herbaceous materials, agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid and alkaline pretreated biomass, and the solid fraction of fermentation residues.

To determine the percentage composition of the ash in a feedstock, the sample placed in a muffle furnace for about an hour, with the lid removed and the temperature set to 600°C. After an hour, the crucible is placed in a desiccator until the sample has cooled [42]. Ash is the weight of the residue (W_{ash}) obtained after complete combustion of the sample (with no carbons left in the sample). The percentage of ash in fuel on a dry base ($\%Ash_{dry}$) can be express as.

$$\%Ash_{dry} = \frac{W_{ash}}{W_{dry}} \times 100 \quad (2.4)$$

Fixed carbon

Fixed carbon is carbon left after a part of the carbon is transformed into a carbonaceous material called pyrolytic carbon during the pyrolysis process. Fixed carbon is not a fixed quantity, it varies with the rate of heating, but its value, measured under standard conditions, gives a useful evaluation parameter of the fuel. For gasification analysis, FC is an important parameter because in most gasifiers the conversion of fixed carbon into gases determines the rate of gasification and its yield [39]. The FC content in dry basis can determine by taking the difference between 100% and the sum of the MC, VM, and Ash percentages of the sample.

$$\%FC_{dry} = 100 - \%MC_{dry} - \%VM_{dry} - \%Ash_{dry} \quad (2.5)$$

Where: the four proximate analysis results are in dry basis.

2.3.4 Ultimate Analysis

The ultimate analysis is the determination of the fundamental constituent elements of the hydrocarbon fuel/compounds. The ultimate analysis gives the chemical composition and the higher heating value of a fuel. The chemical analysis usually determines carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S) content of the moisture-free fuel on a weight percentage basis, and the moisture and ash content.

The ultimate analysis is relatively complicated, expensive and required advanced equipment compared to proximate analysis. The following ASTM standards are available for determination of the ultimate analysis of biomass components. Carbon, Hydrogen E-777 for RDF, Nitrogen E-778 for RDF and Sulfur E-775 for RDF [39]. During ultimate analysis of a feedstock, care must be taken not to include the hydrogen content presented in moisture, if so the hydrogen from the water must be reduced from the total hydrogen content of the ultimate analysis. Moisture and ash for ultimate analysis the result from proximate analysis can be used, and the ultimate analysis values sum to 100%.

$$C + H + O + N + S + Ash + MC = 100\% \quad (2.6)$$

Different researchers analyze the ultimate analysis of MSW by categorizing each constituent materials of the waste individually. So the elemental composition of the whole MSW can be calculated using their weight ratios of each constituent material and the elemental composition of the individual materials using eq.(2.7)[13].

$$Y_{mixture} = \sum_{i=1}^n Y_i \times X_i \quad (2.7)$$

Where: Y_i is weight ratio material i , X_i is the elemental composition of material i .

2.3.5 Heating Value Analysis

Heating (calorific) value is the measure of the amount of heat produced from complete combustion of a specific amount of fuel, and it measured as a unit of energy per unit mass or volume of a substance. The heat of combustion of fuels expressed by either as the higher heating value (HHV) or lower heating value (LHV). The high heating value of the fuel determined by oxidation of the fuel with pure oxygen in a bomb calorimeter, and measuring the heat released during complete combustion of the fuel, and the product come to a temperature of 25°C. Whereas, the lower heating value measured when the water is in the vapor state. The lower heating value can determine by subtracting the heat of vaporization of water vapor generated during combustion of fuel from the higher heating value [39]. The relationship between HHV and LHV expressed.

$$LHV = HHV - h_g \left(\frac{9H}{100} + \frac{MC}{100} \right) \quad (2.8)$$

Where: LHV , HHV , H , and MC are lower heating value, higher heating value, hydrogen percentage, and moisture percentage, respectively on an as-received basis. Here, h_g is the latent heat of steam in the same units as HHV (i.e., 2260kJ/kg).

Many researchers put efforts to correlate heating value with the elemental compositions of a feedstock. The very popular correlation of heating value with elemental composition noticed by Boie, Dulong, Gaur, and Reed, and others [45], [46]. The heating value can estimate with considerable accuracy, the calculated value agrees with the measured value with an absolute error of 2.1% for many biomass materials [43]. Eqs. (2.9), (2.10) and (2.11) are the empirical equations proposed by Boie, Dulong, and Gaur and Reed respectively.

$$HHV(\text{kJ kg}^{-1}) = 35160 \times C + 116225 \times H - 11090 \times O + 6280 \times N + 10465 \times S \quad (2.9)$$

$$HHV(\text{kJ kg}^{-1}) = 33823 \times C + 144250 \times H - 18031 \times O + 9419 \times S \quad (2.10)$$

Where C , H , S , O , and N are the elemental mass fractions of carbon, hydrogen, sulfur, oxygen, and nitrogen in the fuel.

$$HHV(\text{MJ kg}^{-1}) = 0.341 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times \text{Ash} \quad (2.11)$$

Where C , H , S , O , N , and Ash are the wt % of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash in the fuel.

Similarly, the heating value of gasification product (syngas) can be calculated using the percentage composition of each gas in the mixture and the heating value of the gases. The lower heating value of the product gas depended on the volume percentage of CO, H₂, and CH₄ in the bio-syngas and could calculate as follow [47]:

$$LHV = X_{H_2}LHV_{H_2} + X_{CO}LHV_{CO} + X_{CH_4}LHV_{CH_4} \quad (2.12)$$

Where: X was the volume percentage of each gas component. The lower heating values of H₂, CO and CH₄ are 11.2 MJ/Nm³, 13.1 MJ/Nm³, and 37.1 MJ/Nm³, respectively.

2.3.6 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a useful method used for material or solid fuel characterization. The TGA monitors the weight loss of a substance as a function of temperature or time when the sample specimen subjected to a controlled temperature program in a controlled atmosphere. The experimental results of a TGA could present for analysis as derivative thermogravimetry (DTG) and thermogravimetry (TG). In the analysis, the material behavior in TGA, the use of DTG result makes easy identification of critical temperatures in the decomposition of the sample for further analysis.

TGA applies to most industries to characterize materials or solid fuels, for example, it can be used to provide a measure of the renewable content of RDF by dividing the combustible fraction of the fuel into cellulosic and petroleum-derived materials [14]. The analysis helps in determining reaction chemistry of solid samples where one of the products is in the gaseous state, proximate analysis, pyrolysis kinetics of decomposition or thermal stability of solid fuel in an inert atmosphere [46] in the isothermal or dynamic temperature mode. Figure 2.4 illustrates a typical mass loss behavior (intervals) of an RDF during pyrolysis and oxidation process under TGA analysis. As the figure shows in the decomposition of constituent materials the interval between the temperature of 180°C to around 400°C, the biogenic materials decompose. The petroleum-derived materials decomposed in the interval of 400°C to around 570°C.

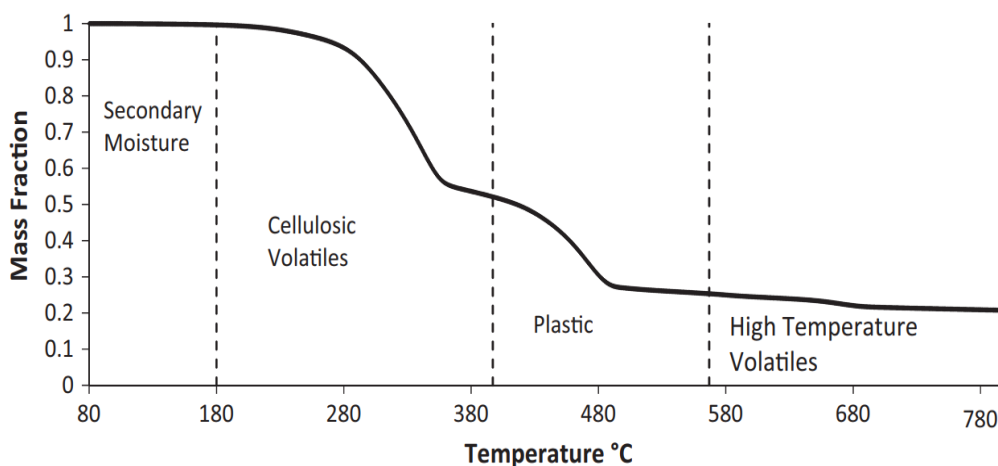


Figure 2.4 Mass loss intervals during TGA temperature ramp [14]

2.4 Theory of Gasification

Thermal waste treatment processes including combustion, gasification, and pyrolysis to recover energy from waste in the form of heat and/or power. Gasification is a thermochemical conversion of a solid or liquid carbonaceous fuel (feedstock) by partial oxidation process into useful energy, chemicals, fuels, or mechanical and electrical power [12], [39], [42], [48–50]. The thermochemical conversion changes the chemical structure of the carbonaceous fuel by the application of high temperature [12] from partial oxidation of the fuel itself or by using external heat supply at the controlled condition. The addition of gasification agent at high temperature facilitates the conversion of large molecular structure compounds and solid char to low molecular structure compounds through different chemical reactions and physical processes. The four-major physio-chemical processes take place in gasification process split into drying, pyrolysis, combustion, and reduction.

As shown in Figure 2.5, pyrolysis, gasification and combustion are a separate thermochemical conversion technology and different products can be gained from the application of pyrolysis, gasification and combustion processes and different energy and matter recovery systems can be used to treat these. Only gasification conversion technology by itself comprised of pyrolysis, gasification and combustion stages within the gasification reactor. In the case of auto-thermal (direct) gasification, the three thermal processes take place in one reactor, whereas in allo-thermal (Indirect) gasification combustion process for supplying the energy required for the gasification is occur externally.

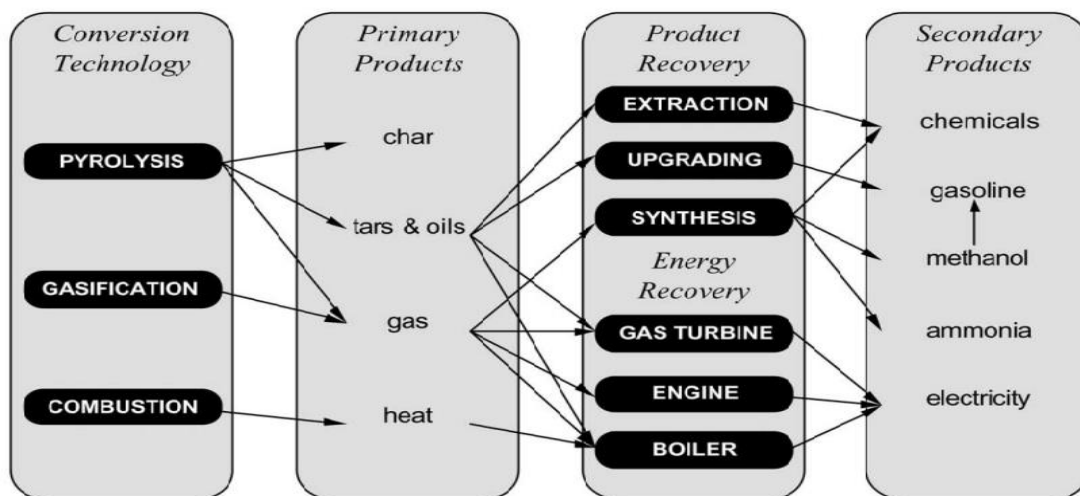


Figure 2.5 Thermal conversion process and products [12]

In gasification process, oxygen, air or steam used as gasifying agents and it participates in the reaction with char, gaseous products, and high hydrocarbons to convert them into low molecular-weight gases. Besides this in the case of direct gasification, the gasifying agents (oxygen/air) use for partial oxidation of the fuel to produce heat for endothermic gasification and pyrolysis processes.

The gasifying agents have a contribution to the composition and the heating value of the gasification product. The gasification with oxygen is not widespread because it involves massive investment for production of oxygen. Similarly, gasification with air also involves substantial investment for purification of the product gas. Recently the steam gasification has become an area of growing interest because it produces a gaseous product having higher H_2 content. Besides, the steam gasification process has the following additional advantages [51]: it is capable of maximizing the gas product with

higher heating rate involved, advantageous residence time characteristics, and the efficient tar and char reduction brought about by steam reforming. However, the steam gasification reactions are endothermic. To provide the necessary thermal energy for gasification air is introduced to burn part of the available feedstock [52] or the heat need to be transferred from external heat supply.

The direct product of gasification referred to as producer gas. It refers to the low heating value gas mixture of mainly carbon monoxide (CO), hydrogen (H₂), carbon dioxide(CO₂), methane (CH₄), other low molecular weight hydrocarbons and nitrogen (N₂) produced if air used as oxidant [53]. The diagram in Figure 2.6 illustrated the composition of product gases depends on the type of gasifying medium used. If oxygen used as the gasifying agent, the conversion path moves towards the oxygen corner. It produces CO for low oxygen and CO₂ for high oxygen. Similarly, if steam used as the gasification agent, the conversion path moves toward hydrogen corner. Then syngas contains more H₂ per unit of carbon, resulting in higher H/C ratio. After purification of product gas, the remaining gas containing primarily of hydrogen and carbon monoxide termed as syngas. Syngas is potentially more efficient to generate electricity using gas turbine than direct combustion of the original feedstock [54], [55] and can be processed further for enhancement of hydrogen.

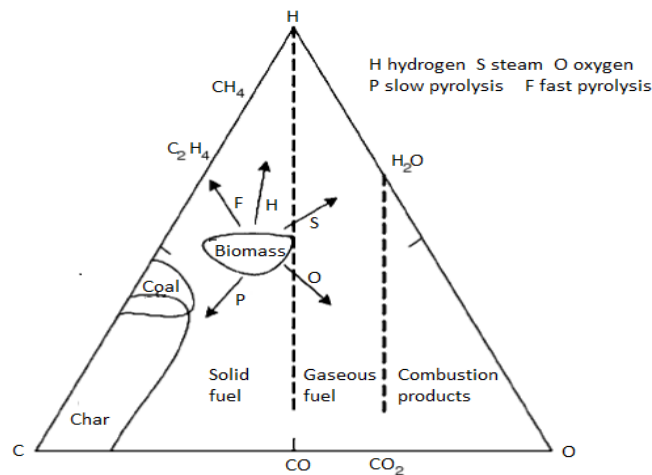
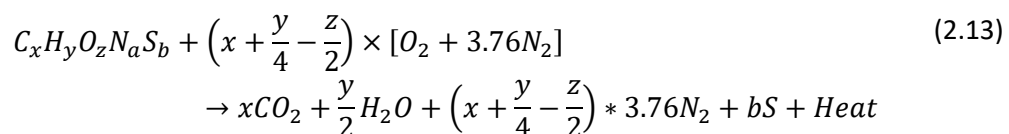


Figure 2.6 C-H-O diagram of the gasification process [39]

In the thermochemical conversion of a feedstock by gasification process, a series of chemical and physical processes take place. The auto-thermal gasification process uses oxidant (air or oxygen) under the stoichiometric requirement for complete oxidation of the specific feedstock, typically around 30% to 70% of the stoichiometric amount required for complete oxidation of the feedstock. The general chemical equation that can be used to estimate the combustion stoichiometry for any carbonaceous fuel with known elemental analysis expressed in eq.(2.13). The generic combustion stoichiometry equation for any carbonaceous fuel given by the empirical equation of $C_xH_yO_zN_aS_b$, with air can express as [42].



where x,y,z, a and b represents the mole fraction of each element in the fuel.

Using chemical equation (eq. (2.13)), a vital gasification process parameter the air-to-fuel ratio by weight required for complete combustion can determine as [42].

$$\frac{Air}{Fuel} \left(\frac{kg}{kg} \right) = \frac{\left(x + \frac{y}{4} - \frac{z}{2} \right) \times [O_2 + 3.76N_2]}{C_x H_y O_z N_a S_b} \quad (2.14)$$

The other important gasification process parameter is an equivalent ratio. It can define as the ratio of the actual fuel to air ratio (F/A) divided by the stoichiometric fuel to air ratio [42]. If this ratio is less than unity it is called fuel-lean conditions and the opposite is fuel-rich conditions.

$$\Phi = \frac{(F/A \text{ ratio})_{actual}}{(F/A \text{ ratio})_{stoichiometric}} \quad (2.15)$$

As mentioned earlier in this section the different phases or zones in the gasifier, which carbonaceous feedstock passes through during gasification conversion into producer gas are drying, pyrolysis, char gasification, and combustion. In those sequential phases series of thermochemical and physical processes take place during gasification reaction, but these phases do not have any physical boundaries between them and occur in rapid successions approximately in 1second if the feedstock particles are in small size [53]. These virtual zones discussed as follow.

Drying

Most biomass resources have high moisture content on harvest or during collection in the case of MSW. The typical moisture content of freshly cut wood ranges from 30% to 60% and may exceed 90% in some types of biomass [39]. The high moisture content of the feedstock affects the conversion efficiency of a gasifier. Moisture that is present in a feedstock is considered to have a negative impact on the gasification, due to the amount of energy absorbed during the vaporization process [39], [56]. Before the feedstock feed to a gasifier, it is essential at list removing a certain amount of external or surface moisture from the feedstock by energy efficient way.

The typical moisture content of a feedstock in which a gasifier handle reported in the different literature is around 10%-20% of moisture [39], [42]. The small percentage of inherent and surface moisture left in the feedstock after pre-drying, removed in the gasifier unit in drying phase of gasification. The irreversible moisture removal from the feedstock takes place in the temperature range of 100-200 °C [39], [42]. The steam from the drying process involved in the subsequent chemical reactions or mix with the product gas as moisture. Drying phase of gasification is an endothermic process, the heat used for the endothermic reaction comes from the partial oxidation of the feedstock in combustion phase of the direct gasification, while it supplied from an external source in indirect gasification.

Pyrolysis

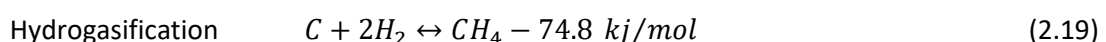
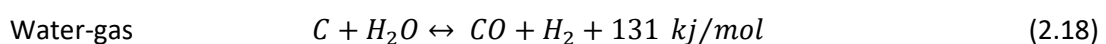
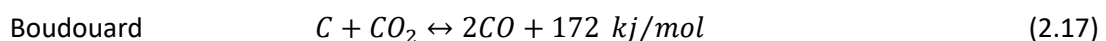
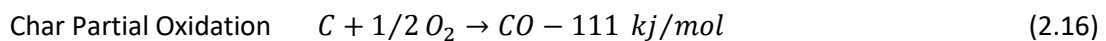
Pyrolysis is an irreversible breaking down (lysis) of carbonaceous material by heat (pyro) without application of any oxidant medium. When a carbonaceous material subjected to a high temperature about 350°C in the absence of air or oxygen, it decomposes into three phases liquid, gas and solid. The relative quantity of the liquid, gas and solid in pyrolysis phase of solid fuel gasification highly depend on the residence time and final temperature reached by the fuel during the reaction.

The product of pyrolysis process are solid (mostly chare or carbon), condensable liquid (tars, heavier hydrocarbons, and water) and noon condensable gases (CO_2 , H_2O , CO , C_2H_2 , C_2H_4 , C_2H_6 , C_6H_6 , etc.) [39], [42], [53]. Long residence time during the pyrolysis phase, gives a favorable condition for decomposition of medium molecules into the small molecules, such as hydrogen, carbon monoxide, carbon dioxide, methane, and other. [47]. Whereas, in short, residence time the medium molecules will condensate and form high melting points and pour points tars and oils and enter the oxidation zone of the gasifier.

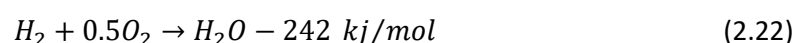
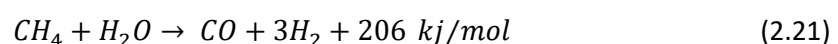
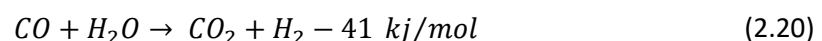
The temperature required for pyrolysis process generally above $300^\circ C$ [42]. Since the process is an endothermic the energy required for the process retrieve from partial oxidation of the fuel or external heat supply. The gas phase products of pyrolysis are composed of mainly carbon monoxide and hydrogen. These products are the primary goal of this study, which is the extraction of hydrogen from these produced gases, and from the other two phases of pyrolysis product (solid and liquid phases). Hydrogen can be extracted or enriches in the subsequent solid-gas reactions and tar cracking processes of the gasification process.

Char gasification

Char gasification reaction occurs after pyrolysis phase of the gasification process in the reactor. In this phase there are four significant reactions involves between residual char and carbon dioxide, gasification agents (air, oxygen, and steam) introduced into the oxidation zone [39], [53]. Among these four reactions, carbon-oxygen (char partial oxidation) and carbon-hydrogen (methanation) reactions are exothermic reactions supplies vital energy to drive the other endothermic reactions in the gasification process, while the two reactions carbon-water (water gas), and carbon-carbon dioxide (Boudouard) are endothermic. The significant gas-solid reactions occurred in gasification process summarized as following from eqs. (2.16) to (2.19).

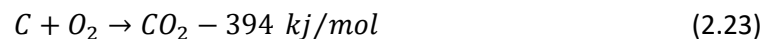


In practice, the contact time between char and gaseous reactants at elevated temperatures is usually insufficient to achieve equilibrium, as a result up to 10wt% of the feedstock appears as char in the gasification products [53]. The typical gas phase reactions take place in gasification process are water gas shift, steam methane reforming and hydrogen partial combustion reactions shown below respectively.



Combustion

Gasification is a partial oxidation process which uses less oxidant than the oxidant required for complete combustion of a fuel. To provide necessary heat of reaction that required for heating, drying, and pyrolysis phases a certain amount of exothermic combustion reaction is allowed in gasification [39]. In gasification typically around 30% to 70% of the stoichiometric amount of oxidizing agent (pure oxygen or air) is used to generate enough heat to gasify the remaining unoxidized fuel [42]. In a combustion reaction, a minor amount of the carbon entirely oxidized to carbon dioxide (CO₂), water and releases the required heat for the remaining gasification phases. Eq. (2.23) is the main combustion reaction take place in the gasification reactor.



2.4.1 Gasification Technologies

A gasification plant includes the gasifier reactor and other auxiliary equipment to facilitate upstream and downstream processes. For gasification process, different reactor designs are used depending on the feedstock characteristic, the desired gasification product, and other factors. Although there are many ways to characterize gasifier reactor types, the way fluids or solids transport through the reactor is one possibility to characterize gasifier reactor types. There are four main types found [25].

- Quasi-non-moving or self-moving feedstock
- Mechanical-moved feedstock
- Fluidically-moved feedstock
- Special reactors

As mentioned in the literature review section of gasification technology, the two main MSW or biomass gasification reactors configuration used commonly are fluidized bed reactors and fixed bed reactors. Fixed bed reactor categorized under quasi-non-moving or self-moving feedstock reactor type, while fluidized bed reactor categorized under fluidically-moved feedstock type.

The fluidized bed gasifier is more complicated in operation and constructing, and it requires more investment in comparison to fixed bed gasifier requires less investment, and it is more suitable for smaller capacity MSW treatment [27]. An appropriate range of application for each, the fixed bed type is used for smaller units (10kWth-10MWth); the fluidized bed type is more appropriate for intermediate units (5MWth – 100MWth) [39].

The other way to classify gasifiers is according to energy providing method for a gasification process since the gasification is an endothermic process which takes place at high temperature. The energy needed for the gasifying of the solid feedstock to flammable gas fuel supplied either by combusting the part of the feedstock within gasification reactor (direct/auto-thermal) or by supplying from external energy sources (indirect/ allo-thermal).

The direct/auto-thermal gasification is a process in which the thermal energy for gasification provided by combustion of part of the feedstock inside the reactor. In this process only one reactor used, and the gasification agent has a direct contact with the product gas. In the case, air used as a gasifying

medium the presence of high percentage composition of the nitrogen affects the heating value of the product gas.

Indirect/allo-thermal gasification is a process in which the thermal energy for gasification supplied from an external energy source. So, part of the feedstock combusted entirely in a separate reactor and the energy transported to the gasification reactor. In this case, there is no direct contact between flue gas from combustion and product gas.

2.4.2 Fixed-bed Gasifiers

In a fixed (or moving) bed gasifiers, the feedstock process in bulk and the feedstock covered in almost all the volume of the reactor. One of the essential characteristics of fixed/moving bed reactor is that it has distinct reaction zones within the reactor such as drying, pyrolysis, combustion, and reduction. However, the relative position of these zones moves up and downwards depending on the fuel characteristics and operating conditions. One of the advantages of fixed-bed gasifiers is the higher temperature in fixed bed gasifiers minimizes the need for installation of gas purification system for purifying the tar present in product gas [25].

Fixed bed reactors further classified according to the way the gasifying agent fed through the reactor. Thus, the main types of fixed bed reactors are updraft (countercurrent), downdraft (concurrent) and cross draft (crosscurrent) gasifiers. As the names imply, countercurrent mass flow means that the feedstock and the gasifying agent (e.g., air, oxygen or steam) flow in opposite directions; the opposite applies to the concurrent (Figure 2.7 and Figure 2.8) respectively [39].

Updraft Gasifiers

Updraft gasifiers are the oldest and simplest gasifiers. They have the advantages of high reliability, high efficiency, low specific emissions and feedstock flexibility and the disadvantage of high tar content which can be solved when the gasifier used for thermal applications [27]. As illustrated in Figure 2.7, in updraft gasifiers the raw fuel feed to the reactor from the top of the gasifier while the gasifying agent enters the gasifier through the bottom of the fixed bed and, thus the gas and solids are in countercurrent mode. As the raw fuel moves in countercurrent to air or oxygen, the processes occurring are drying, devolatilizing, reduction and char combustion, with unburned char and ash, exiting via a rotating grate at the bottom of the gasifier.

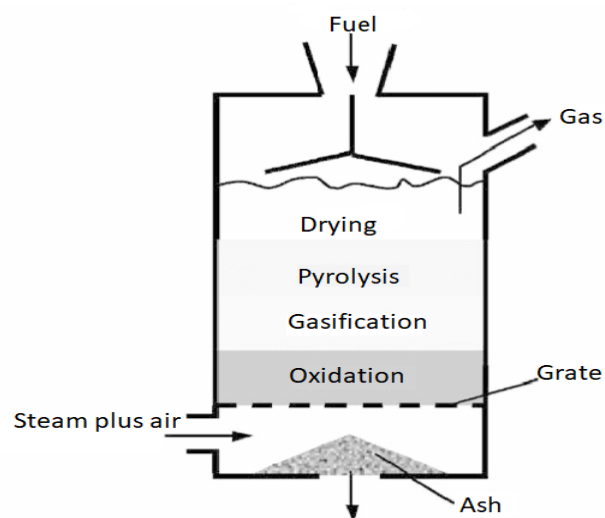


Figure 2.7 Schematic of an updraft gasifier [39]

Air or oxygen entering the bottom of the gasifier reacts with char in the combustion zone to form, CO_2 and H_2O at temperatures as high as 1200°C in the dry-ash gasifier, and $1500\text{-}1800^\circ\text{C}$ in the slagging gasifier, which are large-scale commercial updraft gasifiers [39]. The hot gas from combustion zone provides the energy to drive endothermic processes drying, pyrolysis and char gasification of the fuel. In the pyrolysis section, the hot gas pyrolyzes the fuel to tar, char, and gases. In the char gasification zone, CO_2 and H_2O react with char produced in pyrolysis section to make CO and H_2 . Above the pyrolysis zone, the gases and pyrolytic vapors dry the entering fuel and exits on the top of the reactor. Typical product exit temperatures are relatively low ($80^\circ\text{C}\text{-}100^\circ\text{C}$) [53].

Downdraft Gasifier

The schematic diagram of a downdraft gasifier shown in Figure 2.8. In downdraft gasifier, the fuel introduced on the top of the gasifier the same as that of updraft gasifier. The gasifying agent enters at the middle level of the gasifier above the grate and the product gas flow down concurrently through the gasifier reactor. Since the decomposed products from the endothermic pyrolysis and drying zone are forced to pass through the combustion zone of around 1200 to 1400°C , the tar cracked and reduced to non-condensable gaseous products. Therefore, the gas quality is enhanced, allowing the installation of less complicated gas purification for downstream processes.

In the downdraft gasifier air contacts, the pyrolyzing fuel from pyrolysis zone before it contacts the char and supports a flame. The heat from the burning volatiles maintains the pyrolysis. When this phenomenon occurs within a gasifier, the limited air supply in the gasifier rapidly consumed, so that the flame gets richer as pyrolysis proceeds. At the end of the pyrolysis zone, the gases consist mostly of about equal parts of CO_2 , H_2O , CO , and H_2 . The flame in a limited air supply called "flaming pyrolysis," Flaming pyrolysis produces most of the combustible gases generated during downdraft gasification and simultaneously consumes 99% of the tars. It is the principal mechanism for gas generation in downdraft gasifiers [43].

Compared to the updraft gasifiers, the gas outlet temperature is high in downdraft gasifiers which are generally above 700°C [53]. So, this high heat content at the exit of downdraft gasifiers can be used for district heating and/or other thermal energy-intensive applications. Also, the characteristic of shorter ignition time to bring the plant up to working temperature of downdraft gasifier compared to updraft gasifier makes it attractive in the distributive district heating system.

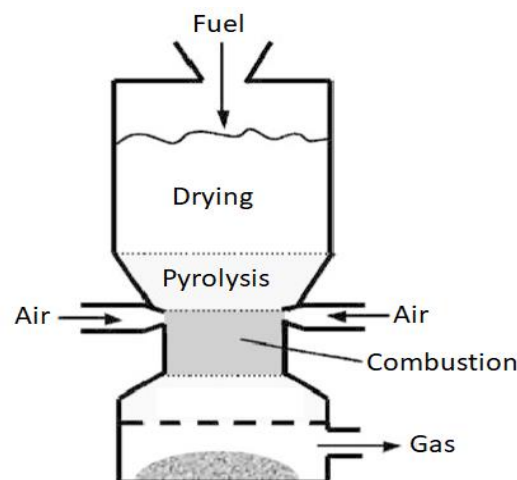


Figure 2.8 Schematic of a throated-type downdraft gasifier [39]

Cross-Draft Gasifier

In a cross-draft gasifier, the fuel feed to the gasifier from the top the same as those reactors types discussed above. Air injected through a nozzle from one side of the gasifier reactor and left from the other side. The air primarily used for gasification of charcoal with the meager amount of ash content [39]. Cross-draft gasifiers have very few applications and can hardly be credited with any advantage beyond good permeability of the bed [57].

2.4.3 Fluidized-bed Gasifier

Fluidized-bed technologies offer alternative and reliable options to other Waste-to-Energy technologies because of their ability to handle the waste of widely varied properties and the many advantages in controlling emissions. There are over 200 plants in commercial operation in Europe and Japan [50]. The two principal types of fluidized bed reactors for gasification of biomass are bubbling and circulating beds. They differ in respect of fluidizing velocity and gas path. Bubbling beds have relatively low gas velocities, in circulating beds velocities are close to pneumatic flow. Minimal solids are transported out from bubbling beds, with circulating beds entrained solids recycle after passing a cyclone. Fluidized beds have excellent heat and material transfer between the gas and solid phases with the best temperature distribution, high specific capacity and fast heat-up [25] such that there is no tendency for softening and melting (and consequent agglomeration) of any of the solid components in the fluidized bed [50].

The fluidized bed gasifiers, as illustrated in Figure 2.9 suspend the mixed feedstock particles and the bed materials by upward-blowing bubbles of fluidizing gas. The upwards and sideways coalescing movement of bubbles provides intense agitation and mixing of the bed particles, which make fluid beds ideal for applications where high mass and heat transfer rates are required. In such gasifiers, the particles initially heated to above the ignition temperature of the fuel, and then gasification takes place when the fuel delivered into or onto the heated fluidized particles. The fuel burns partly by the oxygen within the fluidizing gas (air, oxygen, steam-oxygen) delivered by a fan upwards through the bed particles. During steady-state gasification, the temperature controlled by the opposing effects of the heat input from the burning fuel in the bed, versus outgoing heat in the devolatilised gases and further heat 'consumed' by endothermic reactions in the gas-phase (e.g., steam reforming, water gas-steam carbon, etc.) [50].

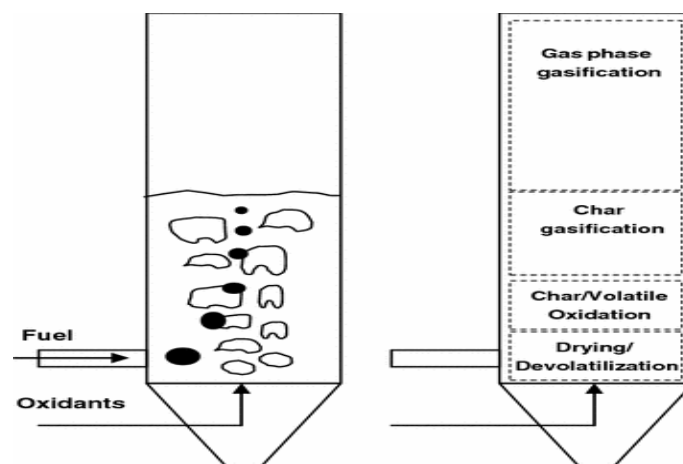


Figure 2.9 Generic bubbling fluidized-bed reactor schematization and process description [50]

2.4.4 Water Gas Shift Reaction (WGSR)

Hydrogen production methods by gasification of carbon-based feedstock produce mainly a mixture of H_2 and CO , namely syngas. Thus, water-gas-shift (WGS) reaction is an essential exothermic chemical reaction used to enhance the yield of hydrogen at the expense of carbon monoxide. This reaction is a crucial step in all carbon-based fuel processing aimed at producing and upgrading hydrogen for downstream applications [58]. The water-gas shift reaction is an exothermic reversible reaction usually takes place in the presence of a catalyst and the reaction which prefers formation of reactants at higher temperatures. WGS reaction preferred in the temperature range of 250–400 °C whereas revers WGS preferred at higher temperatures [28]. The overall reaction corresponds to the conversion of carbon monoxide and water into carbon dioxide and hydrogen, expressed by eq.(2.24). The chemical equation suggests that oxygen in steam can be extracted to convert CO into CO_2 , thereby transform the steam into hydrogen.



The performance of the WGS reaction influenced by different operational conditions. The critical parameters influence the yield of hydrogen in WGS reaction include the catalyst type, residence time of reactants in a catalyst bed, reaction temperature and CO /steam ratio [59]. According to the reaction temperature or catalyst type, the WGS reaction falls into two categories: high-temperature (HT) shift reaction and low-temperature (LT) shift reaction. The catalysts commonly used in high-temperature shift reaction is an iron–chromium-based catalyst, whereas copper– zinc-based catalyst frequently adopted in the low-temperature shift reaction. The two catalysts termed after their operating temperature as a high-temperature catalyst (HTC) and a low-temperature catalyst (LTC) respectively [59], [60].

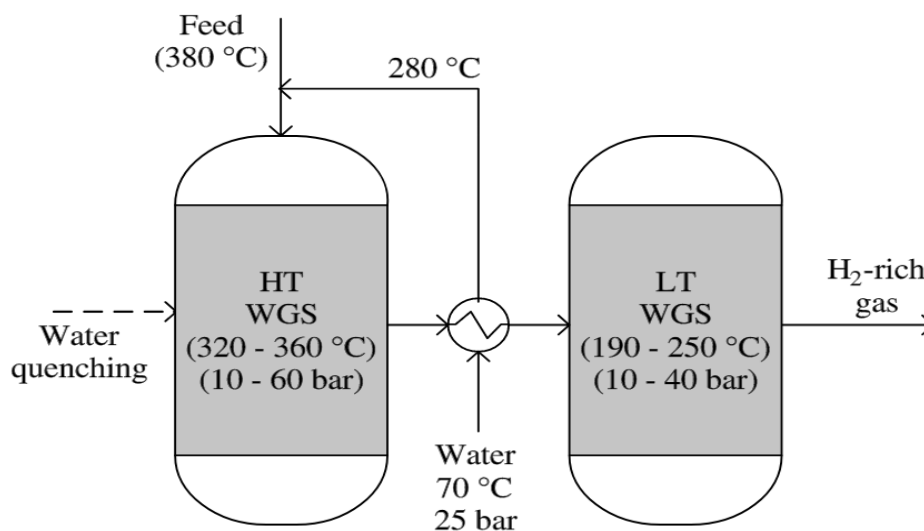


Figure 2.10 Conventional two-stage process diagram of the WGS reaction unit [61].

As mentioned above, the typical WGS reaction is carried out in two stages as illustrated in a schematic representation of the two steps conventional process for WGS reaction (Figure 2.10). Mendes et al., [55] explained the operation of typical WGS reaction in a typical industrial process as follow.

In the first step of the process the cold syngas (at about 350-450°C) from the upstream process feed to the high temperature (310-450 °C) reactor, at a pressure of (10-60 bar). The reaction in this stage

takes place in the presence of a Fe-based catalyst and reduces CO concentration down to 1-5% with the outlet stream temperature of (400-450°C). This stream cools down to 200°C. Keeping the inlet temperature at least about 20°C above the dew point of the feed gas is recommended to avoid water condensation in the catalyst pores and its subsequent deactivation. In some operations, water is injected between the stages to adjust the steam/gas ratio before entering an LT carbon monoxide shift reactor, operating in the range of 190-250°C in the catalyst bed are observed, and an outlet stream with a CO concentration less than 0.5% is obtained.

2.5 Mass and Energy Balance

In this section, the conservation of mass and conservation of energy laws on control volume system are discussed. The two laws of physics provide the basis for the mass balance and the energy balance. The balances will apply to the steady-state system. Mass and energy balance in energy conversion processes which include chemical reaction is complicated than an energy conversion process which doesn't include chemical reaction because chemical constituents change, and energy released from the rearrangement of chemical bonds [62].

2.5.1 Mass Balance

For a control volume at steady state conditions, the net quantity of mass in the control volume is constant with time. The rate of change of mass within the control volume becomes zero. For a control volume system having 'i' number of inlet and 'e' number of exit, the mass balance equation at steady state can be expressed as follows.

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \quad (2.25)$$

Where \dot{m}_i and \dot{m}_e are the instantaneous mass flow rates at the inlet and exit, respectively.

In an energy conversion system where a chemical reaction involves, chemical compounds are not conserved as they flow through the system, but the chemical elements making up these compounds are conserved. Thus, the mass balance of the system could be determined on either an elemental or molar basis.

Mixtures of reactants or products consist of N constituents, then the total mass, m , and a total number of moles, n , are given by:

$$m = m_1 + m_2 + \dots + m_N = \sum_{i=1}^N m_i \quad (2.26)$$

$$n = n_1 + n_2 + \dots + n_N = \sum_{i=1}^N n_i \quad (2.27)$$

2.5.2 Energy Balance

For a chemically reacting system, the energy balance equation formulated from heat, work, kinetic energy, potential energy, and enthalpy associated with mass flowing into and out of the control volume does not consider changes in the chemical composition of the system nor the chemical energy absorbed or released during these reactions. It is more convenient to present energy conservation in a molar formulation rather than a mass formulation when a chemical reaction occurs [62].

As illustrated in the diagram of enthalpy change as a function of temperature (Figure 2.11) the enthalpy of the reactants and products has a unique enthalpy-temperature relationship. From the diagram, the energy balance equation of the reaction can formulate.

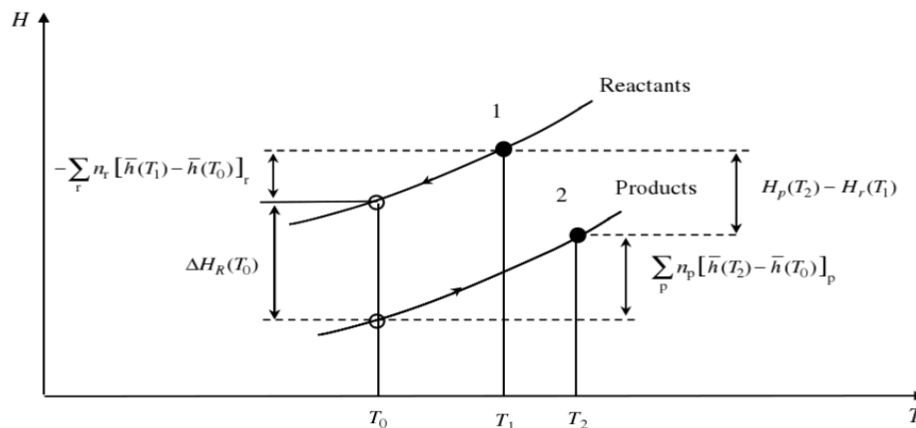


Figure 2.11 Relationship between mixture enthalpy and temperature for a chemically reacting system [62]

The enthalpy change (the amount of heat) for non-isothermal chemical reactions can calculate from the relationship:

$$H_p(T_2) - H_r(T_1) = \sum_p n_p [\bar{h}(T_2) - \bar{h}(T_0)]_p + \Delta H_R(T_0) - \sum_r n_r [\bar{h}(T_1) - \bar{h}(T_0)]_r \quad (2.28)$$

Where $H_p(T)$ and $H_r(T)$ are the mixture enthalpy (kJ) of the product and the reactants, n_p and n_r the moles of the reactants and the products, respectively, $\bar{h}(T)$ is molar enthalpy (kJ/kmol) and $\Delta H_R(T_0)$ is the enthalpy of reaction.

The energy released or absorbed by the chemical reactions (enthalpy changes) for isothermal chemical reactions at constant temperature (T_0) become the enthalpy of reaction $\Delta H_R(T_0)$. The heat/enthalpy of reaction of a chemical reaction can be calculated using enthalpy of formation of chemical compounds in reactant and product from their elemental and standard state as:

$$\Delta H_R = \sum_p [n_p \bar{h}_f^o]_p - \sum_r [n_r \bar{h}_f^o]_r \quad (2.29)$$

Where \bar{h}_f^o is enthalpy of formation, n_p and n_r are the moles of the reactants and the products.

The enthalpy of formation for common chemical compounds found in different thermodynamic books. Because of a wide range of variability of biomass and waste enthalpy of formation need to be formulated for specific feedstock. Enthalpy of formation for fuel can be used in various thermodynamic calculations for the fuel sample, whether gasification to hydrogen or combustion to flue gas[62]. This value can be determined using the heating value of the fuel and the complete combustion of MSW chemical equation.

3 Materials and Methods

3.1 Introduction

In this chapter, the experimental method implemented for characterization of MSW performed in the laboratory, The MSW gasification plant design and the simulation of gasification in Aspen plus simulation software discussed. In the material and experimental procedure section, the MSW sampling method and the critical waste feedstock characteristics in thermochemical conversion of the feedstock discussed. Also, the method of thermogravimetric analysis performed discussed. The plant design section discusses both direct and indirect gasification systems. In the simulation method section, the method and process described in the simulation of MSW gasification and assumptions taken in simulation process described.

3.2 Material and Characterization Procedure

3.2.1 MSW Sampling

Collecting a sample for thermochemical characteristic analysis of MSW is less straightforward due to highly physically and chemically heterogeneity of waste. In this work, the plan was to analyze representative waste samples from waste incineration plants in Kristiansand (Returkraft), Avfallnorge or Mepex Consult AS. However, unfortunately, it was not possible to get the representative sample from those mentioned companies; the sample, therefore, collected from waste containers as an individual material category which treated by incineration, rather than the entire MSW. The picture in Figure 3.1 shows the heterogeneity of waste piles in incineration plants.



Figure 3.1 Picture of waste piles in Returkraft

As only a few grams of the sample used for thermochemical characteristic analysis, the waste sample in this work was carefully sampled to make it representative of the average large waste pile generated in Norway. The samples collected from different combustible waste categories which have high percentage composition in Norwegian waste categories according to 2015 waste scenario as listed in Table 2.1.

Modeling of the percentage composition of the sample materials used in the characterization of the waste performed on the bases of Table 2.1 for wood waste, paper and cardboard, plastics and mixed waste. Mixed waste is a waste that is not subjected to any presorting or from where some categories

have been sorted out like (plastics, paper, Clothes and textiles, leather and rubber, diaper – bind, etc.). Though the mixed waste contains a lot of combustible materials, only plastics, and paper used for test sample modeling.

As per a report from Avfall Norge in 2009, the household mixed waste delivered to Norwegian incinerators comprise of 15.4% paper, 7.8% plastic bags in weight and the rest is wet organic and another type of wastes [63]. This data is used to model the percentage composition of paper and plastic in mixed waste from all types of sources, assuming that the mixed waste generated from all sources have a similar physical composition as that of household mixed waste. Then the calculated data from the mixed waste (paper and plastic bags) added to the respective waste category in Table 2.1 and the percentage composition of the sample waste prepared according to physical composition data given in Table 3.1.

Table 3.1 Physical composition model of the sample waste for thermochemical characterization

| The physical composition of sample waste | | |
|---|----------------------|--------------|
| Waste type | (1000 tonnes) | Wt. % |
| Wood waste | 677 | 49 |
| Paper and cardboard | 384 | 28 |
| Plastics | 311 | 23 |
| Sum | 1372 | 100 |

The sample wastes collected according to the percentage composition of the sample wastes model in Table 3.1, from the University of Agder, student house and Dahlke high school waste containers. During the collection of the sample, it has been tried to make it as representative as possible using self-experience and consulting experienced people in this area.

In the plastic waste category, the plastic waste sample includes various polyethylene, plastic bags, and packaging plastics. The paper and cardboard waste sample comprises packaging box, magazine, newspaper and other diver's types of paper wastes. The wood waste sample mostly collected from Dhalke high school waste container, the waste includes sawdust and different kinds of wood waste types. This waste sample considered as representative of an average of the Norwegian waste treated in incineration plants.

3.2.2 Sample Preparation

The waste taste sample was prepared for the proximate, ultimate and TGA analysis from the collected waste category separately for each material category. The test sample was collected during the winter season so that the collected waste samples had a high moisture content. Each waste category stored for 2 to 15 days at room temperature to let the moisture content reduces before comminution. Due to unavailability of milling machine which mills the waste sample size of small as 0.25mm in the laboratory, the comminution technique used for the three air-dry constituent teste samples (plastic, wood and, paper and cardboard) performed by manual knife milling and sieving, therefore it was such a time-consuming task. The picture of the three test sample categories manually milled shown below in Figure 3.2.



Figure 3.2 Manually knife milled paper and cardboard, wood and plastics

The total weight of the comminuted test sample for the analysis of the diverse materials of plastic, wood, and paper and cardboards was 16.72g, 8.92g and 8.15g respectively. Table 3.2 shows the weight of test sample acquired from comminution of the test sample and the sieving. Sieving performed into two sieve sizes 0.25 and 1mm sieve sizes. The plastic materials are relatively resistant to size reduction, and this resistance causes the ground material to become diminished as it passes through the sieves.

Table 3.2 Prepared test sample weight and size

| Sieve size (mm) | Paper and cardboard (g) | Plastic (g) | Wood (g) |
|---------------------|-------------------------|-------------|----------|
| Total Milled sample | 8.15 | 16.72 | 8.92 |
| < 0.25 | 1.17 | 0.27 | 2.2 |
| <1 | 6.18 | 7.88 | 5.23 |

After sieving of individual test samples, the next step was mixing of the sample according to their percentage composition as given in Table 3.1 to prepare the representative test sample. As shown in Table 3.3, 1g and 10g of test sample prepared out of the sample size, which passed through the 0.25 mm and 1 mm sieve size and collected from the bottom tray respectively. The two prepared mixed test samples were stirred to make the test sample homogeneous as much as possible both manually and by using magnetic stirrer. Those samples used in the characterization of the waste according to a specific sample size requirement of test standards.

Table 3.3 Mixture of the test sample

| Material | Percentage composition (wt. %) | 0.25 mm Size (g) | 1mm Size (g) |
|---------------------|--------------------------------|------------------|--------------|
| Wood | 49 | 0.49 | 4.9 |
| Paper and cardboard | 28 | 0.28 | 2.8 |
| Plastics | 23 | 0.23 | 2.3 |
| Sum | 100 | 1 | 10 |

3.2.3 Proximate Analysis

As mentioned in the theory section proximate analysis, determine the moisture content, volatile matter, ash content, and fixed carbon. The analysis can be conducted using simple laboratory equipment such as a drying oven, a furnace, and a balance. The equipment is available at the University of Agder, Grimstad campus laboratory and utilized for proximate analysis of the test sample prepared. In the MC, VM and ASH content testes three duplicate test samples of MSW with the same percentage composition was tested to minimize the error due to mixture homogenization and technical error. The test results of the duplicate samples help in providing the average value and the standard deviation between the duplicates.

Moisture content test

Although as-received moisture content of the waste is significant in designing and operation of thermochemical conversion plant, knowing the air-dried moisture content of the test sample in this work helps calculate the other constituent of the waste sample. For the moisture content measurement, three test samples of the air-dried mixed sample with a weight of 1g each used from the 10g mixed sample of less than 1mm particle size (Table 3.3). The three weighted test samples in crucibles without lid placed in the drying oven with the oven set temperature of 105°C for two days. Most standards recommend that usually drying performed overnight or until the weight of the sample becomes constant.

The time given for drying the teste sample was quite enough for vaporization of the moisture in the sample. After two days the crucibles containing the oven-dried sample were removed from the drying oven and placed in a glass desiccator to avoid moisture gain from the room, before once again being weighted. The difference in weight between oven dried and air-dried samples give mainly the inherent moisture content of the sample waste and some part of surface moisture left after air drying. The moisture content of the air-dried MSW test sample in the dry or wet basis can be determined using the weight difference before and after oven drying. Eq.(2.1) can be used to calculate percentage composition of moisture content in dry basis.

Volatile mater test

The volatile matter (VM) was driven off in a closed crucible by heating the MSW test sample to 900 °C under a controlled condition and measuring its weight loss, excluding the weight of moisture dried off at 105 °C. The method used during laboratory taste for determination of the volatile matter performed explained as follows.

First, the three clean and dry crucibles with a lid weighed, and approximately 1g well mixed-test sample with a particle size of less than 1mm is put in each crucible and weighed again. The measurements noted and, the test samples placed simultaneously in the furnace with a furnace temperature of 900°C for seven minutes. After seven minutes the crucibles removed from the furnace and put in the decanter to avoid weight gain while cooling the lab atmosphere.

After putting the samples in a decanter for about two hours, the samples were measured to find the loss in weight after thermal decomposition, the weight loss during decomposition includes the moisture content and volatile matter of the test sample. Using the measurements before and after thermal decomposition of the test sample the percentage composition of volatile matter on dry-basis

can be determined using eqs. (2.2), (2.3) by excluding the weight of moisture dried off at 105 °C in the analysis of moisture content of the test sample.

Fixed carbon and Ash content test

Standard test method for ash in biomass ASTM E1755 covers the determination of ash, expressed as the mass percent of residue remaining after dry oxidation (oxidation at $575 \pm 25^\circ\text{C}$) [64]. The method used to determine the ash content of the MSW test sample in this work adopted from this standard.

For the ash content measurement three duplicate well-mixed sample with a weight of 1g, each used from the test sample of less than 1mm particle size. The three crucibles without lid containing the test samples placed in the furnace simultaneously. The furnace temperature programmed to reaches 550°C progressively. First the furnace temperature increases from ambient temperature to 250°C gradually within 50 minutes, with a heating rate of approximately $5^\circ\text{C}/\text{min}$ and then the temperature increases to 550°C within 30 minutes, with a heating rate of $5^\circ\text{C}/\text{min}$. At 550°C the furnace temperature kept constant for 20 hrs. The long retention time gives the test sample room to terns entirely to ash.

The percentage composition of ash in the test sample calculated taking the weight left after combustion and using eq. (2.4).

As discussed in the previous chapter, the percentage composition of fixed carbon of the MSW sample is hundred percent minus the sum of percentage composition of moisture content, volatile matter, and the ash content in specific basis (wet or dry).

3.2.4 Ultimate Analysis

The percentage composition of carbon, hydrogen, nitrogen in the MSW test sample was measured by using PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, available at the University of Agder laboratory. The instrument determines the carbon, hydrogen, nitrogen, sulfur or oxygen content in organic and other types of materials, by choosing the desired mode option (CHN, CHNS or oxygen mode). The principle of determining the elemental composition of a sample is, based on the classical Pregl-Dumas method, samples combusted in a pure oxygen environment, with the resultant combustion gases measured in an automated fashion [65]. The picture of the ultimate analyzer utilized in this work shown in appendix A. (Figure A-1).

The experiments were replicated nine times to determine their repeatability. The experimental data presented in this thesis corresponding to the measured results are the mean values of the nine runs carried out. In the ultimate analysis the test sample of size less than 0.25mm used for the determination of hydrogen, carbon and nitrogen content of the test sample. The experiment carried out in each test sample with the same test procedure presented as follow.

First, a tin vial was weighed, with and without test sample in, the measurement data directly transfer to the ultimate analyzing instrument from the connected measurement. Then the well-mixed test sample from the particle size of less than 0.25mm was put in the tin vial, weighed again and the data transferred to the instrument. The net mass of the samples used for elemental analysis was approximately in the range of between 1 to 2mg, then each encapsulated sample in the tin vial was placed on the integral 60-position autosampler.

The instrument was set to The CHN mode, to determine carbon, hydrogen, and nitrogen. During the test, the sulfur column was not functioning. So, since the percentage composition of sulfur content

was essential data in Aspen plus simulation software for simulation of solid feedstock, it was taken from relevant literature in this work. The analysis starts by running two test calibrating material (Acetanilide) with known percentage composition of carbon, hydrogen, and nitrogen to assure optimal analyzer performance. After checking the calibration of the instrument, three blank runs carried out to purge the system, followed by nine test sample of MSW, in every three-test sample of MSW run three blanks run was conducted to purge the system which helps to remove the remains from preceding run.

A list of the nine-run results has collected by using the computer with a specific software connected to the instrument. The percentage composition of constituent elements was analyzed, and the average has taken for each constituent element. The average result obtained from the direct measurement was in air-dried base since the teste sample was on the air-dried basis. The result converted to dry basis and the hydrogen content from moisture reduced from the measured percentage hydrogen composition. As mentioned the percentage composition of sulfur have taken from literature, while the ash content is the ash obtained in the proximate analysis. The oxygen percentage composition can calculate by using eq.(2.6).

3.2.5 Thermogravimetric Analysis

Thermogravimetric analysis was carried out on MSW sample using a thermal analyzer (Mettler Toledo TGA / DSC1) available at University of Agder Microscopy laboratory. The experiment carried out on two duplicate MSW samples of approximately 19.5 mg to ensure the accuracy of the experimental results. The MSW sample composition was the same as that used in proximate and ultimate analysis with the particle size of less than 0.25 mm. The composition of MSW sample was as listed in Table 3.3. The samples were air-dried at room temperature before and after comminution for around 30days and well-mixed by thorough shaking. The picture of the thermogravimetric analyzer utilized in this work shown in appendix A. (Figure A-2).

The TGA experimental method for the two duplicate samples adopted from Robinson et al. [15]. The adopted method starts with drying of the process then followed by pyrolysis (thermal decomposition) in the presence of inert gas and finally ends with complete combustion. In these processes inert and oxidation, the medium was used as per process type. The four-stage TGA program adopted presented as follow:

- Isothermal at a temperature of 80°C for eight minutes under inert gas (Argon) atmosphere with a flow rate of 50ml/min.
- Dynamic in the temperature range of 80°C to 800°C and temperature rate of 25°C/min, under inert gas (Argon) atmosphere with a flow rate of 50ml/min.
- Isothermal at a temperature of 800°C for five minutes under inert gas (Argon) atmosphere with a flow rate of 50ml/min.
- Isothermal at a temperature of 800°C for ten minutes under oxidant gas (oxygen) atmosphere with a flow rate of 50ml/min.

The experimental work started by inserting the four-stage TGA program into the control computer connected to the TGA analyzer and then followed by the weighting of the empty 150µl alumina crucibles. In the next step, approximately 19 mg of the well-mixed MSW sample by thorough shaking was placed within two 150µl volume each alumina crucibles. After placing several blank and the two

crucibles with the sample on TGA analyzer, the experiment run started with blank experiments to gain the baselines to use as corrections.

The TG results of the experimental data of the two MSW sample exported from the TGA control computer as a text file format. The result further converted to an excel file format and checked for errors then the average value was taken to extract the first derivative of TG result (DTG) for further analysis.

3.3 MSW Gasification Plant Design

The two-feasible gasification systems for hydrogen production from MSW by gasification and followed by WGS reaction illustrated in Figure 3.3 and Figure 3.4. The former uses only steam gasifying medium which is an endothermic process (allo-thermal/ indirect), whereas the later one could use oxygen/air and steam as a gasifying agent which is an exothermic process (auto thermal/ direct). In both systems, the WGS reaction has a similar process.

For and preexist CHP/DH plants powered by MSW the indirect gasification configuration is a feasible solution. Since in these plants the MSW combustion reactors already exist the surplus heat and the heat generated during less heat demand periods could be utilized for the gasification process so that addition of gasifier agent steam increased the yield of hydrogen as is discussed in the literature and simulation results discussed in the result section of this thesis.

The schematic diagram of hydrogen production plant with allo-thermal/indirect gasifier illustrated in Figure 3.3. The pre-processed MSW feed to the gasifier and the existing incineration plant. The feedstock feed to the preexisting plant produces electricity and/or heat, the heat from this plant uses both for district heating and gasification process to produce hydrogen-rich product gas in the presence of steam. The product gas from the gasification process cleaned and cooled in gas cleaning and cooling system and then send to the WGS reactor for enhancement of hydrogen and followed by compression for storage after cleaning and cooling of the product from WGS reactor. The surplus heat from the gasification process utilized for producing steam and use as a gasifying agent in gasifier and WGS reactor. The surplus heat from the WGS reactor could utilize for district heating using the existing grid infrastructure.

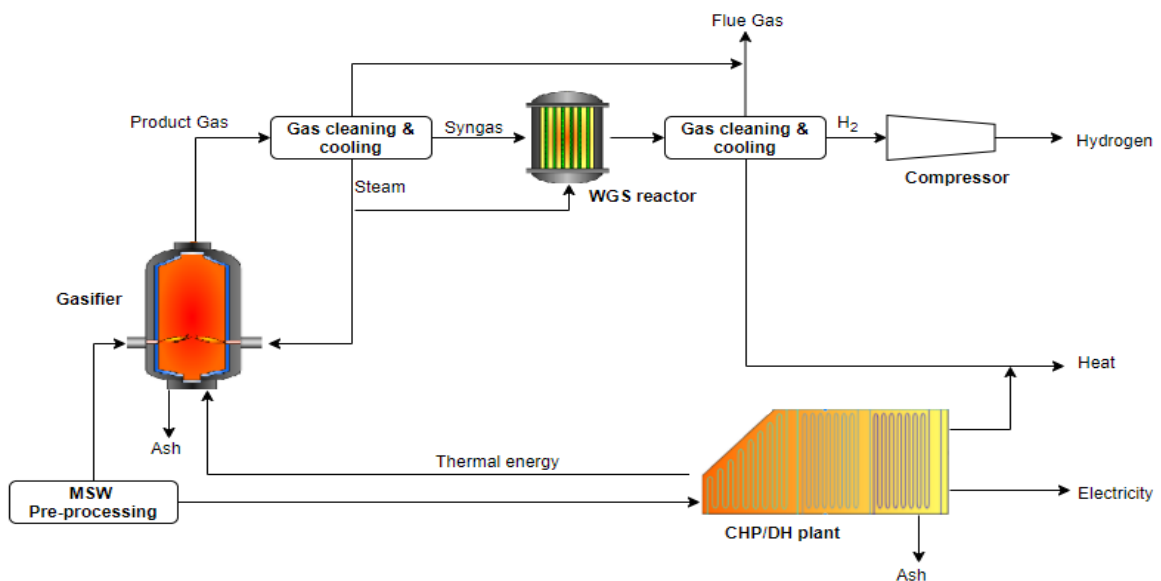


Figure 3.3 Schematic diagram of hydrogen production plant with allo-thermal/indirect gasifier

For direct gasifier process the heat for gasification process supplied by partial combustion of the pre-processed MSW, unlike indirect gasification in which the heat supplied from the external heat source. This plant is feasible for a new incineration plants construction to integrate gasifier with a district heating plant in focus of hydrogen production. As illustrated in Figure 3.4 the pre-processed MSW feed to the gasifier and partial combustion of the MSW takes place in the presence of air, besides air steam also can admit to the gasification reactor to enhance the composition of hydrogen in the product gas. The process after gasification is similar to that of indirect gasification discussed in the case of the indirect gasification process. The surpluses heat from gasification reactor, product gas cooling, and WGS reactor could used for district heating. The two hydrogen production plants are simulated, and yield of hydrogen and the heat of the system per kg of MSW is presented in the next chapter.

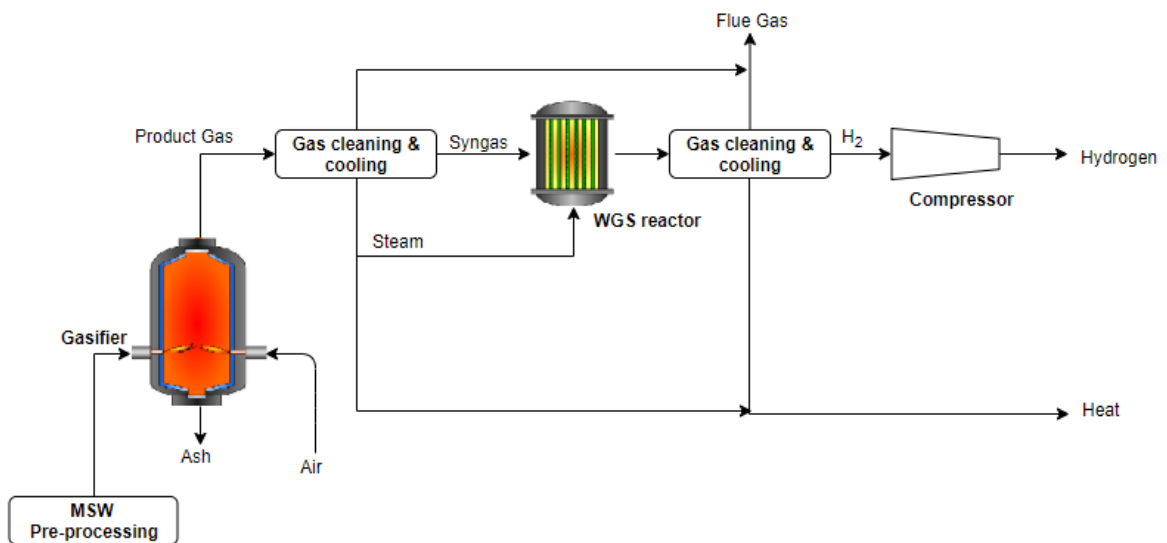


Figure 3.4 Schematic diagram of hydrogen production plant with auto thermal/direct gasifier

3.4 Simulation Method

In this study, comprehensive process model developed and simulated for auto-thermal and allo-thermal MSW gasification system. The model developed in an atmospheric fixed bed reactor and followed by atmospheric water gas shift reactor using the Aspen Plus V9 commercial process simulation software. The simulation models predicted the yield of hydrogen and the surplus heat produced in the system. Sensitivity analysis also carried out to investigate the effects of different operating parameters such as gasification temperature, equivalence ratio, and steam to MSW rate on the yield of hydrogen gas in the gasification reactor. Similarly, the effect of temperature and steam flow rate in WGS reactor is simulated.

The simulation for the process of MSW gasification and water gas shift reaction is set up based on thermodynamic equilibrium, and chemical equilibrium among the overall process. For the equilibrium modeling of the system stoichiometric and nonstoichiometric methods are used. The bases for simulations in Aspen plus is the schematic diagram of the plants illustrated in Figure 3.3 and Figure 3.4 using downdraft fixed-bed reactor. Besides gasification and water-gas-shift reaction process, the model includes the pre-drying process of the MSW.

3.4.1 Assumption

The following assumptions were introduced in this study to model the whole gasification process:

- The process is in steady state, and the reactions reach chemical equilibrium.
- The gasification product stream contains only H₂, CO, CO₂, CH₄, N₂, H₂O.
- Tar and other heavy hydrocarbons were considered negligible.
- The separators are ideal.
- Carbon fully converts to the gaseous product.
- The temperature of the output of gasifier and WGS reactors inside the reactors considered isothermal.
- The product of water-gas-shift reaction contains only H₂ and CO₂.

3.4.2 Process Simulation of Gasifier

Simulation, or mathematical modeling, of a gasifier, may not give a very accurate prediction of its performance, but it can at least provide qualitative guidance on the effect of design and operating or feedstock parameters [39].

Gasifier simulation models may classify into the following groups :

- Thermodynamic equilibrium
- Kinetic
- Computational fluid dynamics (CFD)
- Artificial neural network

The Aspen plus process simulation software has been used by different investigators to establish reaction process models and solve computational problems of biomass, coal and MSW gasification process. Examples include Deng et al. , [66] have used the Aspen plus software to predict and analyze the municipal solid waste pyrolysis and gasification process in an updraft fixed bed reactor. The model forecast and analyze the target performance parameters such as syngas composition, lower heating value and carbon conversion rate under different conditions of the gasification temperatures, and ratios and types of gasifying agents.

In Chen et al. , [27] study, Aspen plus software is used to investigate the effect of flue gas on syngas composition and conversion characteristics by simulation of MSW gasification using updraft fixed bed reactor. Keche et al. , [67] developed a model for the gasification of biomass in an atmospheric downdraft-fixed bed gasifier using the Aspen plus simulator. The results obtained through the model validated with the experimental results of a downdraft gasifier developed and tested by the authors with four different types of feedstocks.

In those mentioned studies and other studies simulating a variety of steady-state processes involving many units are performed. The simulation was in the basis of thermodynamic equilibrium and the chemical equilibrium determined by minimization of the Gibbs free energy at equilibrium. In this work, also the same approach used to predict the performance of the system.

3.4.3 Aspen Plus Simulation Software

Aspen plus is a problem-oriented process simulation computer program that is used to facilitate the physical, chemical and biological calculations. It often exploited to model steady-state chemical processes that involve solid, liquid and gaseous streams under defined condition by using mass and

energy balance equations and phase equilibrium database [68]. The program used in most computational thermochemical processes simulation by using extensive built-in physical properties database and user-specified data.

Thermal conversion of solid fuels involves a lot of complex reactions. Thus, solving by hand leads to human error and takes time. Aspen plus simulation software play a significant role in minimizing these two problems and gives the simulation result in a different format to make the analysis accessible and user-friendly. Aspen plus simulation software allows the prediction of the behavior of a process by using fundamental relationships: mass and energy balances, and phase equilibria and chemical equilibrium. For solid state process simulation which involves heat and mass balance requires a suitable physical property model for solid components [69].

In Aspen plus all unit operation models need property calculations to generate results. The most often requested properties are fugacities for thermodynamic equilibrium. Enthalpy calculations are also often requested. Fugacities and enthalpies are often sufficient information to calculate a mass and heat balance [70].

Aspen plus property method selection assistant suggest more property methods which used to specify the models used to calculate the nonconventional solid hydrocarbons components properties. The PENG-ROB property method is one of the recommended methods for hydrocarbon processing applications. The equation of state proposed by Peng and Robinson is the basis for the PENG-ROB property method, and the equation for this model is:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \quad (3.1)$$

Where: P is Pressure, T is Temperature, R is ideal gas constant, V is Molar volume, the constant 'b' which is related to the size of the hard spheres and the parameter 'a' can be regarded as a measure of the intermolecular attraction force [71].

Nonconventional components are solid compounds that do not participate in chemical or phase equilibrium, the only physical properties that calculate for nonconventional components are enthalpy and density [70]. In coal enthalpy and density calculation, HCOALGEN and DCOALIGT models used, these models are applied in different literature to calculate nonconventional solid biomasses. The HCOALGEN model estimates the enthalpy based on proximate analysis, ultimate analysis, and sulfur analysis, the enthalpy calculates at standard states as:

$$H = \Delta_f h + \int_{T^{ref}}^T C_p dT \quad (3.2)$$

Where: $\Delta_f h$ is the heat of formation, T^{ref} is arbitrary reference temperature, C_p is heat capacity at constant pressure.

The heat of formation can be calculated from the heat of combustion because of the combustion products, and elemental composition of the components are known.

$$\Delta_f h = \Delta_c h + \Delta_f h_{cp} \quad (3.3)$$

Where: $\Delta_c h$ is the heat of combustion, $\Delta_f h_{cp}$ is the sum of the heats of formation of the combustion products multiplied by the mass fractions of the respective elements in the nonconventional components.

3.4.4 Process Description

In the MSW gasification and water-gas-shift reaction processes, the main stages used in this work are pre-drying, decomposition, gasification and water gas shift reaction. In both direct and indirect gasification processes the models in all stages are the same except for the gasification stage. In the gasification stage, air is used as a gasifying medium for direct gasification while steam used in the indirect gasification process. Also, in the direct gasification process the hydrogen yield of the process tested by adding steam beside air as a gasifying medium. The surplus heat from gasification and water gas shift reactors are retrieved using a heat exchanger and used in gasification and water gas shift reactors. The left-over heat after the two reactors used in district heating system.

The components present in the simulation entered as conventional and non-conventional components. For the two component types entered the property methods selected using Aspen plus property method selection assistant. One of the suggested property methods for this simulation was PENG-ROB thermodynamic methods to calculate properties of conventional components. The HCOALGEN and the DCOALIGT models used to calculate the nonconventional solid (MSW) properties (enthalpy and density). The models used by these methods for calculation of properties discussed in section 3.4.3.

The process starts by vaporization of the moisture content of the feedstock in the pre-drying stage as per required amount, in this simulation process, the moisture content of the feedstock fed to the gasifier contains around 15% moisture. Before the gasification stage, the pre-dried feedstock decomposed into its constituent chemical elements, ash, and water, these data used from the proximate and ultimate analysis of the experimental characterization performed in the lab (Table 4.1 and Table 4.2). The Aspen plus simulation model flowsheet of the direct gasification illustrated in Figure 3.5.

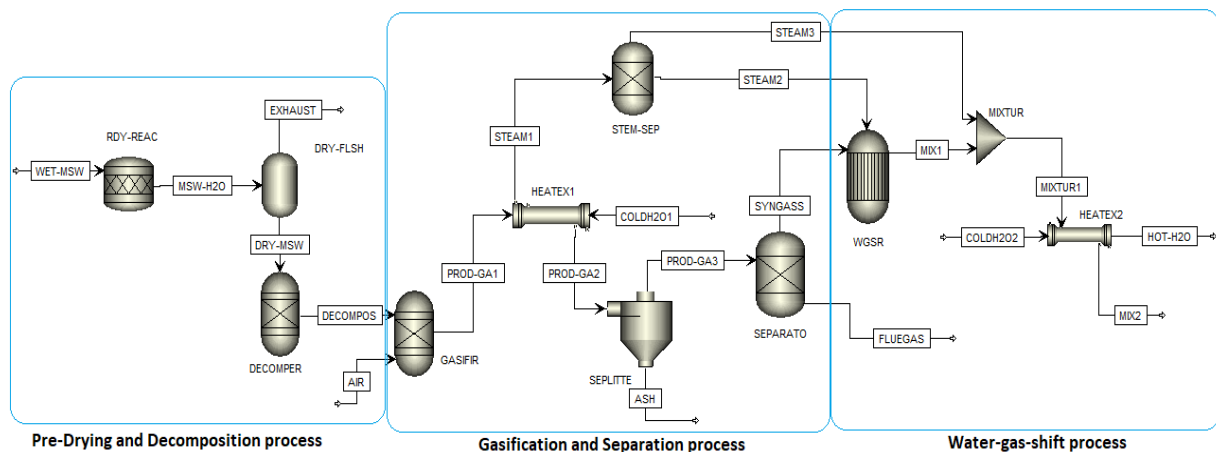


Figure 3.5 Process flowsheet of direct gasification system with air as a gasifying agent

In gasification reactor, the thermochemical reaction takes place, by minimization of the Gibbs free energy, the reaction reaches a stable equilibrium condition. Then after separating syngas from gasification product of a mixture of solid, liquid and mixture gases, the syngas sends to water gas shift reactor to increase the yield of hydrogen. Table 3.4 describes the Aspen plus name of the block and the model name of the blocks in the present model.

Table 3.4 Description of model blocks

| Aspen plus block name | Model block name | Aspen plus block name | Model block name |
|-----------------------|------------------|-----------------------|------------------|
| RStoic | DRY-REAC | SSplit | SEPLITTE |
| Flash2 | DRY-FLSH | Sep | STEM-SEP |
| RYield | DECOMPER | Sep | SEPARATO |
| RGibbs | GASIFIR | RGibbs | WGSR |
| HEATEX1 | HEATX | Mixer | MIXER |

MSW pre-drying

Aspen plus consider solid fuel as a non-conventional component and is defined in the simulation model using the ultimate and proximate analysis of the fuel. As mentioned in chapter two a gasifier handling capacity of moisture in the feedstock is around 10%-20% moisture content. Therefore, part of the moisture portion of the non-conventional component present in the feedstock removed in the drying section of the process.

The drying and decomposition section of the process flowsheet illustrated in the first section of Figure 3.5. The raw feedstock stream 'WET-MSW' is fed to the drier 'DRY-REAC' block, the stream specified as a non-conventional solid component with the ultimate, proximate analysis and particle size distribution input. In the stoichiometric reactor (DRY-REAC) block, at 200°C reactor temperature, a portion of moisture present in non-conventional component convert into conventional component liquid H₂O. The (DRY-REAC) block was supplemented and controlled by external FORTRAN statement to reduce and control the moisture content of the feedstock to 15% on a wet basis. After the MSW dried, a DRY-FLSH block is used to separate the exhaust vapors from the MSW, and dried product exits the dryer through DRY-MSW stream with 15% moisture content.

Before feeding the dried MSW to the GASIFIR block, the feed decomposes into its constituent chemical elements. The decomposition performed in the DECOMPER block. For this simulation, the actual yield distribution was calculated using calculator block from the component attributes for MSW in the feed stream (DRY-MSW) to the DECOMPER model. The decomposed components forwarded to the gasifier block though DECOMPOS stream.

Gasification process

In the second section of the process flowsheet in Figure 3.5 the gasification process and separation of flue gas from fuel gas is illustrated. The gasifying medium and decomposed MSW fed to the gasification block. In this block, the RGibbs model is used to simulate gasification of the decomposed MSW in the presence of the gasifying medium. The RGibbs model's chemical equilibrium by minimizing Gibbs free energy. A description of the different Aspen plus reactor blocks are given in Table 3.5.

The heat from product gas and the ash from the gasification process retrieved in 'HEATEX1' block and send to the cyclone through 'PROD-GA2' stream for the separation of solid ash. The steam from the heat exchanger send to 'WGSR,' and the rest send to the second heat exchanger for adjustment of the output temperature. Following the removal of ash, the syngas separated takes place in separator reactor 'SEPARETO' from the gasification process. The syngas then fed to the water gas shift reactor for enhancement of hydrogen. Like as that of gasification reactor in water gas shift reaction RGibbs model is used. After water gas shift reaction, the mixture gas containing hydrogen passes through a heat exchanger for extraction of surplus heat in the mixed gas. The heat used for heating water at a temperature of 100°C for district heating application. The flowsheet of the direct gasification with the addition of steam and air, and the indirect gasification depicted in the Appendix Figure B-2 and Figure B-3 respectively.

The description of commonly used reaction and separation blocks in Aspen plus simulation software listed as follow.

Table 3.5 Description of Aspen plus simulation software reactor blocks

| | |
|--------|--|
| RYIELD | RYield block is used to simulate a reactor with a known yield. The reactor decomposes the nonconventional solid into its constituent elements. This reactor is useful when reaction stoichiometry and kinetics are unknown, and yield distribution data or correlations are available. |
| RSTOIC | RStoic models a reactor when: Reaction kinetics is unknown or unimportant, Stoichiometry is known, the extent of reaction or conversion can specify. Rstoic can handle reactions that occur independently in a series of reactors. It can also perform product selectivity and heat of reaction calculations. |
| RGIBBS | RGibbs reactor models single-phase chemical equilibrium, or simultaneous phase and chemical equilibria. RGibbs is used to model reactions that come to chemical equilibrium. RGibbs calculates chemical equilibrium and phase equilibrium by minimizing the Gibbs free energy of the system. This reactor block requires the thermodynamic specifications, and it does not require reaction stoichiometry to calculate chemical and phase equilibrium. |
| SEP | Sep combines inlet streams and separates the resulting stream into two or more streams, according to splits specified for each component. It can specify the splits for each component in each substream. |

4 Results and Discussion

4.1 Introduction

In this chapter, the experimental characterization of MSW performed in the laboratory and the simulation results of gasification process presented and discussed. In the MSW characterization section of this chapter, proximate analysis, ultimate analysis and TGA analysis results presented and discussed. In the process simulation section, the present model validated using other works in literature and against theoretical hydrogen yield of the chemical reaction of the MSW. Also, the whole process hydrogen yield, sensitivity analysis results and the mass and energy balance of gasification and water-gas-shift reactors presented and discussed.

4.2 MSW Characterization

4.2.1 Proximate Analysis Result

The experimental data presented for the proximate analysis in this thesis corresponding to the measurement results are the mean values of the three duplicate samples of MSW test carried out. As discussed in the method section, three duplicate samples are used to test MC, VM, and ash. The proximate analysis results of the three duplicate samples presented in Appendix A (Table A-1). The sample FC content determined by the difference of hundred percent to the sum of the average percentage value of MC, VM and ash tests from the three duplicate samples (eq.(2.5)). In Table 4.1, the results presented together with the result reported by Hla and Roberts [13] for comparison. Hla and Roberts reported the results for measured reconstituted sample and calculated from an individual sample of combustible components in Greater Brisbane, Australia.

Table 4.1 Proximate analysis results of present sample and from literature

| Parameters | Present result | Measured [13] | Calculated [13] |
|-----------------------|----------------|---------------|-----------------|
| Moisture (%wb) | 6.3 | N/A | N/A |
| Volatile matter (%db) | 78.6 | 77.4 | 78.4 |
| Fixed carbon (%db) | 9.0 | 15.1 | 14.5 |
| Ash (%db) | 12.4 | 7.6 | 7.2 |

The study on municipal solid waste characterization conducted in Greenland by Eisted and Christensen [17] indicated that the chemical composition of the material fractions in Greenland was similar to the composition of material fractions in Danish household. This study shows that chemical composition and a material fraction of municipal solid waste dependent on geographical location, socioeconomic status, and other reasons.

The comparison of the results in Table 4.1 shows some differences; the differences could be due to the reasons mentioned above. Thus, the present finding can give a reasonable approximation of average Norwegian municipal solid waste proximate analysis. Though the two study locations are in entirely different geographical location, they have some similarity in economic issue and lifestyle. Therefore, it can be concluded that the proximate analysis obtained in this work suggests that the method used for sampling of the municipal solid waste using statistical data was reasonable. However, for the as-received moisture content of the waste since it depends highly on the geographical location, the waste sorting and categorization method in a specific area and season in which the sample

analyzed. Therefore, it is entirely reasonable to study the as-received moisture content of MSW for a place in which the incineration plant operates.

4.2.2 Ultimate Analysis Result

The elemental analysis of MSW samples was determined using the methods described in section 3.2.4. The experimental data of carbon, hydrogen and nitrogen corresponding to the measurement results are the mean values of the nine runs carried out. The ultimate analysis results of the nine duplicate samples presented in Appendix A (Table A-2). The oxygen (O) content determined by difference (eq.(2.6)), and the ash content is the same as a result found in the proximate analysis. As mentioned in the method section of this work, the ultimate analyzer in the lab determines only carbon, hydrogen, and nitrogen, the sulfur content in this work taken from relevant literature [13], [15]. In those mentioned literature the mass percent composition of sulfur ranges from 0.18 to 0.21 %, in this work the sulfur content approximated to 0.2%.

In general, the results obtained were as expected, most chemical characteristics of MSW samples presented in Table 4.2 are the typical chemical composition of biomass, since mass percentage composition of the MSW sample in this study dominated by biomass which is around 77%. The result also has not a considerable deviation from results reported by the different investigator on MSW characterization listed in Table 1.1 [13], [15], [17]. The results from the ultimate analysis together with the result from [13] presented in Table 4.2 showed that carbon and oxygen were the most dominated chemical elements in the municipal solid waste.

Table 4.2 Chemical composition of MSW sample

| Element | C (%db) | H(%db) | N(%db) | O(%db) | S(%db) | Ash(%db) |
|-------------------------|---------|--------|--------|--------|--------|----------|
| Present sample | 51.6 | 6.3 | 0.8 | 28.7 | (0.2) | 12.4 |
| Measurement [13] | 52.8 | 6.4 | 1.29 | 31 | 0.18 | 7.6 |

The general chemical equation of the studied municipal solid waste can be approximated using the ultimate analysis data provided in Table 4.2 as $CH_{1.5}O_{0.4}N_{0.014}S_{0.002}$. This general chemical equation can use to determine the stoichiometric air-to-fuel ratio of combustion as it is discussed in section 2.4 and the air-to-fuel ratio became approximately eight.

The atomic H/C and O/C ratios of the waste sample found out to be approximately 1.5 and 0.4 respectively. Plotting atomic H/C and O/C values in Van Krevelen (VK) diagram (Figure 2.2) gives behavior of the MSW. The point in the diagram lies outside the biomass and above the peat region, the reason is the presence of plastic in the sample, and the heating value is quite higher than the biomass according to the increasing trend of the heating value shown in the diagram.

4.2.3 Heating Value Calculation

The heating value of a feedstock is an essential parameter in the design of any thermochemical conversion plant. The energy content of the municipal solid wastes profoundly affected by the moisture content of the waste. The energy content of a feedstock can be measured by two methods, experimentally in a laboratory using bomb calorimeter or can be calculated using different empirical formulas. These empirical formulas determine the heating value of a feedstock by using the ultimate analysis of the feedstock. In this work, the second approach was applied and calculated using the

empirical formulas mentioned in section 2.3.5 (eqs. (2.9)-(2.11)) and the elemental analysis data of the MSW presented in Table 4.2. The heating value of the analyzed MSW presented in Table 4.3.

Table 4.3 Heating value of the analyzed MSW and heating value of MSW from literature

| Formula | Boie | Dulong | Reed | Average |
|-----------------------------------|------|--------|-------|---------|
| HHV _{db} (MJ/kg) | 22.3 | 21.3 | 21.7 | 21.8 |
| HHV _{db} from literature | | | | |
| Literature | [13] | [15] | [16] | [17] |
| HHV _{db} (MJ/kg) | 22.5 | 22.2 | 18.97 | 21.2 |

The HHV_{db} of municipal solid waste was calculated and found out 22.3 MJ/kg, 21.3 MJ/kg and 21.7 MJ/kg by using the empirical formulas proposed by Boie, Dulong, and Gaur and Reed respectively. The heating value of the MSW sample is in a good agreement with the heating values reported in [13], [15]. These results from those literature used as reference point to get a picture of the heating value of an MSW. The HHV_{db} obtained in this work was higher than HHV_{db} of wood, paper, cardboard and lower than plastic reported in [13], [15], [17]. So, the presence of plastic in MSW has the advantage of increases the overall heating value of the waste, though fossil fuel nature of the plastic requires high consideration in fuel gas cleaning for downstream use, flue gas control system and ash characteristics.

4.2.4 Thermogravimetric Analysis Result

Figure 4.1 illustrates the TGA profile of drying, devolatilization and combustion result obtained for the average of the two experiments performed as a function of time. First, in TGA program curve, the temperature of the furnace increased from room temperature to 80°C gradually and held at 80°C for eight minutes to drive out the moisture present in the sample with the help of inert purging gas (Argon). In this phase, the weight loss of 3% corresponds to moisture, and the weight of the sample became constant until devolatilization phase.

During devolatilization phase, the temperature increases at a rate of 25°C/min until it reaches 800°C in an inert gas atmosphere. As illustrated in the figure, the highest weight loss in devolatilization phase occurred in two steps first around the 25th minute and the second was around the 30th minute. The occurrence of the weight loss in two steps is due to the heterogeneity of the waste, which is the cellulosic and polymer components, this phenomenon discussed below. In the next stage, the temperature was held at 800°C for five minutes with the inert gas atmosphere to give room for the rest volatile mater left to drive out. In this temperature ramp and isothermal phases, the weight loss corresponds to volatile matter, and constant weight reached. At this point, the left-over weight of the sample contains only ash and fixed carbon.

The oxidation phase of the experiment was so fast the high furnace temperature gives a favorable condition for the exothermic carbon combustion reaction eq.(2.23). After the introduction of oxygen in the furnace the oxidation completed within two minutes and the weight of the sample kept constant for around eight minutes, so rest was ash.

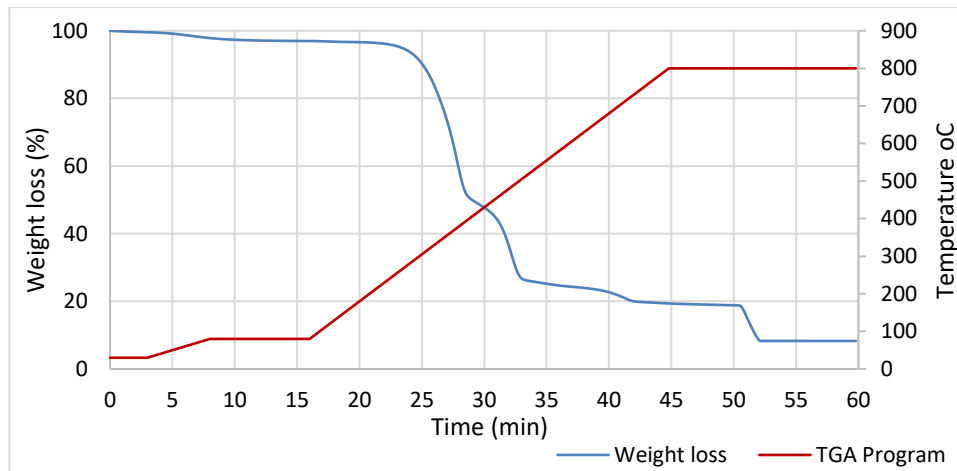


Figure 4.1 A weight loss of the sample and TGA program curve as a function of time

Because of the expense and time constraint in the proximate analysis using standards proposed as alternative thermogravimetry or differential thermogravimetry can be used to predict proximate analysis of fuel, this method though not an industry standard [39]. Thus, from the measured weight loss-vs-time graphs, a quantitative value of moisture content, volatile matter, and ash content can be predicted by the constant weight lines. The fixed carbon can calculate by using eq. (2.5).

Table 4.4 Comparison of proximate analysis of MSW by standard analysis and TGA analysis

| Parameters | Standard | TGA Result |
|-----------------------|----------|------------|
| Moisture (%wb) | 6.3 | 3.04 |
| Volatile matter (%db) | 78.6 | 80.6 |
| Fixed carbon (%db) | 9.0 | 10.9 |
| Ash (%db) | 12.4 | 8.5 |

The moisture content of the air-dried test sample obtained in the TGA is too low compared to the standard method. The first reason could be the sample was held at room temperature for around fifteen days after the standard proximate analysis performed. Consequently, the extra moisture content might vaporize during this period. The other could be the first isothermal temperature of 80°C phase could not be enough to evaporate inherent moisture content of the sample so that these reasons could make a change on the result of moisture content from TGA. In the case of volatile matter, the TGA results relatively in good agreement with a standard method with only 2.5% deviation. Similarly, for fixed carbon and ash content result shows some difference from the standard analysis. Some of the reason for the deviation could be due to residence time, sample homogeneity, noise on TGA and other technical issues.

The result of TGA analysis shown in Figure 4.2 it shows the mass loss and rate of mass loss of the MSW sample as a function of reaction temperature. This analysis is an essential tool in the characterization of a feedstock for further study of the kinetic parameters of thermochemical decomposition of the feedstock. In this work, the pyrolysis and combustion characteristics of the MSW investigated. Although the analysis of the gasification phase of TGA was an essential tool for the study of the kinetic parameters of the gasification, the gasification phase not included in this study.

As shown in Figure 4.2 the two picks of maximum mass losses at around 373.5°C and 482.6°C in the DTG curve are evidence to the devolatilization of volatile matter from biogenic materials and petroleum-derived polymers respectively. The decomposition of cellulosic materials generally finishes at a temperature lower than 400°C, and the petroleum-derived polymers usually begin at temperatures higher than 400°C and end around 500°C [14]. After the volatile material is driven out of the sample and only char and ash remain, char may then determined by switching the gas flow to oxidant (oxygen or air). Thus, local maximum pick at 717.3°C is the mass loss due to the combustion of carbon in the presence of oxygen.

Using the method used by Robinson et al. , [14] the onset and the end set temperatures of mass loss for biogenic materials, petroleum-derived polymers and char decomposition determined as follow. For determination of the onset and end set points for a mass loss in the process, a tangent line is drawn at the point in the TGA curve where the rate of mass loss reaches a local maximum. The connection point of two tangent lines before the local maximum is the onset point while after the local maximum is the end set points.

The first mass loss interval, attributed to the devolatilization of volatile matter from cellulosic materials, found out to be approximately the onset temperature is 320°C, and an end set temperature of 387°C. The second mass loss interval, attributed to the devolatilization of volatile matter from petroleum-derived polymers, has an onset temperature of approximately 450°C and an end set temperature of 500°C. For char decomposition, the maximum mass loss was at around 717.3°C and the onset temperature of the mass loss of char found at approximately 670°C while the end set temperature was almost around 740°C.

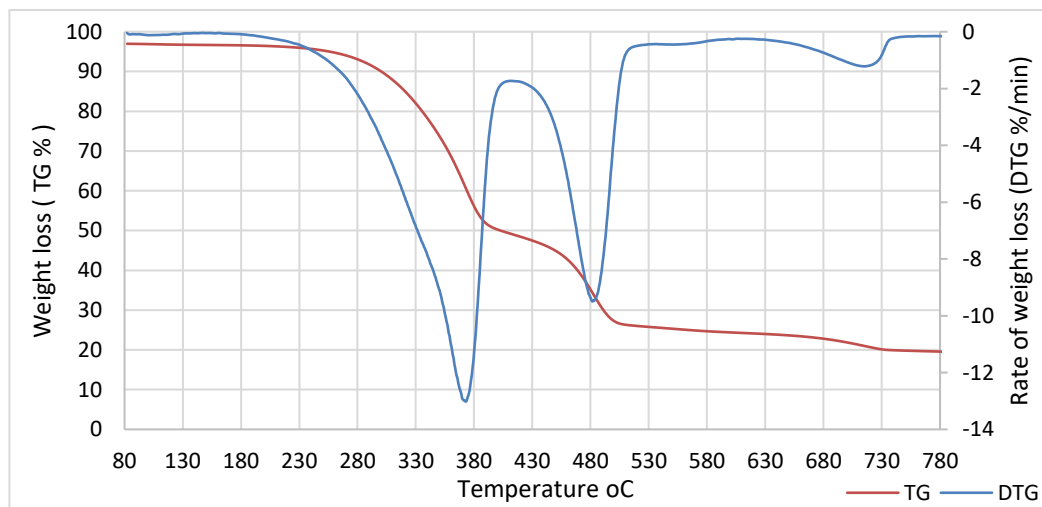


Figure 4.2 The TG and DTG curves of MSW

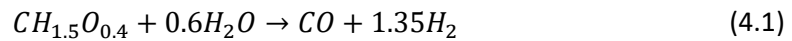
4.3 Process Simulation

4.3.1 Model Validation

This section deals with the validation of the developed simulation model using two methods. The first method was by comparing of the predicted hydrogen yield of the gasification process and water gas shift reaction with the theoretical attainable hydrogen yield of the dry ash free municipal solid waste. The second model validation method conducted by comparing the present model output with existing experimental result. The predicted producer gas composition of the developed simulation model using

steam as a gasifying agent compared with an experimental study conducted on hydrogen-rich gas production via steam gasification of biomass in a research-scale fluidized bed by Fremaux et al. , [72]. Though the experimental research was on a fluidized-bed reactor, the gas composition pattern of this validation taste can use to see the performance of the present model.

The balanced general chemical equation of the dry ash-free municipal solid waste and steam as a gasifying agent in gasification stage and water gas shift reaction by neglecting the sulfur and nitrogen content of the MSW written as:



The possible attainable theoretical maximum hydrogen yield under the assumptions of dry and ash free MSW can be calculated from the balanced chemical equations, eqs. (4.1), (4.2). The maximum theoretical hydrogen yield of steam gasification (eq. (4.1)) and water gas shift reaction (eq. (4.2)) calculated 236g H₂ per kg of dry ash free MSW. This yield of hydrogen is used to validate the present model. Practically the theoretical yield of hydrogen cannot achieve due to the molecular structure of MSW, the uncontrolled and complex decomposition the fuel undergoes upon heating, and system losses and irreversibility's [23].

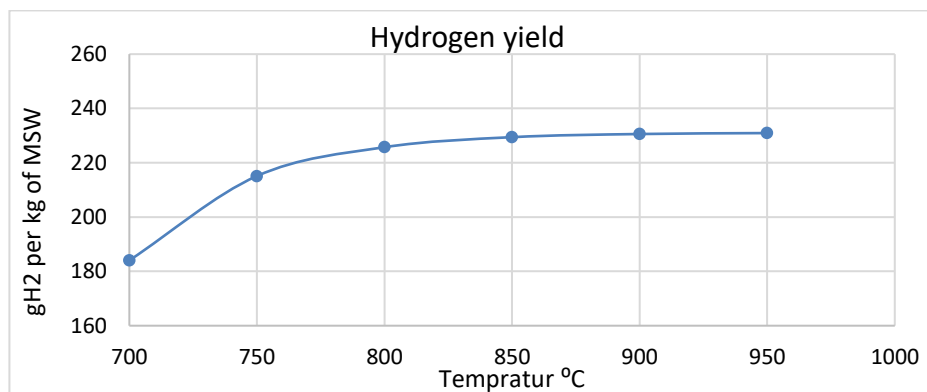


Figure 4.3 Hydrogen yield of the model from MSW at a different gasification temperature

Figure 4.3 illustrated the hydrogen production attained by the present simulation model both from gasification and water gas shift reactors. The simulation performed with MSW to steam and carbon monoxide to steam ratio of the same as that of eqs. (4.1), (4.2). The hydrogen yield increases with the increasing of gasification reactor temperature at a constant water-gas-shift reactor temperature of 300°C and atmospheric gasifier and water-gas-shift reactors pressure.

The highest attained hydrogen yield in this simulation model was 230.9 gH₂ per kg of dry ash free MSW at a temperature of around 950°C, and above this temperature, the yield becomes almost constant. The lowest is 184.1 gH₂ per Kg of dry ash free MSW at 700°C. The result shows that the hydrogen yield of the present model had no a big difference with the theoretical maximum yield of the MSW, the differences range from around 2.2% to 22% of the theoretical yield at 950°C and 700°C respectively. The reasons for the reduction of the hydrogen yield compared to the theoretical yield could be: The participation of hydrogen in the formation of methane and water in the simulation and miss much of the optimum condition for the two reactors.

The second model validation method conducted by using wood residue characteristics used by Fremaux et al. Their experimental study on the effect of steam to biomass ratio between 0.5 to 1 at gasification temperature of 700°C used for comparison of the present model. The characteristics (proximate and ultimate analysis) of wood residue used in their experimental study adopted for validation of the present model given in Table 4.5

Table 4.5 Proximate and Ultimate Analysis of wood residue

| Proximate analysis (wt%) | | Ultimate analysis (wt%) | |
|--------------------------|-------|-------------------------|-------|
| Moisture | 5.01 | C | 50.26 |
| Volatile matter | 77.71 | H | 6.72 |
| Fixed carbon | 16.94 | O | 42.66 |
| Ash | 0.34 | N | 0.16 |
| | | S | 0.20 |

Figure 4.4 shows the comparison of the percentage composition of product gas in experimental steam gasification of residue wood performed by Fremaux et al. and by simulation of gasification with steam as gasifying agent modeled using Aspen plus software in this work. The result from the present model shows that similar trends as they found in the experiments study of Fremaux et al. The same approach was used by Pala et al. , [28] on validating of their simulation model and they also found a similar trend as it was in the present work.

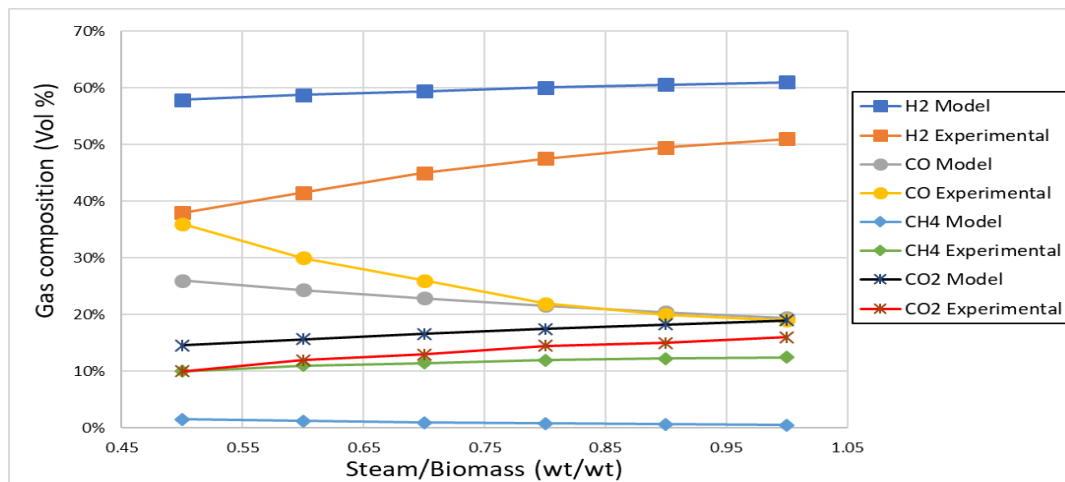


Figure 4.4 Comparison between model and experimental (Fremaux et al. , [72]) results at the gasification temperature of 700°C

The model predicted higher hydrogen concentrations than the experimental study done by Fremaux et al. on the same feedstock. Pala et al. , [28] reason out that the reason for the higher hydrogen concentrations as that the model does not consider the formation of tar and higher hydrocarbons. The same in this work also tar and higher hydrocarbons are neglected so the reason could be the same here. The other reason could be the experimental study was conducted in fluidized bed reactor, but the present work was in fixed bed. As we can see in Table 1.2, the hydrogen yield of the fluidized bed reactor is lower compared to a fixed-bed reactor with air as a gasifying medium. The concentration of CH₄ underestimated in this model, which was an entirely common problem in the equilibrium modeling [47].

4.4 Mass and Energy Analysis

4.4.1 Mass Balance

As discussed in theory section (2.5.1) mass is conserved in both gasification reactor and water gas shifter reactor. In the steady state control volume, Aspen plus model the mass into a block is equal to the mass out of the block. This balance of mass carried out through elemental analysis of the constituent elements of the MSW and the compounds produced after the process. Besides the constituent elements of the combustible organic part of the MSW, the attribution of the inorganic compound (ash) considered.

The primary inputs compounds into the gasifier are the MSW constitute of C, H, O, N, S, ASH and H₂O from moisture and oxidant medium. The outputs considered C, H, O, N, S, ASH, CO, CO₂, CH₄, SO₂, and H₂O. In water gas shift reactor, the inputs are CO, H₂, and H₂O, and the outputs are H₂, H₂O, CO₂ and unconverted CO. The result in Table 4.6 from the simulation shows that elemental balance was kept constant in gasification and the water-gas-shift reaction section of the model in both direct and indirect gasification systems.

From Table 4.6 we can observe that the mass percentage of an element at the inlet of the reactors is equal to the sum of the mass percentage of the same element at the output either as an element or in a molecular compound.

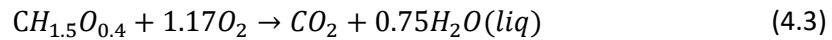
Table 4.6 Gasification and WGS reaction section mass balance for direct and indirect gasification model

| Component | Direct Gasification model | | | | Indirect Gasification model | | | |
|------------------|---------------------------|------|-------------|------|-----------------------------|------|-------------|------|
| | Gasifier (wt%) | | WGS Reactor | | Gasifier (wt %) | | WGS Reactor | |
| | IN | OUT | IN | OUT | IN | OUT | IN | OUT |
| H ₂ | 1.9 | 2.1 | 3.9 | 7.3 | 3.7 | 7.2 | 6.5 | 9.7 |
| N ₂ | 50.2 | 50.2 | - | - | 0.5 | 0.5 | - | - |
| O ₂ | 22.9 | 0.0 | - | - | 16.9 | 0.0 | - | - |
| S | 0.1 | 0.0 | - | - | 0.1 | 0.0 | - | - |
| C | 15.7 | 0.0 | - | - | 30.3 | 0.0 | - | - |
| CO | 0.0 | 31.3 | 58.4 | 10.8 | 0.0 | 63.0 | 57.0 | 12.2 |
| CO ₂ | 0.0 | 8.4 | 0.0 | 74.9 | 0.0 | 11.9 | 0.0 | 70.3 |
| CH ₄ | 0.0 | 0.0 | - | - | 0.0 | 0.0 | - | - |
| H ₂ O | 5.4 | 4.0 | 37.7 | 7.0 | 41.2 | 9.8 | 36.5 | 7.7 |
| ASH | 3.8 | 3.8 | - | - | 7.3 | 7.3 | - | - |
| SO ₂ | 0.0 | 0.1 | - | - | 0.0 | 0.2 | - | - |
| Total | 100 | 99.9 | 100 | 100 | 100 | 99.9 | 100 | 99.9 |

4.4.2 Energy Balance

The first step to calculate the energy released due to the thermochemical reaction is finding the enthalpy of formation of the compounds in reactant and product of the balanced chemical equation. For most of the compounds, the enthalpy of formation tabulated in thermodynamic books. For the MSW as discussed section 2.5.2, it can be calculated using the average of the three results of the

heating value of the MSW found in section 4.2.3 ($HHV_{db} = 21.8 \text{ MJ/kg}$) and using formulated generic combustion stoichiometry equation.

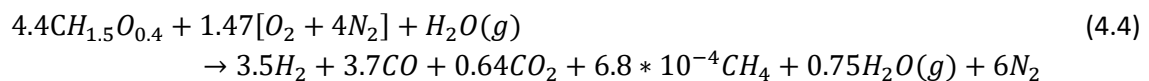


The result found by using the above stoichiometry equation and the heating value the MSW to calculate the enthalpy of formation of MSW and the other substances involved in gasification process found from different books listed in Table 4.7.

Table 4.7 Enthalpy of formation of substances involved in the gasification process

| Substances | Formula | h_f° (kJ/kmol) |
|-----------------|-------------------|-----------------------|
| MSW (sample) | $CH_{1.5}O_{0.4}$ | -174,030 |
| Oxygen | O_2 | 0 |
| Hydrogen | H_2 | 0 |
| Nitrogen | N_2 | 0 |
| Carbon monoxide | CO | -110,530 |
| Carbon dioxide | CO_2 | -393,520 |
| Water (g) | H_2O | -241,820 |
| Water (liq.) | H_2O | -285,800 |
| Methane | CH_4 | -74,850 |

The chemical equation was formulated using mass composition of the substances from the gasification process performed in Aspen plus. In the formulation of the chemical equation, the ash free MSW with a moisture content of 17% considered, and the sulfur and nitrogen content of the waste sample neglected. The balanced chemical equation (eq. (4.4)) proves the mass balance of the system in molar balance basis, besides aiding in the calculation of the heat of reaction for the constant temperature at 900°C gasification process.



Using eq.(2.29) the heat of reaction at a constant temperature of the direct gasification found out to be $\Delta H_R = 165.2 \text{ MJ/kmol}$ the result showed the overall reaction is an endothermic reaction at a temperature of 900°C. However, a typical chemical reaction is not an isothermal process as illustrated in Figure 2.11 the relationship between mixture enthalpy and temperature for a chemically reacting system.

For the WGS reactor, the chemical reaction took place formulated using reactant and product of the simulation in Aspen plus and formulated as follow. The chemical equation illustrated the mass balance of the reaction by molar balance.



The heat of reaction for a constant temperature of 300°C WGS reactor was calculation using eq.(2.29), and it was found out to be $\Delta H_R = -196.17 \text{ MJ/kmol}$ the result shows the reaction is an exothermic reaction, which is in agreement with the theory of forward reaction of the water gas sift reaction discussed in section 2.4.4.

4.5 Sensitivity Analysis

4.5.1 Direct Gasification

Sensitivity analysis is a tool to analyze how a process reacts to varying critical operating and design variables. Sometimes it may be useful to see how the results vary with changes in inputs, either because they are uncertain or because they represent a range of applications. In Aspen plus sensitivity analysis tool, it is possible to perform “what if” studies by varying one or more flowsheet variables. The sensitivity analysis results and discussion of direct gasification (Auto thermal) process to study the effect of temperature and equivalent ratio in gasification and effect of temperature in the water gas shift reaction presented as follow.

In this study, the moisture content of MSW was used to be 15% in all the following simulations performed. The moisture from MSW may also be involved in chemical reactions, such as water gas shift reaction, water gas reaction, and steam methane reforming reaction, and affect the chemical reaction equilibrium and change the component distribution in the product gas [47].

Effect of Gasification Temperature

The effect of gasification temperature on the product gas composition at an equivalent ratio of 0.3 was studied because the temperature is the most important operating variables for MSW gasification. Figure 4.5 shows the gas composition obtained from direct gasification of MSW as a function of gasification temperature in the range of 550 to 1000°C with the increment of 50. The percentage composition of N₂ not displayed in the figure and its content can calculate by subtracting the sum of other components from 100%. Similarly, the trends of product gas percentage composition in direct gasification with air and steam as gasifying agent illustrated in Figure B-2.

Le Châtelier’s Principle states that a change in pressure, temperature, or concentration will push the equilibrium to one side of the equation. As expected, the trends shown in Figure 4.5 are in good agreement with chemical reaction laws stated: raising reaction temperature favors the endothermic reactions, while the reverse is true in an exothermic reaction. In the result obtained the concentration of H₂ and CO increased with the increase of gasification temperature while the concentration of CO₂ and CH₄ decreased as the gasification temperature increased. A null value for methane concentration was usually predicted in equilibrium modeling above 800 °C [47]. The result shows that H₂ increasing from approximately 18% at 550°C to maximum point 24% at 750°C and then slightly reduced to 23% at 1000°C. CO shows a dramatic increase in the temperature range of 550°C to 750°C from approximately 6% to 26% and then slightly reaches 28% at 1000°C. Quite similar general gas composition trends were reported by [27], [47] for their study of the effect of gasification temperature. In general, the product gases are sensitive bellow gasification temperature of 700°C, above this temperature, the change in product gas composition is quite small.

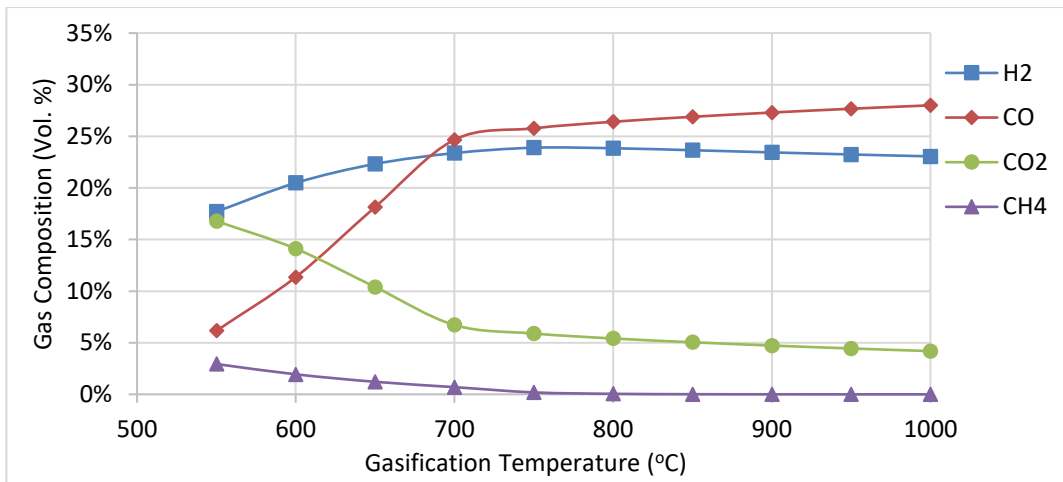


Figure 4.5 Effect of gasification temperature on product gas composition in direct gasification only air as a gasifying agent

The gas composition trends attributed to the endothermic and exothermic chemical reactions from eq. (2.16) - (2.23). The endothermic reaction is more sensitive to changes in temperature. Therefore, the endothermic reaction will increase faster with increasing temperature than the exothermic reaction will. The increase of H₂ concentration in the product gas as a function of temperature attributed to endothermic water gas and steam methane reformation reactions. The increasing of gasification temperature provides the necessary energy for these endothermic reactions which are the most significant contributor of H₂. Similarly, the primary CO contributor Boudouard, water-gas and steam methane reformation reactions get the necessary energy for endothermic reactions. Thus, the CO concentration increases with increasing the gasification temperature. Besides the increasing of H₂ and CO in steam methane reformation endothermic reaction, it decreases the concentration of CH₄ with increasing gasification temperature.

The decreasing CO₂ concentration with increasing gasification temperature could be because of the Boudouard reaction and reverse reaction of water gas shift reaction. As mentioned in section 2.4.4 in forwarding water-gas-shift reaction the favorable temperature is in the range of approximately 200-400°C. Increasing the temperature above this favor for the reverse reaction of water gas shift, so that it could be the reason for the reduction in the concentration of CO₂ product gas.

Effect of Air Equivalence ratio

Air equivalence ratio represents the ratio of the actual amount of air introduced to the amount of stoichiometric air needed for complete combustion. The effect of equivalence ratio on percentage composition of product gas presented in Figure 4.6. Equivalence ratio was increased from 0.35 to 0.75 (fuel-lean condition) in increments of 0.25 by increasing the air flow rate while holding mass flowrate of MSW constant at constant gasification temperature of 900°C.

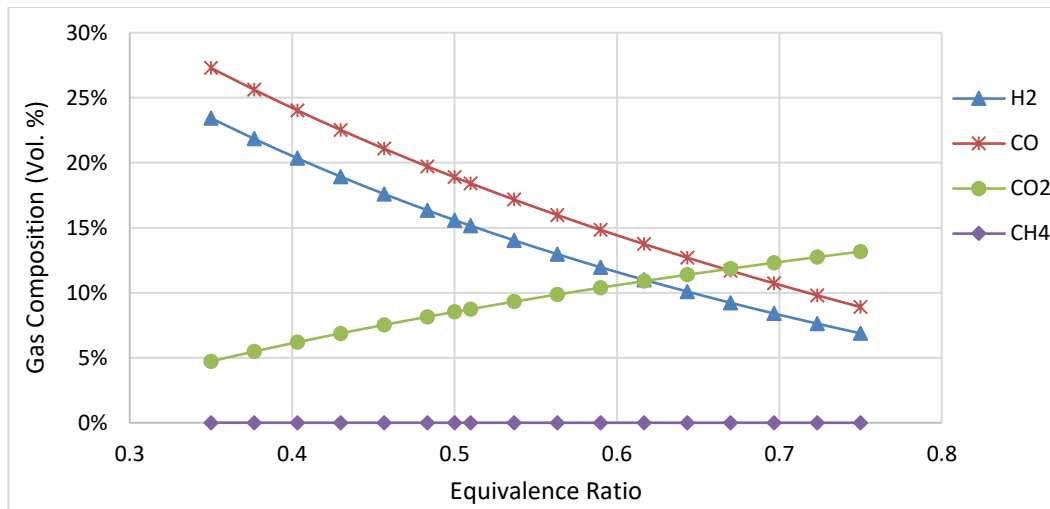


Figure 4.6 Effect of equivalence ratio on product gas composition

In the study of the effect of equivalence ratio on the percentage composition of the gas, the trends were opposite to that of trends obtained in the effect of gasification temperature study this is because air reached gasification is favorable for combustion than gasification. It can observe that the percentage composition of H₂ and CO decreased with increasing of equivalent ratio while percentage composition of CO₂ increases with increasing equivalent ratio. It can be concluded that product gas composition in direct gasification using air as a gasifying agent is highly sensitive to equivalence ration.

As mentioned above the concentration of methane was underestimated in this model, which was an entirely common problem in the equilibrium modeling [47]. Quite similar trends in gas composition were reported by [23], [27] in the study of the effect of equivalence ratio, except that hydrogen had high percentage composition than carbon monoxide. The reason for the domination of the percentage composition of hydrogen in those studies was the introduction of steam in the gasification process to produce hydrogen enrich product gas.

Effect of Temperature in WGS reaction

Figure 4.7 shows the result of the effect of water-gas-shift reaction temperature on percentage composition of H₂, CO, and CO₂. The simulation performed at steam to carbon monoxide ratio of 0.6, and the water-gas-shift reaction temperature was increased from 200°C to 750°C in an increment of 50°C. The gasification parameters of the gasifier held constant, at a temperature of 900°C and equivalence ratio of 0.3.

As expected, from the thermodynamic equilibrium that the concentration of hydrogen and carbon dioxide reduced with increasing temperature while the concentration of carbon monoxide increases with temperature. The phenomenon is due to that the preference of the backward endothermic shift reaction at high temperature than forwarding shift reaction of an exothermic process.

The result obtained for the study of the effect of temperature in the water-gas-shift reaction in this work was in good agreement with the result reported by [28], in the report percentage conversion of carbon monoxide and carbon dioxide reported and the trend shows similarity with the result obtained from the present model.

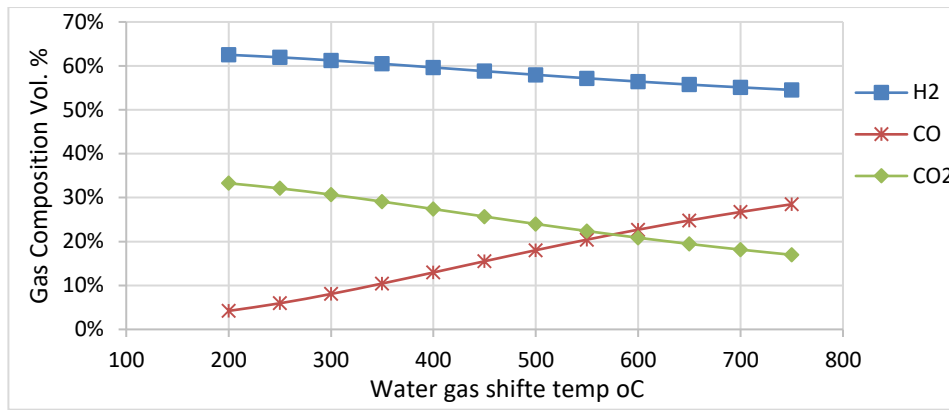


Figure 4.7 Effect of the WGS temperature on the gas composition

4.5.2 Indirect Gasification

The simulation of indirect gasification was performed using a gasifying agent of steam and with external energy supply. The sensitivity analysis results and discussion of indirect gasification (Allo-thermal) process to study the effect of gasification temperature and steam to MSW ratio on the gas composition of product gas presented as follow. Since in the indirect gasification, there is no nitrogen contamination with the product gas the presence of nitrogen only from the municipal solid waste nitrogen content and is negligible.

Effect of gasification Temperature

The effect of gasification temperature on the product gas composition studied by holding steam to municipal solid waste ratio steady at 0.6, because the temperature is one of the most important operating variables for MSW gasification. Figure 4.8 shows the gas composition obtained in indirect gasification of MSW as a function of gasification temperature in the range of 550 to 1000°C with the increment of 50.

It can observe from the result that the concentration of hydrogen increased slightly from approximately 48% at 550°C to maximum point 57% at 800°C and kept constant until 1000°C. Like direct gasification, the composition of carbon monoxide shows a fast increase in the temperature range of 550°C to 750°C from approximately 9% to 36% and then slightly reaches 40% at 1000°C. Trends obtained in the product gas composition compare well with results of Pala et al. , [28] from a simulation performed in gasification temperature range of 750°C to 950°C and constant steam to biomass ratio of 0.6.

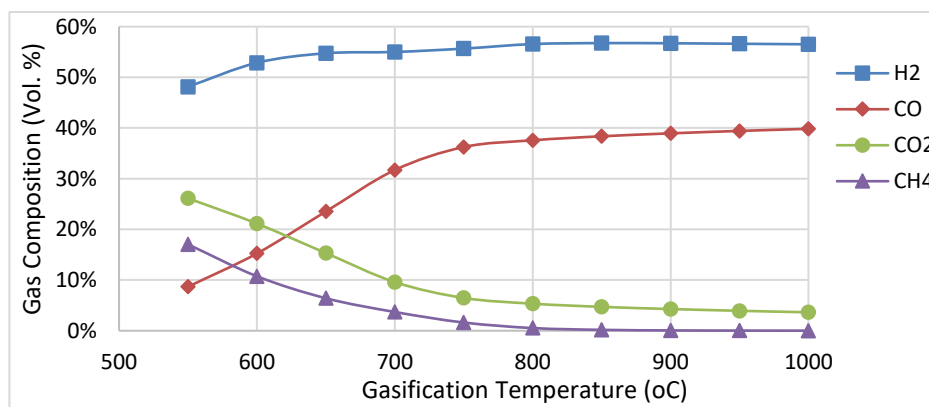


Figure 4.8 Effect of gasification temperature on product gas composition in indirect gasification

As expected, the trends shown in Figure 4.8 are in good agreement with chemical reaction laws stated: raising reaction temperature favors the endothermic reactions, while the reverse is true in an exothermic reaction. The gas composition trends obtained had similar trends as that of discussed in direct gasification Figure 4.5. The concentration of hydrogen and carbon monoxide increased with the increase of gasification temperature while the concentration of carbon dioxide and methane decreased as the gasification temperature increased.

The presence of hydrogen in steam plays a significant role in increasing the composition of hydrogen in the product gas. Therefore the hydrogen composition trend dominates the other compositions. The addition of steam gives a favorable condition for endothermic water gas reaction and steam methane reformation thus, increase the yield of hydrogen and carbon monoxide. The increasing of the gasification temperature with addition of steam as gasification medium provides the necessary energy and reactant for those endothermic reactions which are the most significant contributor of hydrogen and carbon monoxide.

Effect of Steam to MSW ratio

The result of the sensitivity analysis of the effect of steam to MSW ratio on product gas percentage composition depicted in Figure 4.9. The simulation was performed at a gasification temperature of 900°C and steam to MSW ratio increases from approximately 0.3 to 1 by increasing the steam flowrate while mass flowrate of MSW held constant. The result showed that the concentration of H₂ and CO₂ increases with increasing steam to MSW ratio while the concentrations of CO and CH₄ decrease with increasing steam to MSW ratio. Similar trends have reported in [28] at gasification temperature of 900°C for wood residue

The increase in hydrogen and carbon dioxide with increasing steam flow rate resulting from the conversion of carbon monoxide and methane via water gas shift and steam methane reforming respectively. Thus, the composition of carbon monoxide and methane decreases. The result showed that the effect of steam to MSW ratio on the hydrogen concentration was weak. Therefore, it is advantageous to feed only a low amount of steam because it can lead to an inconsiderable value of hydrogen-rich gas, and high amount of steam to MSW ratio will reduce the activity of the water gas shift reaction [72]. Also, the production of steam is an energy-intensive process [28].

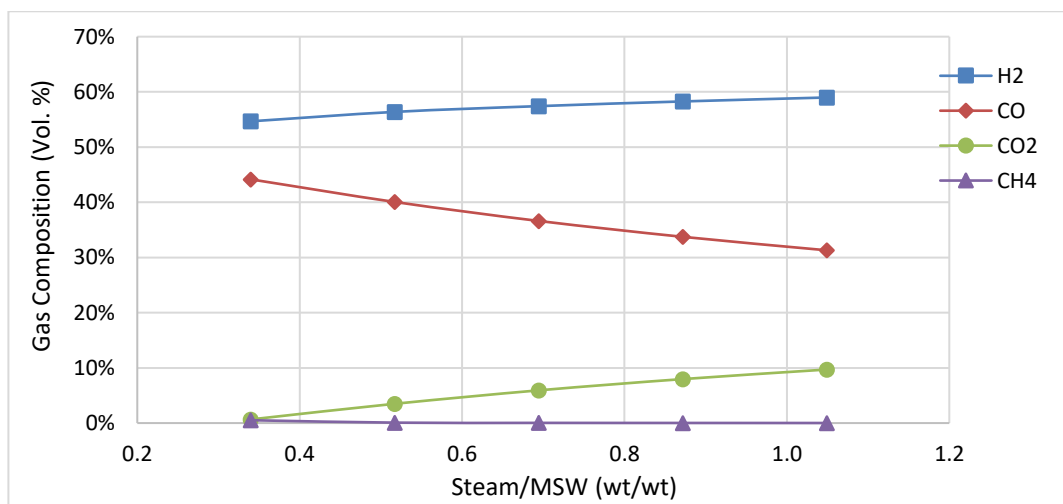


Figure 4.9 Effect of steam to MSW ratio on product gas composition in indirect gasification

4.6 Hydrogen Yield

The overall prediction of hydrogen yield of the whole process by gasification and followed by WGS reaction performed in three different process setups at atmospheric pressure. The main differences in the setups were the type of gasifying medium and the way energy is supplied for the gasification process. The performed simulations were in direct and indirect gasification, using air, steam and air/steam as gasification medium. The result of the simulation, for hydrogen yield as a function of steam to syngas ratio in the water-gas-shift reactor for the three setups presented in Figure 4.10. The gasification and water-gas-shift reactors parameters used in the simulation presented in (Table 4.8). In the three process setups, steam gasification was indirect gasification while the other two were direct gasification.

Table 4.8 Gasifier and WGS reactor parameters

| Setups | Gasification Reactor | | | WGS Reactor | | |
|--------|----------------------|------------------|--------------------|-------------|------------|-----------------------|
| | Gasification Agent | Equivalent Ratio | Steam to MSW Ratio | Temp. (°C) | Temp. (°C) | Steam to Syngas Ratio |
| 1 | Air | 0.25 | - | 1000 | 300 | 0.2-1 |
| 2 | Air & Steam | 0.25 | 0.5 | 930 | 300 | 0.2-1 |
| 3 | Steam | - | 0.5 | 1000 | 300 | 0.2-1 |

The first setup executed with air as a gasifying agent in the direct gasification system. The lowest hydrogen yield obtained was 112 g H₂/ kg of dry-ash free MSW, and the highest yield was 169 g H₂/ kg of dry-ash free MSW at steam to syngas ratio of 0.2 and 1 respectively. The temperature by partial combustion of MSW in the Gibes gasification reactor was 1000°C, which is in the range of a typical downdraft gasifier reactor temperature.

In the second setup besides air, steam was admitted as a gasifying agent in the first setup. As illustrated in Figure 4.10 the hydrogen yield improved by 11.6% at 0.2 steam to syngas ratio, and with increasing steam to syngas ratio, the yield became almost the same as that of the first model. In this model, the temperature of the Gibes gasification reactor reduces to 930°C due to the addition of steam at a temperature of around 300°C.

The third setup was indirect gasification with steam as a gasifying agent. In the third set up the hydrogen yield improvement was quite high and almost constant relative to the two setups through the whole range steam to syngas ratio. In this setup hydrogen yield increases by 48% at 0.2 steam to syngas ratio and 31% at 1 steam to syngas ratio over that of the first setup. In this setup, the temperature in the reactor supplied and kept constant at 1000°C.

The highest hydrogen yield potential attained out of the three setups was in the steam gasification which was 222 g H₂/kg of dry ash free MSW, representing 94% of the MSWs maximum theoretical hydrogen yield calculated in section 4.3.1.

In agreement with Le Châtelier's principle, the WGS reactor parameters studied, the yield of hydrogen increasing with the increase of steam to syngas ratio. Whereas, increasing temperature showed decreasing trend of hydrogen yield (Figure 4.7). According to Le Châtelier's Principle increasing concentration of reactant let the reaction to the product side, whereas increasing temperature in an exothermic reaction (eq.(2.24)) favors the reaction to the reactant side.

The result showed that addition of steam in gasification a positive impact in hydrogen yield since the hydrogen content of the steam contributes to increasing the concentration of hydrogen. The major problem associated with steam gasification is the production of tar, which causes blockage in the pipes and equipment [72]. Although direct gasification using air as gasification agent overcome the problem, in another hand the high concentration of nitrogen in syngas required high demand in the separation of nitrogen in downstream. The same with using oxygen as gasification agent it required high demand in the separation of oxygen in upstream. The choice of appropriate gasification media is a tradeoff among those mentioned. The performance of gasifier type reasonably handles those issues among gasifier types listed in Table 1.2 is fixed bed downdraft gasifier.

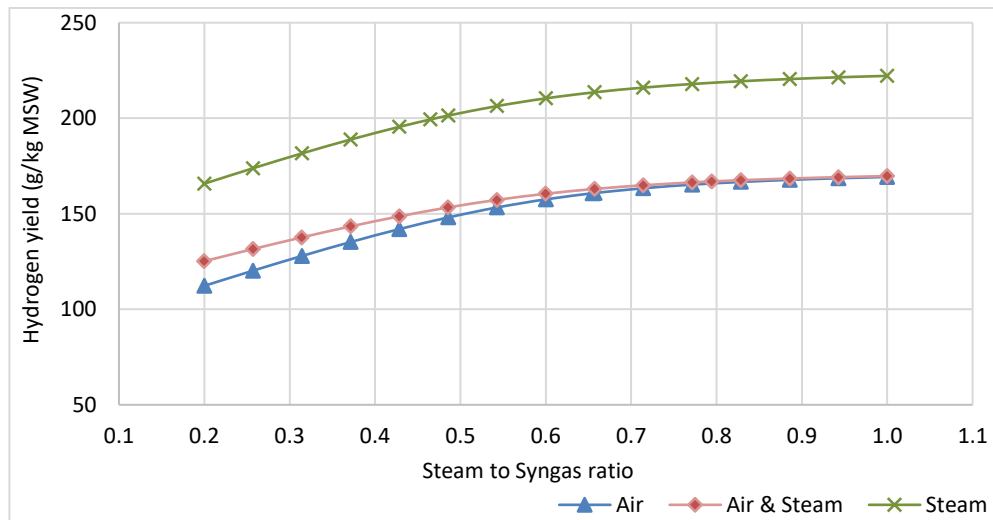


Figure 4.10 Hydrogen yield from the gasification and WGS reactors with gasification agent of air, steam and air/steam as a function of steam to syngas ratio

4.6.1 Hydrogen and Heat Production

The amount of hydrogen and heat can be delivered for district heating per one kilogram of municipal solid waste was predicted for the three setups discussed above. The simulation performed by holding steam to syngas ratio constant 0.6 for the first and second setups and 0.5 for the third setup. The reason for the reduction of steam to syngas ratio in the third setup was that the thermal energy content of the product gas from gasifier was not enough to produce steam for both gasification and WGS reactors. Therefore, in the WGS reactor steam to syngas ratio reduced to 0.5 while steam to MSW held as it is in Table 4.8 to deliver steam both for gasification. In this prediction of deliverable heat, it was assumed that the temperature of the hot water delivered for the district heating was 100°C and power generation from thermal energy not considered.

Setup 1.

In the first setup, the thermal energy with a temperature of around 1000°C from the gasification reactor used to heat water to 300°C using a heat exchanger. Part of the steam used in WGS reactor the rest mixed with excess thermal energy from WGS reactor used to heat water at room temperature to 100°C, this thermal energy is the excess energy which used for district heating. The process flowsheet of the simulation model of setup 1. Illustrated in Figure 3.5.

Hydrogen and heat output of this setup per one kilo of MSW with the same gasification and WGS reactors parameters as given in Table 4.8 and at steam to syngas ratio of 0.6 was, 157g of hydrogen

and the excess thermal energy heats 9.3 liters of water to 100°C per one kilo of MSW at atmospheric pressure.

Setup 2.

The second setup was the same as that of first except the temperature reduces to 930°C due to the addition of steam in the gasification reactor. The steam generated from the thermal energy in product gas used in WGS reactor and the gasification reactor as a gasifying medium with air. The excess thermal from the two reactors used for district heating system. The process flowsheet of the simulation model of setup 2. Illustrated in Figure B-1.

Hydrogen and heat output of this setup per one kg of MSW with the same gasification and water-gas-shift reactors parameters given in Table 4.8 and at steam to syngas ratio of 0.6 was, 165.3g of hydrogen and the excess thermal energy heats 7 liters of water to 100°C per one kg of MSW at atmospheric pressure.

Setup 3.

In the third setup only, steam used as a gasifying agent and the thermal energy for gasification supplied from an external source. The product gas temperature reached 1000°C and used to produce steam for both gasification and WGS reactors then the excess heat used to heat water for district heating. The thermal energy from the gasification reactor in this setup the exact amount of steam required for gasification and WGS reaction. The excess heat for district heating retrieves from the thermal energy in the output of WGS reactor. The process flowsheet of the simulation model of setup 3. Illustrated in Figure B-3.

Hydrogen and heat output of this setup per one kilo of MSW with the same gasification and WGS reactors parameters given in Table 4.8 and at steam to syngas ratio of 0.5 was, 199.6g of hydrogen and the thermal energy heats 4 liters of water to 100°C per one kilo of MSW. In this setup the hydrogen and heat production did not consider the source of energy for gasification, it was given per kilogram of MSW gasified.

A practical gasification plant hydrogen yield and deliverable heat for district heating per kilogram of MSW could reduce for the three setups discussed above. The reasons could be

- Formation of tar and heavy hydrocarbons
- Conversion efficiency
- System loss
- Heterogeneity of MSW and other

4.6.2 Feasible Gasification Technology

For the MSW gasification process, feasible gasification technology suggested by the author after revising literature, studying the theory of gasification technologies and the results from the simulation is fixed-bed downdraft gasifier. Some of the reasons for the author to come to this conclusion was listed as followed.

- Waste particle handling capacity of diameter up to 100 mm and high ash content feedstock possible
- The simplicity of the design, construction, and manufacturing of the gasifier is not complicated
- Low tar and phenols in the product gas

- Proven gasification technology for MSW gasification
- High exit gas temperature, which is attractive for district heating
- High thermal efficiency
- Relatively clean gas is produced which is minimize the effort of cleaning for downstream process
- Last but not the least is the economic feasibility of the technology. The recent investigation on techno-economy of biomass gasification plant for production of biofuel performed by Mustafa et al. , [30] in Narvik, Norway showed that payback period for a 6 MW downdraft gasification plant and bio-diesel process found out to be four years.

5 Conclusion

To aid planning, designing, operating or upgrading solid waste management system and optimal utilization of energy in solid waste, MSW samples were collected based on Norwegian waste statics and analyzed for their gasification-related properties. The result from the characterization of MSW used for theoretical investigation of the hydrogen yield of the MSW by gasification and water-gas-shift reaction using air and steam as a gasifying medium.

The characterization of MSW performed on the main constituents of the MSW (paper and cardboard, plastic and wood) and most of the thermochemical properties of the waste agreed with other investigations in other countries with similar socioeconomic status as Norway. It justifies the method used for characterization of the MSW was reasonable. The energy content (HHV_{db}) of the MSW calculated by three empirical formulas and found out 22.3 MJ/kg, 21.3 MJ/kg, and 21.7 MJ/kg. The heating values of MSW mainly controlled by moisture content and the presence of incombustible materials in the waste (sorting process). From the present MSW, the maximum mass losses rate occurred in TGA analysis in two stages at around 373.5°C and 482.6°C for the devolatilization of volatile matter from biogenic materials and petroleum-derived polymers respectively. The maximum mass loss rate due to combustion of solid carbon occurred at around 717.3°C.

Theoretical investigation of hydrogen production by direct and indirect gasification of MSW and water-gas-shift reaction in three simulation model setups were conducted and simulated using Aspen plus chemical process optimization software. The highest hydrogen yield potential attained out of the three setups was in the steam gasification which was 222 g H₂/kg of dry ash free MSW, representing 94% of the MSWs maximum theoretical hydrogen yield. At specific operation condition, the hydrogen and heat produced in steam gasification per one kg of MSW were 199.6g of hydrogen, and the excess thermal energy heats 4 liters of water to 100°C. The indirect gasification with steam as gasifying medium showed the highest hydrogen production potential while the direct gasification was the lowest. The addition of steam in direct gasification showed an improvement in hydrogen yield.

The results showed that the theoretical hydrogen yield of specified MSW is quite high and the result obtained from simulation is relatively good. So, by doing further region and season specific investigation on MSW characteristics hydrogen production by gasification and followed by water gas shift reaction in the existing MSW-fired plants would be a promising technology. The technology can play a significant role both in recovering and storing energy in the form of energy carrier hydrogen and reducing the bulk volume of the waste. The modeling approach and the characterization results in this work can be used as a base by other investigators who aim to change their operational strategies and plant designs for MSW management system.

5.1 Recommendations

The waste characterization performed in this work was based on statistical data of the whole country, and this result is not final and binding because waste has location-specific characteristics, so the result gives an insight of the waste characteristics in Norway. Therefore, performing location specific characterization is essential where CHP/DH plant integrates with a gasifier. Besides this, for management and decision-makers, the economic evaluation and life cycle analysis of the whole process is an essential tool for deciding the project. Performing those analysis to show the feasibility of the plant is essential to inform management and decision-makers.

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Appendix A.

Characterization of MSW

Proximate analysis

The test results of the three replicated MSW test sample for proximate analysis listed in Table A-1. In the analysis, each analysis performed using the new sample, and they had the same composition. In the moisture content test of the three depicted sample, the two test results were the same; the third result shows 16% deviation. For the ash content test, the highest deviation among the three tests was around 7%. Similarly, for volatile matter test, the highest deviation was 4.7%. For the deviation of results, the reason could be the samples heterogeneity, the material composition of one sample could differ from other.

Table A-1 The proximate analysis result of the three replicated MSW test sample

| Moisture contents measurement | | | | |
|--------------------------------------|---------------------------|-----------------------------------|-----------------------|--------------------------|
| Sample | Crucible weight (g) | Crucible +sample weight (g) | After test weight (g) | Weight difference (g) |
| C4 | 69.04 | 70.05 | 69.98 | 0.07 |
| C37 | 72.69 | 73.69 | 73.63 | 0.06 |
| C28 | 69.22 | 70.22 | 70.16 | 0.06 |
| Ash contents measurement | | | | |
| Sample | Crucible weight (g) | Crucible +sample weight (g) | After test weight (g) | Weight difference (g) |
| C19 | 67.68 | 68.68 | 67.798 | 0.118 |
| C30 | 74.59 | 745.59 | 74.702 | 0.112 |
| C25 | 74.75 | 75.75 | 74.87 | 0.12 |
| Volatile matter | | | | |
| Sample | Crucible + Lid weight (g) | Crucible + Lid +sample weight (g) | After test weight (g) | VM + moisture weight (g) |
| A | 13.9 | 14.878 | 14.0771 | 0.8009 |
| B | 14 | 14.96 | 14.1752 | 0.7848 |
| C | 14.02 | 15.02 | 14.1982 | 0.8218 |

Ultimate analysis

The elemental analysis performed using PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The picture of the analyzer is shown in Figure A-1.



Figure A-1 PerkinElmer 2400 Series II CHNS/O Elemental Analyzer

Table A-2 shows the results of the nine runs performed in elemental analysis of the MSW replicated sample. The runs were performed as listed in the table after every three runs there three blank runs were performed to purge the system.

Table A-2 Ultimate analysis result of the nine runs performed in the lab

| Ultimate Analysis | | | | |
|-------------------|---------------|-----------|------------|------------|
| Run Details | | Results | | |
| Run | Sample Weight | Carbone % | Hydrogen % | Nitrogen % |
| Test 1 | 1.24 | 43.95 | 5.89 | 0.68 |
| Test 2 | 1.98 | 47.47 | 6.83 | 0.53 |
| Test 3 | 1.64 | 47.5 | 6.95 | 0.81 |
| Test 4 | 1.81 | 48.32 | 6.78 | 0.48 |
| Test 5 | 1.39 | 49.8 | 7.24 | 1.06 |
| Test 6 | 1.84 | 50.01 | 7.28 | 0.77 |
| Test 7 | 1.57 | 48.5 | 6.94 | 0.67 |
| Test 8 | 1.12 | 49.51 | 7.14 | 1.22 |
| Test 9 | 1.82 | 49.55 | 7.41 | 1.18 |

TGA analysis

The thermogravimetric analysis performed using Mettler Toledo TGA / DSC1 thermal analyzer. The picture of the analyzer is shown in Figure A-2.

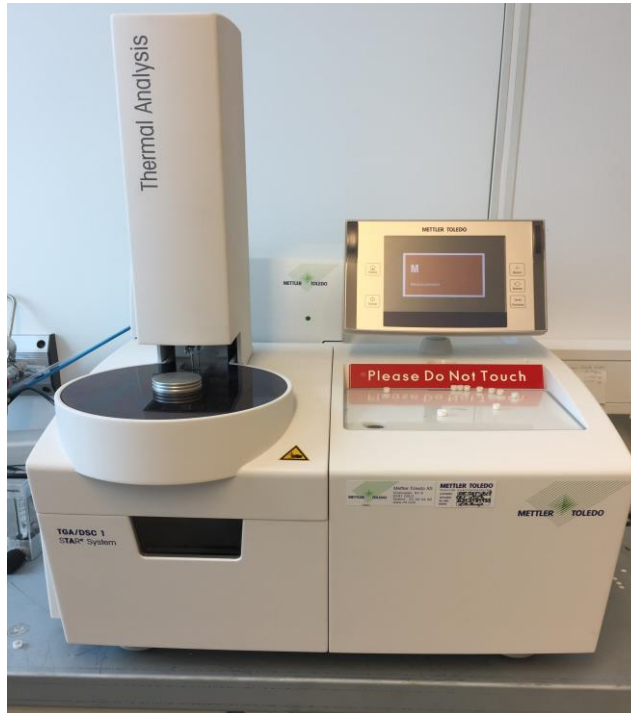


Figure A-2 Mettler Toledo TGA / DSC1 thermal analyzer

The TGA results of the two replicated samples were almost similar as it can be seen in the graphs the results are overlapped.

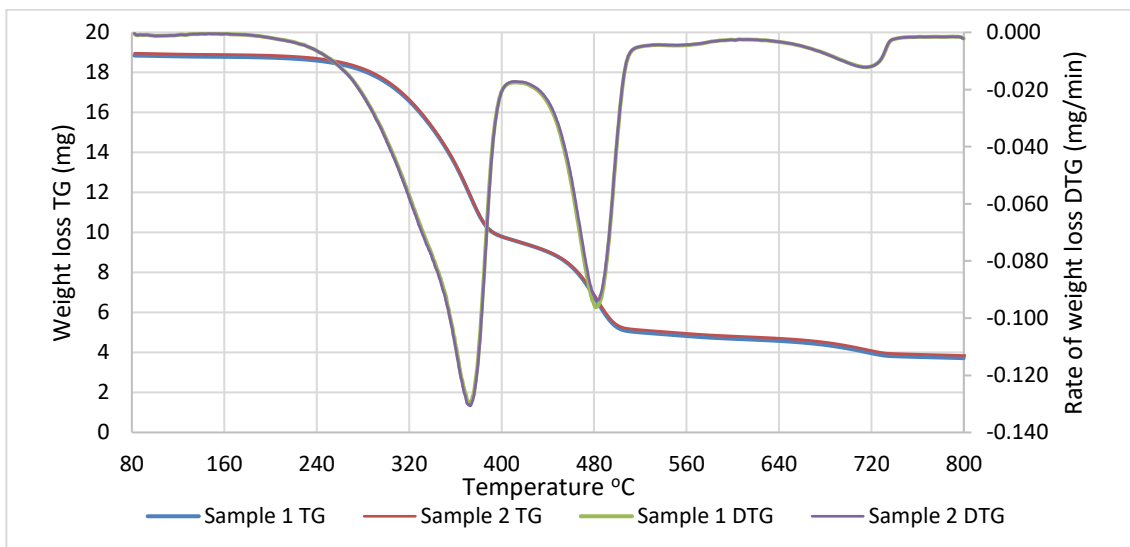


Figure A-3 TG and DTG curves of the two replicated MSW test samples

The heat flow from TGA analysis shows the exothermic and endothermic behavior of the two MSW samples in Figure A-4. The two samples have similar heat flow curves as a function of sample temperature

The slight decrease in the curve indicated the absorbed energy for moisture evaporation, devolatilization of cellulosic materials and petroleum-derived polymers, at a temperature where the local pick of the DTG curve obtained as discussed in TGA result section.

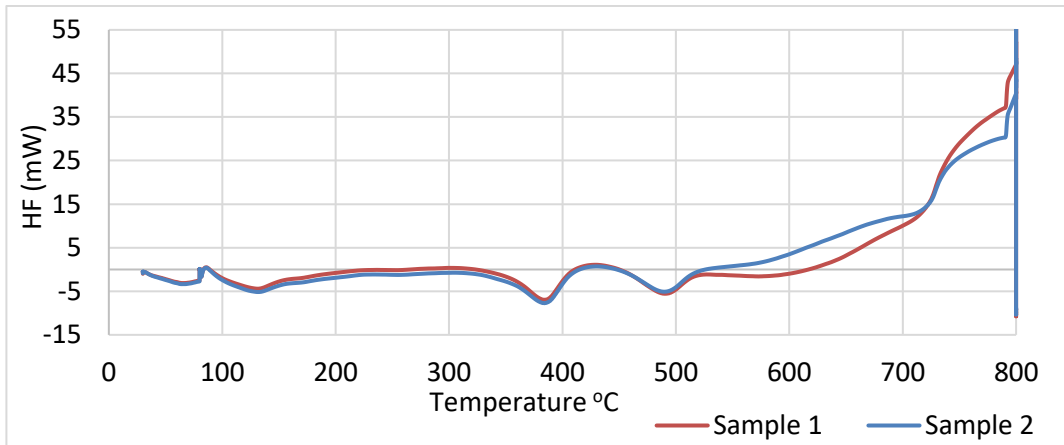


Figure A-4 Heat flow curves of the two replicated MSW test samples

Appendix B.

Simulation of the process

Direct gasification with air and steam as gasifying agent

Figure B-2 illustrated the hydrogen production and heat retrieval system of direct gasification with air and steam as a gasifying agent. In this system, the steam used both for gasification and water gas shift reactions the rest used for district heating.

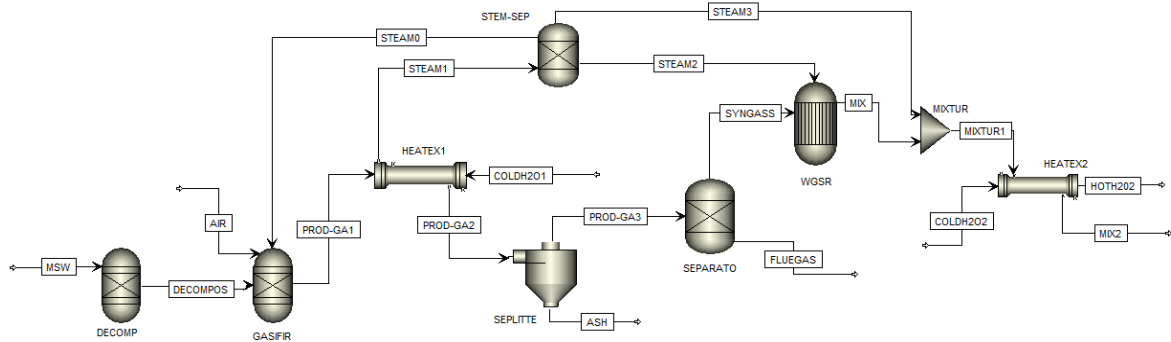


Figure B-1 Process flowsheet of direct gasification system with air and steam as a gasifying agent

Effect of Gasification Temperature

The effect of gasification temperature on the percentage composition of product gas shown in Figure B-2. The simulation performed in direct gasification system with air and steam as a gasifying agent, with the equivalent ratio of 0.3 and steam to MSW of 0.5. The trends of the percentage composition of gases are similar except due to the addition of steam the hydrogen composition increases whereas, carbon monoxide decreased. In this graph, the composition of hydrogen is slightly reduced with increasing temperature this could be due to the preference of the backward endothermic shift reaction at high temperature than forwarding shift reaction of an exothermic process.

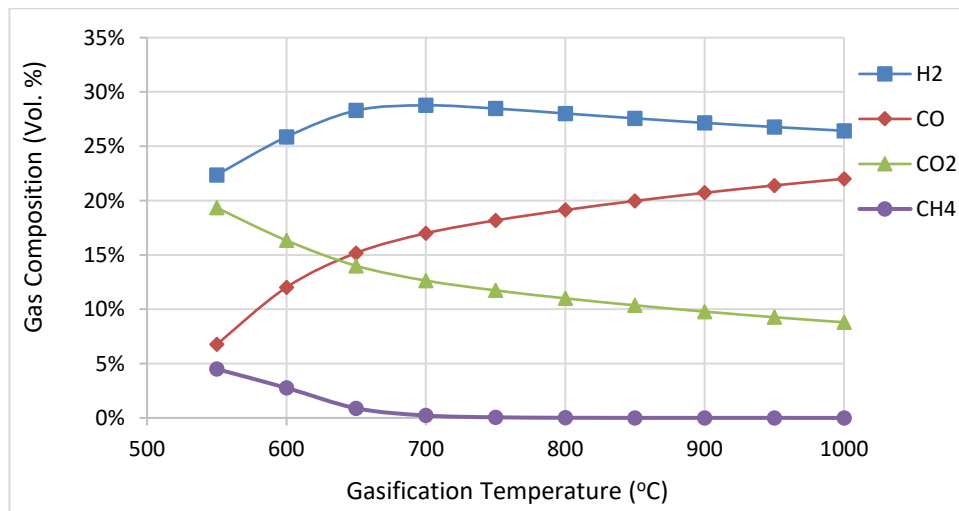


Figure B-2 Effect of gasification temperature on product gas composition in direct gasification with air and steam as a gasifying agent

Indirect gasification with air and steam as gasifying agent

Figure B-3 illustrated the indirect gasification system with steam as a gasifying agent. In this system, the excess heat from gasification reactor used to produce steam for gasification and water gas shift reaction. In the system since the high steam content is used for gasification process less heat is used for district heating only excess heat from water gas shift reactor.

